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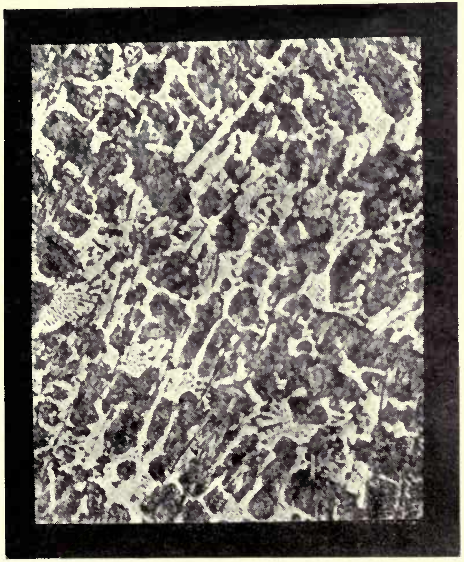

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PREFACE.

The author's object in writing this book has been to present, within the compass of a single volume, the results of many researches on the nature and properties of cast and malleable cast iron, and the scientific principles underlying their manufacture. These researches are for the most part scattered widely throughout the journals of technical societies, magazines, and periodicals, and it is hoped that, collected together in their present form, they will prove of greater value to metallurgical students, engineers, and manufacturers. Much of the subject-matter is the result of the author's own investigations in this field, and embodies many years' experience.

The metallurgy of cast iron presents problems of profound interest, upon which much light has been thrown by the equilibrium diagram of the iron carbide system. The author has, therefore, conceived it best to start with a description of this diagram and of the nature and constitution of those alloys. The succeeding chapters deal with the influence of the other constituents, such as silicon, phosphorus, sulphur, manganese, and the rarer elements. The remainder of the volume is devoted to the consideration of the influences incidental to the modes of manufacture, such as the casting temperature, shrinkage and contraction, and heat treatment generally.

Many of the researches described consist of the work of eminent metallurgists at home and abroad, and it has been the author's endeavour to afford a fair presentation of their views. At the same time, he has drawn largely upon his own practical experience, which he trusts may be useful to those who, like himself, are actively interested in the manufacture of castings, as well as to students and others.

His thanks are due to the Professors and staff of the Metallurgical Department of the Sheffield University, and to Mr J. F. Crowley and other friends, for the interest they have evinced in the preparation of the book. He also desires to take this opportunity of thanking the Councils and Secretaries of the several Societies and Institutions which have accorded him permission to reproduce illustrations from papers read before such Societies. Last, but not least, his thanks are due to the publishers, Messrs Charles Griffin & Co., Ltd., who have been willing to include his work amongst the valuable treatises which they have, from time to time, published in their "Metallurgical Series."

W. H. HATFIELD.

15 Oakdale Road,
Sheffield.

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CAST IRON

IN THE LIGHT OF RECENT RESEARCH.

INTRODUCTION.

One of the greatest triumphs of the present age is the Modern Blast Furnace, which in the course of a single day now produces hundreds of tons of molten iron. The ores from which the iron is smelted are contaminated with various oxides and earths with which they are found associated, and the reducing action which produces the metallic iron liberates at the same time considerable quantities of other elements, which are subsequently found in the product of the furnace. As the iron approaches and passes through the fusion zone, large quantities of carbon are taken up from the fuel, and it is then that the previously liberated silicon, manganese, and other substances pass into solution, resulting in the production of that most complex and variable substance known as pig iron.

To the metallurgical student, the early developments in the production of iron always present a most fascinating chapter. Although meteoric iron was probably the form in which the metal was first known to the ancients, man very early learnt that a lump of iron ore when thrown upon a fire would become a spongy metallic mass capable of being forged, and from this primary knowledge the rudimentary methods of smelting gradually developed. Amongst primitive peoples the world over, and throughout all history, there is a remarkable similarity in these earliest processes. The method employed by the Celts on the Cheviot Hills of Britain previous to the Roman Invasion was very similar indeed to that at present employed by the African natives on the banks of the Zambesi. The Egyptians imported the greater quantity of their iron from Ethiopia; and it is curious to note that the methods of iron smelting depicted by the ancient Egyptians are almost precisely the same as the one at the present day used by the Abyssinians. Assyria from the earliest times produced quantities of iron, whilst to the Aryans of early India the art of iron working was not unknown. It would seem that, the world over, man even in his earliest stages of development learnt to produce and to value this "precious" metal. Although little advance was made in actual iron smelting, much progress was made in its manipulation, and very early indeed did the art of producing steel arrive, it being no doubt first obtained by the contact of the metallic sponge with the carbon of the fire. The excellence of the

Syrian swords was proverbial in pre-Roman times. As indicating the early appreciation of iron in our own country, the Franciscan, Bartholomew, writing in 1260, said: "Use of iron is more needful to men in many things than use of gold, though covetous men love more gold than iron. Without iron the commonalty be not sure against enemies, without dread of iron the common right is not governed; with iron innocent men are defended, and foolhardiness of wicked men is chastised with dread of iron. And well-nigh no handiwork is wrought without iron; no field is eared without iron, neither tilling craft used nor building builded without iron."[1]

The iron produced by the early methods was relatively pure and, owing to the intense heat required to render it molten, the casting of iron was not possible, and hence the art of the smith was so superbly developed. An examination of the artistic productions of the Middle Ages reveals magnificent castings in bronze and in the precious metals, but in the case of iron we have to be content with the work of the smith. In this connection the following table of melting points will be found of interest, and incidentally will provide the explanation:—

	°Centigrade.
Platinum	1750
Wrought iron	1505
Steel (1·45 per cent. carbon)	1425
Cast iron (3·8 per cent. carbon)	1150
Copper	1084
Gold	1064
Silver	962

It will be seen that the comparatively infusible wrought iron has its melting point brought down by the influence of the addition of about 4 per cent of carbon to within measurable distance of that of copper. It is therefore obvious why the discovery of cast iron and the introduction of the blast furnace in the fifteenth century gave such a vast impetus to the development of the iron industries.

The evolution from the rudimentary methods of iron smelting to the modern blast furnace affords perhaps the most interesting record in metallurgical literature.

In the earliest times the smelting hearths were placed at the top of wind-swept gullies or neighbouring heights, such, for instance, as our numerous local "bole" hills, so that advantage might be taken of the assistance of the prevailing winds. Even by such inadequate means satisfactory lumps of iron were produced. Naturally we find that the first development was the substitution of artificial blast for the somewhat unreliable natural winds. Hence the development of the various types of bellows, some of the most ingenious, in ancient Egypt, India, China, and Africa. One cannot help regarding with interest the early Indian foot bellows and the superb box bellows of China. The introduction of artificial blast must have created quite as great an economic flutter in its time as the latter-day introduction of such improvements in its application as that of Neilson.

The process of smelting on a small hearth supplied with an air blast

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[1] Bennett H. Brough, "Early History of Iron," *Journal of the Iron and Steel Institute*, 1906, No. i.

constituted for centuries the general method of iron production in Europe; and the Catalan Forge, which is illustrated in fig. 1, is typical of the better type of such furnaces. This furnace held its own until comparatively recent times, and is remarkable for the ingenious method of supplying the blast. This was done by a trompe, an apparatus invented in Italy in mediæval times; it consisted of inducing a pressure of air by means of falling water. The furnace itself will be seen to consist of a four-sided hearth into which the ore and charcoal were fed, and the blast was supplied through one tuyère in the manner shown in the illustration.

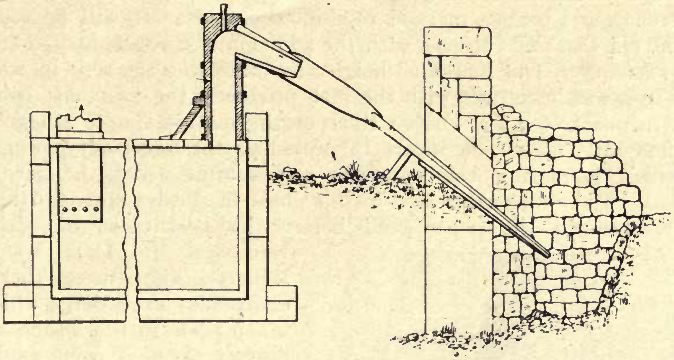
Trompe and Furnace Longitudinal vertical section

Fig. 1.

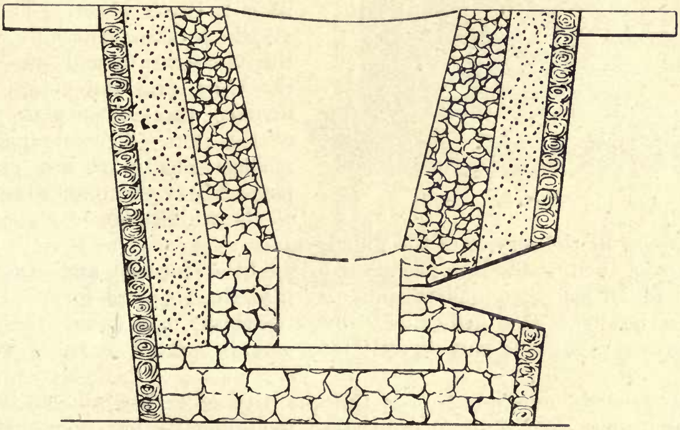

Fig. 2.

The next development would seem to be typified by furnaces of a similar kind to the Osmund, which is so ably described by Percy.[1] Fig. 2 shows

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[1] Percy's *Metallurgy of Iron and Steel.*

the construction, which will be seen to be almost identical in principle with that of the Catalan Forge, with the one difference that it is built with a higher hearth.

The old German Stuckofen, fig. 3, is really the progenitor of the modern blast furnace, and bears a marked resemblance to it. It will be seen to be really the old Osmund furnace, with the addition of a superimposed truncated cone of masonry. This increased height, by increasing the time in which the reduced iron was in contact with the fuel, produced the first cast iron. Our modern furnaces (see fig. 4) owe their origin to this simple stuckofen, and to the ingenuity of our engineers in providing the necessary power for the progressively increasing blast pressure and volume which the development demanded. To anyone interested in this phase of the development the author would recommend the paper read before the Institution of Mechanical Engineers in 1907 by D. E. Roberts, who traced therein the enormous evolution which has taken place in the design and production of the blowing engine.

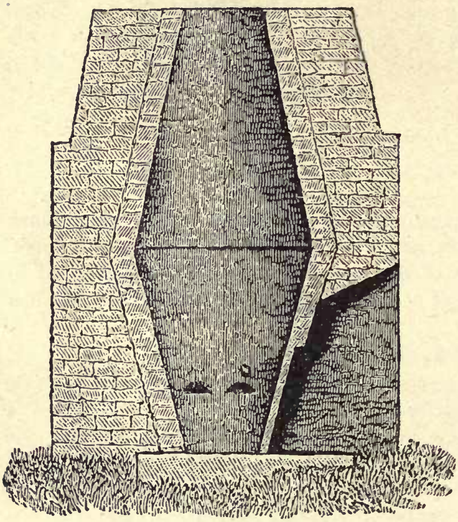

Fig. 3.

The range of composition of the product of the blast furnace is very wide. It is dependent upon many factors, and is determined not only by the class of ore, fuel, and flux which is smelted, but also by the ratio which the weights of the components of the charge bear to each other. The speed at which the furnace is worked, the temperature and condition of the blast, and the design of the furnace, also influence the quality of the iron. Typical analyses of modern pig irons are given on pages 240–4 which afford some idea of the wide range of compositions which is now at the service of the foundryman.

Pig iron, then, is the iron produced in the blast furnace, and cast iron is pig iron which has been melted and cast into the required form. In some instances, however, what are called "direct castings" are made; that is, the blast furnace product is run directly into moulds instead of being cast into pigs.

As previously mentioned, it is the quantity of carbon alloyed with the iron that confers upon it those properties (including its low point of fusion) which have so commended it to industrial usage.

Iron as produced in early times was relatively pure, and consisted of material which under the microscope would have been seen to consist mainly of "ferrite" crystals. It was extremely soft and ductile. The later addition of carbon resulted in the production of steel, and the microstructure then presented in the normal or softened condition the well-known "pearlite" structure, containing either ferrite or free "cementite" according to whether the steel contained more or less carbon than about 0·89 per cent. Relatively, the iron-carbon steels present little difficulty, forming as they do a single iron-carbon system in which the carbon exists in the unhardened condition as massive carbide or as the segregated carbide of the pearlite, and at high temperatures as a solid solution of carbide in iron. Of the elements other than carbon usually present, only manganese substantially modifies the structure. This element, by chemical union with the carbide of iron, materially alters the characteristics of the pearlite, and incidentally the mechanical properties likewise.

With pig or cast iron the problem is rendered much more complicated by the large percentages of other elements present, it being usual to find, along with the carbon, very considerable quantities of manganese, sulphur, silicon, and phosphorus. These elements all individually produce definite reactions with iron, and also, in some cases, with each other, and thus pig iron may present a complex and variable mass of free iron and free carbon, carbides, double carbides, sulphides, silicides, and phosphides. Each individual constituent will have its own particular characteristics, its own thermal phenomena, and, what is also very important, its own coefficient of contraction.

One aspect of the presence of the impurities is, that their influence is greater than the percentage recorded by analysis would lead one to anticipate. It is found that the compounds formed by the various elements present occupy such considerable volume that they have most seriously to be reckoned with. For instance, H. M. Lane, in a recent paper, demonstrated that a No. 2 foundry iron, whilst only containing 6·93 per cent. of impurities, contained by volume 35·73 per cent. of compounds formed therefrom. In fig. 5 will be found a photomicrograph of a sample of ordinary foundry cast iron. The background or matrix consists of silico-ferrite, and this will be seen to be cut up by the graphitic plates and by the phosphide of iron pro-

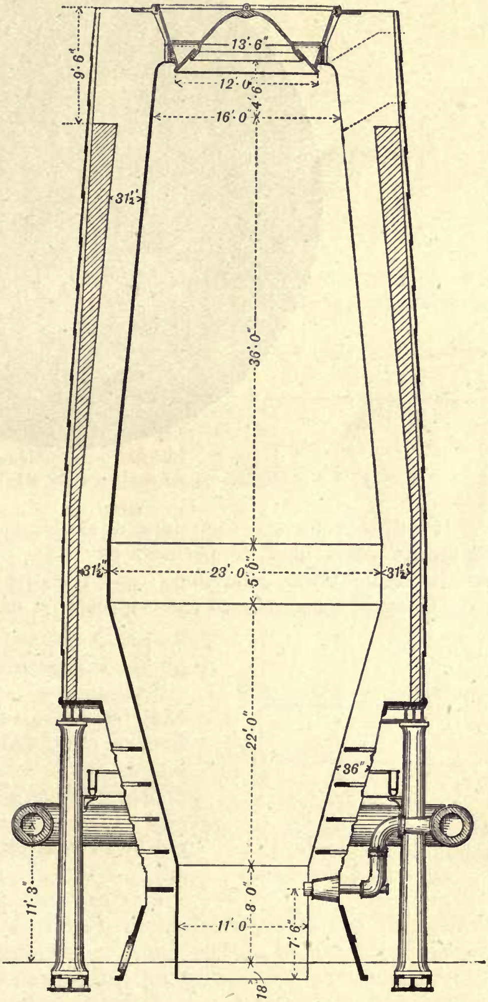

Fig. 4.

duced from the phosphide eutectic originally present in the iron. This micrograph will demonstrate the point of the foregoing remarks.

FIG. 5.—Etched picric acid in alcohol. Magnified 60 diameters.

It will therefore be seen how advantageously the accumulated researches of recent years may be perused by those interested in obtaining the best results under works conditions; and the author hopes that the following pages may prove of assistance to those interested in the study of cast iron.

CHAPTER I.

THE IRON-CARBON ALLOYS AND CAST IRON FROM THE STANDPOINT OF THE EQUILIBRIUM DIAGRAM.

BEFORE the various iron-carbon alloys which come under the category of cast iron can properly be understood, an appreciation of the iron-carbon equilibrium diagram is necessary.

Frederick Guthrie,[1] in his classical researches, worked out the freezing diagrams of various salt solutions, and it is of considerable interest to note that a work which was no doubt considered at the time of its publication to be purely academical should have formed the basis of modern metallurgical research. An invaluable method has thus been provided of correlating the numerous data which have resulted from much varied work.

In fig. 6 will be seen the equilibrium diagram of solutions of common salt (NaCl) in water. It is not proposed here to go into the detail of Guthrie's experiments; those researches, along with others, will be found admirably treated elsewhere.[2] Suffice it that it was demonstrated that the addition of common salt progressively lowered the initial freezing point of water until at the point B (fig. 6) with 23·5 per cent. of NaCl it had reached –22° C. With solutions of this particular percentage of salt the simultaneous freezing of the whole takes place at –22° C., this solution being understood to be of the "eutectic" composition. Further additions of salt progressively increase the initial freezing point, and now the most interesting feature must be recorded. From all the varying solutions containing less than 23·5 per cent. of salt crystals of ice begin to separate out when the primary freezing points, indicated by the curve A–B, are reached, and ice continues progressively to separate until the mother liquor is equal to the eutectic composition. That point is invariably reached at –22° C., when the residual mother liquor simultaneously solidifies. If the solutions which contain more than 23·5

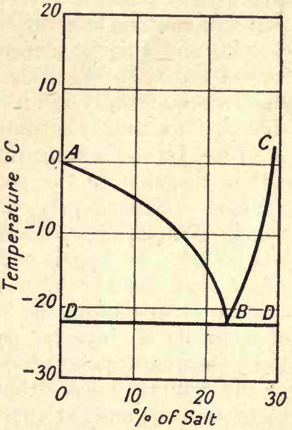

FIG. 6.—Freezing diagram of solutions of sodium chloride (common salt) in water.

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[1] *Physical Magazine*, 1875–8.

[2] Harbord's *Metallurgy of Steel*; Goerens' *Introduction to Metallography*; Desch's *Metallography*.

per cent. are next considered, it will be found that along the primary freezing line B–C pure salt is found to be deposited, and this precipitation also progressively increases with the decrease in temperature, until at – 22° C. only the mother liquor of 23·5 per cent. of salt content is left, and we again have the freezing of the eutectic. This particular composition, known as the eutectic, upon solidification loses its homogeneity, and is found under the microscope to consist of "innumerable plates of ice and salt in mechanical juxtaposition."

Given the "common salt in water" diagram, it is not necessary here to present the innumerable diagrams which have now been worked out, and have gradually and completely, through a long series of aqueous solutions, fusion mixtures, and alloys, confirmed the accuracy and utility of the principles revealed as the result of Guthrie's researches, and the subsequent application of Gibb's Phase Rule.

Pig iron must be considered as a frozen solution of carbon and iron, and it will be seen in the following pages how much simplified the subject becomes if considered from this standpoint.

The iron ore is reduced to iron in the upper regions of the blast furnace, and as the spongy mass of metal descends, carbon is absorbed from the coke. The conditions are such that the molten material invariably becomes a saturated solution of carbon in iron. In the absence of other elements, such iron will contain in solution, at the temperature of freezing, 4·3 per cent. of carbon, and this is therefore the explanation of the normal percentage of carbon found in pig irons. The presence of varying percentages of other elements materially influences this solubility, but for the present it is advisable that we should consider the purely iron-carbon alloys.

The Iron-Carbon Diagram.—We are indebted for the present iron-carbon diagram to the combined efforts of many distinguished metallurgists working independently, and including Roberts-Austen, Osmond, Chatelier, Stead, Arnold, Roozeboom, Heyn, Benedicks, Charpy, Carpenter, Goerens, and Wüst. In fact it is doubtful whether there is any thinking metallurgist whose soul has not been vexed at one time or another in endeavouring to confirm or to confute the various lines suggested at different periods as being of necessity an integral part of this diagram. An admirable treatise,[1] from the Continental point of view, has recently been written upon the development of the diagram; and although it may not even yet be considered quite complete, there is now, at any rate, substantial agreement upon the main issues.

It is interesting, in the light of our present views, to find that Sir W. Roberts-Austen, in his Fifth Report to the Alloys Research Committee,[2] says: "If carburised iron is a solution capable of being either liquid or 'frozen,' it might be anticipated that the constituents of the solid solutions would be recognisable by the microscope, just as individual crystallised salts grouped together can be distinguished by suitable magnification. Patient research conducted with the aid of the microscope, beginning with the work of Sorby in 1864, has during the last thirty-five years proved that this is the case."

To Roberts-Austen, and also to Osmond and to H. Le Chatelier, we are indebted for the first conception of the iron-carbon equilibrium diagram. Working on the hypothesis contained in the above abstract, Roberts-Austen investigated the thermal behaviour of a series of varying carbon-iron alloys, and by collating data already extant he produced the diagram found in fig. 7. The materials which he used varied somewhat: for the higher percentages he

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[1] Wüst, *Metallurgie*, 1909, p. 512.

[2] Institution of Mechanical Engineers.

prepared alloys in the electrical furnace, but for those containing under 2·0 per cent. of carbon he used cemented steel and open hearth samples taken at varying periods from the bath. His standard pure iron was prepared by the electrolytic method.

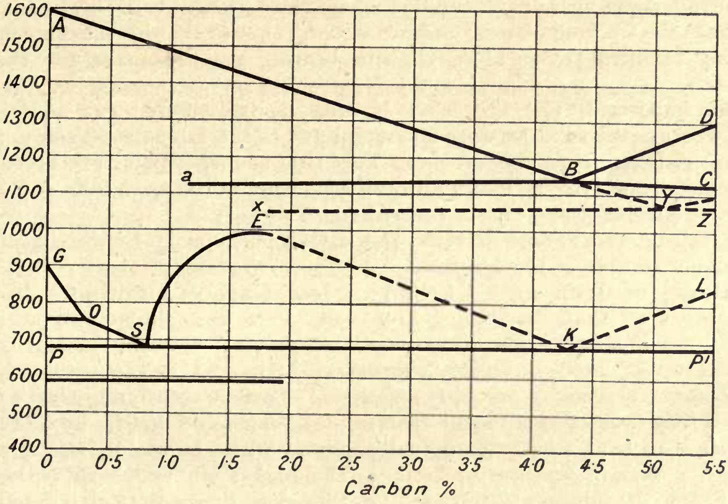

FIG. 7.

The analyses of his materials containing under 2·0 per cent. of carbon are given in the following table:—

Nos.	Carbon.	Silicon.	Sulphur.	Phosphorus.	Manganese.	Arsenic.
	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.
1	1·800	0·008	0·032	0·054	0·391	trace
2*	...	...	...	...	...	...
3	1·740	0·006	0·037	0·046	0·380	trace
4	1·451	0·006	0·029	0·023	0·340	0·004
5	1·461	0·007	0·038	0·025	0·340	0·002
6	1·234	trace	0·030	0·013	0·327	0·004
7	1·161	,,	0·030	0·016	0·290	trace
8	0·927	,,	0·025	0·013	0·293	0·004
9	0·912	,,	0·036	0·010	0·236	trace
10	0·821	,,	0·040	0·008	0·270	0·002
11	0·690	,,	0·038	0·009	0·220	0·004
12	0·540	,,	0·032	0·006	0·280	trace
13	0·434	,,	0·030	0·009	0·270	,,
14	0·342	,,	0·032	0·006	0·270	0·003
15	0·160	,,	0·037	0·008	0·240	trace
16	0·145	,,	0·041	0·006	0·250	,,
17	0·102	,,	0·037	0·008	0·230	,,
18*	...	...	...	...	...	...
19	0·070	trace	0·035	0·008	0·244	trace
20*	...	...	...	...	...	...
21	0·097	trace	0·030	0·007	0·220	0·004
22*	...	...	...	...	...	...
23	0·108	trace	0·033	0·005	0·240	trace
24	0·101	,,	0·034	0·004	0·217	,,
25	0·078	,,	0·033	0·007	0·217	,,

* Nos. 2, 18, 20, and 22 were not analysed.

If reference be made to figs. 6 and 7 it will be seen that, in an analogous manner to the phenomena of salt solutions, the addition of carbon gradually lowers the initial freezing temperature of the iron along the line AB until the point B, which indicates the eutectic composition, is reached, and that further additions again raise the line as indicated from B to D. The line *a*–C indicates the freezing of the "mother liquor," or eutectic, which has a constant freezing temperature of 1135° C., thus bearing out the analogy of the salt solutions.

One important difference, however, must be here pointed out, and that is that, whereas the solid ice does not retain any of the salt in solid solution, the frozen iron retains much carbon. This fact is responsible for the further phenomena observed as indicated by the lines found between 900° to 600° C. in alloys (steels) of low carbon content (fig. 7).

It will be well to here describe this latter phenomena before considering the higher reaches of the diagram.

Alloys of Iron and Carbon of low Carbon Content.—In 1868 Gore observed that on cooling iron wire there was, whilst still at a red heat, "a sudden dilation which was not present in other metals experimented upon," and he later demonstrated that at this temperature the iron became, on cooling, strongly magnetic. Barrett, continuing Gore's work, showed that in heating also, the reverse phenomenon occurred, and he further showed that hard steel wire actually glowed when, in cooling down, it had reached a certain temperature still in the region of "red heat." Osmond, working with the newly devised Le Chatelier pyrometer, elaborated and extended these observations, and to him we are indebted for the establishment of the well-known critical points occurring in steel. Tschernoff having discovered that there was a critical temperature associated with the hardening of steel, which he designated by the sign "A," Osmond named his points obtained during cooling as *Ar* 1, *Ar* 2, and *Ar* 3. To distinguish the absorptions of heat taking place during heating from the evolutions taking place during cooling, he named the former *Ac* 1, *Ac* 2, and *Ac* 3.[1] The explanation of these phenomena is still a subject of discussion; indeed the actual facts concerning them are even as yet not quite agreed upon. For instance, whilst in a low carbon steel some investigators would claim the *Ar* 2 to be one single evolution of heat, Arnold and M'William claim, and apparently with good reason, that it consists of two distinct evolutions. Taking the data generally, however, it would seem to be that there is a fair agreement, and it may be well here to record the explanation.

The author would refer to an admirable paper recently published by W. C. A. Edwards.[2] That worker has made a most successful attempt to reconcile the varying theories evolved from time to time to solve the problem of hardening and the various changes taking place at these critical points. It would be well here to explain that many metallurgists were of opinion that the iron existed, in the different critical ranges, in varying allotropic modifications, and that it was to the properties of one of them retained by quenching that the hardening was due; Arnold, however, put forward the hypothesis that it was due to the formation of a subcarbide $Fe_{24}C$, produced by the chemical combination of the carbide and ferrite of the pearlite, preserved by

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[1] In these symbols *A* is the initial letter of the French word *arrestation* or arrest, while *r* stands for *refroidissement* (cooling) and *c* for *chauffage* (heating).

[2] *Jour. Iron and Steel Inst.*, vol. ii., 1910.

quenching. It would seem, in the light of recent discussion, that the correct explanation will be found in a compromise between these two theories. In the first place, iron without carbon will not produce the tool steel hardness so well known in Sheffield and elsewhere. In the second place, the properties of iron do vary sufficiently in the critical ranges to entitle them, by somewhat stretching the original meaning of the word, to the description of allotropic modification. To quote Edwards, pure iron "cooling from the melting point to the ordinary temperature passes through three distinct ranges of temperature, viz. from 1505° C. to 900° C., 900° C. to 760° C., and 760° C. to 0° C. The significance of these ranges will be evident if the incontestable difference in the properties of the metal when at temperatures within the above-mentioned limits are considered. For example, iron between 1505° C. and 900° C. is non-magnetic, and will readily dissolve carbon or carbide of iron; from 900° C. to 760° C. it is still non-magnetic, but it is almost without action upon carbon; and below 760° C. it is magnetic, and incapable of dissolving carbon. Now, the thermal change at 900° C. can be explained only by considering that at that temperature there is a rearrangement of the molecules within the mass, which may or may not be accompanied by an external change of crystalline form. The marked difference in physical properties strongly supports this view. In addition to this evidence, Rosenhain and Humphrey have shown that iron at temperatures between 760° C. and 900° C. is harder when at temperatures either just above 900° C. or just below 760° C." This hardness is in no way comparable with the quenched steel hardness, but at the same time the work of Rosenhain and Humphrey certainly provides additional evidence of the variation of the properties of the iron in the critical ranges. It will now be well to refer to the diagram in fig. 7 during this subsequent argument. The addition of carbon gradually lowers the *Ar* 3 point until at ·45 per cent. (O in the diagram) it synchronises with *Ar* 2. If we, however, examine a steel containing ·25 per cent. of carbon it will be found that it consists of a homogeneous solid solution down to *Ar* 3 (along the line G–O), which in this case occurs at 840° C. Evidence would then point to iron containing less, if any, carbon commencing to fall out of solution, hence the evolution of heat; the remaining solid solution therefore continues gradually to become richer in carbon (like salt solutions) by a gradual precipitation of iron at gradually lowering temperatures. Hence the continual evolution of heat which Arnold has designated the "fourth recalescence." When 760° C. is reached the *Ar* 2 change takes place, and the precipitated iron becomes magnetic and absolutely incapable of holding carbon in solution. Micrographically the iron, after passing 760° C., consists of ferrite crystals, amongst which are to be seen the areas of solid solution or "hardenite." On further cooling to about 700° C. (indicated by the line PP′) a further evolution of heat takes place owing to the iron completely throwing out of solution the remaining carbide, with the production of pearlite.

With gradual increase in carbon content it is found that the *Ar* 2.3 point is gradually depressed until at the point S only one critical point is to be observed. This eutectic point for the solid solution, it will be seen, occurs at 0·89 per cent. of carbon, *i.e.* the percentage fixed by Arnold in his "Carbon and Iron" research as being the composition at which the whole of the section consists of pearlite. If, therefore, we cool from 900° C. iron containing ·89 per cent. of carbon, the homogeneous solid solution persists down to the point

A 1.2.3 (S in the diagram), at which temperature the pearlite is produced by resolution of the solid solution.

It will be well here to consider the theory of hardening: whether the carbide is in chemical union or merely in solution above this *Ar* 1.2.3 is immaterial; the essential fact is that if the iron is quenched above this critical point the iron is trapped in its pre-pearlite condition, and then we obtain from this 0·89 per cent. carbon steel the maximum hardness. It is somewhat tempting here to discuss at length the theoretical considerations underlying the phenomena of hardening, but it is considered outside the scope of the work. Any student interested in the subject is referred to the paper by Edwards, and the subsequent discussion.

Alloys of Iron and Carbon of high Carbon Content.—If now we take an iron containing, say, 1·40 per cent. of carbon and allow it to cool from 900° C., it will be found that the homogeneous solid solution persists down to the temperature marked by the line SE; we shall then have the separation of free carbide gradually taking place (compare again the salt solutions) until the eutectic composition of ·89 per cent. C. is reached, and then, on further cooling, the resolution of the pearlite takes place when the *Ar* 1.2.3 point is reached at 700° C. (line PP′, fig. 7).

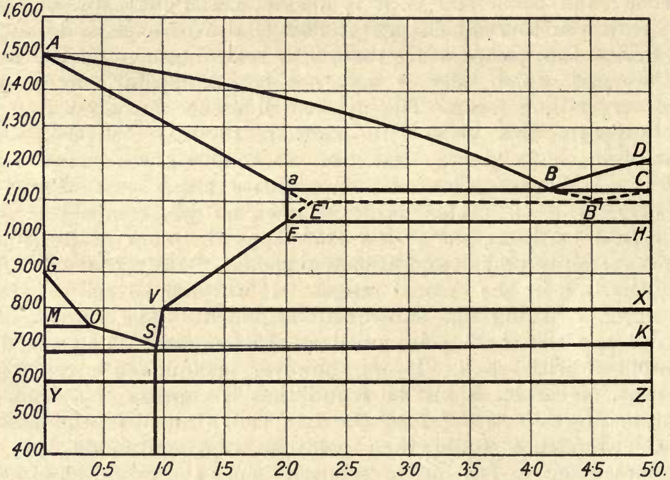

FIG. 8.

Further additions of carbon gradually raise the temperature at which the homogeneous solid solution can exist without the precipitation of free carbide until we arrive with over 2·0 per cent. of carbon at the primary iron-carbon eutectic line E–C, see fig. 10, at which the 4·3 per cent. eutectic solidifies. Before, however, discussing the matter further, we must consider the work of other investigators in building up the higher region of the diagram.

An interesting paper by Stansfield helped further to evolve the Roberts-Austen diagram, although some of his hypotheses have not survived the results of recent work. In 1900 Roozeboom gave his much-discussed paper before the Iron and Steel Institute, entitled "Iron and Steel from the Standpoint of the Phase Rule." It was a highly theoretical work, based upon the researches of Roberts-Austen and Osmond. His classical diagram is given in fig. 8. It will be seen that whereas Roberts-Austen fixed the line marking the commencement of freezing, Roozeboom also added the line AE′, indicating the end of the freezing range, by connecting up the eutectic freezing line with the point A. As shown by Wüst and others, his other suggestion was not so fortunate; he suggested that the line *a*–C represented the *formation of a solid solution graphite eutectic mixture, followed at a lower temperature by a line at which the reaction between this solid solution and the graphite took place, which resulted in the formation of the carbide.* Objections were raised in many quarters to this hypothesis, since varying metallurgical practice was not in accord with it. Le Chatelier instanced the malleableising processes as an example. However, the very considerable discussion which the paper provoked did much to advance the subject; and in 1904 Carpenter and Keeling, at the National Physical Laboratory, worked out the thermal phenomena of a very complete series of iron-carbon alloys. The table on p. 14 will be found to give the results of their observations.

As a result of this research, Roozeboom abandoned his theory as to the formation of graphite, and became convinced that graphite, and not carbide, was the stable phase. He, however, held to Stansfield's suggestion as to the existence of the two systems iron-graphite and iron-iron-carbide.

Roozeboom's conception of the freezing process is well expressed by Wüst in the following words:—

A. *The Stable System.*—Mixed crystals separate from the fluid melt at temperatures AB, see fig. 8, the composition of which is represented by A*a*. The limit to which carbon can be held in solution by iron in this range is 2 per cent. From those melts containing between 2 and 4·3 per cent. of carbon mixed crystals separate, until at 1130° C. the eutectic, consisting of saturated mixed crystals and graphite, solidifies. From melts containing more than 4·3 per cent. carbon primary graphite separates out along BD, until finally the graphite mixed crystals eutectic is reached.

B. *Freezing of the Iron-Iron-Carbide System.*—Mixed crystals separate from this fluid mass along AB, whose composition is represented by AE′. The solubility of the carbide in this range being greater than that of graphite, the point E representing the saturated mixed crystal corresponds to a higher concentration than the former point "*a*," and the eutectic freezing point must also occur at a lower temperature. Without any special reason, Roozeboom tried the eutectic horizontal line EB′ at 1100° C. Hypereutectic alloys deposit primary iron-carbide along the line B′C, and finally the mixed crystal iron-carbide eutectic at 1100° C.

The line EH was intended to represent the limit of the range in which the solubility of the graphite in the solid solution was constant, and Roozeboom considered that, commencing along this line, a further separation of graphite took place.

It will be seen that the question to be settled was, How and when is the graphite formed? Roozeboom's work was of interest, but by no means brought us to the final solution of this problem. The theory advanced at this stage was that the carbon was in solution in the iron in the elementary form, and that graphite was formed by deposition direct from the solution. The subject was much discussed by Continental metallurgists, and several able papers and modified diagrams were produced, the chief amongst which was that of Benedicks, given in fig. 9.

That worker, as a result of a careful study of the results to hand, designed

THE RANGE OF SOLIDIFICATION AND THE CRITICAL RANGES OF IRON-CARBON ALLOYS.

Alloy No.	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	Alloy No.
	Carbon per cent.	Range of Solidification.		Ar.m.c.	Ar. 3.		Ar. 2.		Ar. 1.		Ar. 0.	
		Beginning.	End.	Beginning.	Beginning.	Maximum.	Beginning.	Maximum.	Beginning.	Maximum.	Beginning.	
1	0·01	..	..	..	901	900	784	762	..	..	616	1
2	0·02	1504*	1470*	..	900	890	795	762	..	..	600	2
3	0·05	..	..	..	905	884	780	762	..	..	..	3
4	0·12	1504†	1470†	..	894	838	774	762	693	688	600	4
5	0·16	1498†	1465†	..	872	837	771	762	697	693	576	5
6	0·17	1497†	1450†	..	..	..	..	..	..	..	..	6
7	0·24	1492†	1448†	..	890	merged	..	762	696	693	611	7
8	0·38	1479†	1416†	..	..	..	778	762	700	699	..	8
9	0·47	1482†	..	..	..	..	777	762	..	703	587	9
10	0·53	1473†	1404†	..	..	..	762	730	..	700	617	10
11	0·61	1469†	1394†	..	..	..	780	merged	merged	699	593	11
12	0·80	1457‡	1351‡	..	..	..	..	..	..	(704)	..	12
13	0·80	1454†	..	..	..	..	..	..	..	(695)	..	13
14	0·81	1460†	1351†	..	774	merged	..	merged	merged	706 (705)	..	14
15	0·93	1443†	..	..	774	”	..	”	”	699	587	15
16	1·31	1426†	1286†	883	774	”	..	”	”	(711) 695	600	16
17	1·51	1406†	1244†	911	768	”	..	”	”	(713) 684	587	17
18	1·69	1388†	..	985	774	..	..	..	..	(708) 710	..	18
19	1·81	1383†	..	..	..	..	..	..	..	..	..	19
20	1·85	1383†	1179†	(1015) 1030	783	merged	..	merged	merged	(711) 711	..	20
21	1·97	1367†	..	(1042)	..	..	..	..	..	(710)	..	21
22	2·12	1350†	1110†	..	..	..	..	..	..	(714)	..	22
23	2·21	1354†	1107†	..	801	merged	..	merged	merged	714	610	23
24	2·25	1352†	1122†	..	..	..	..	..	..	..	..	24
25	2·25	1348†	1122†	..	..	..	..	..	..	(714)	..	25
26	2·47	1330†	1134†	1035	801	merged	..	merged	merged	708	622	26
27	2·61	1305†	..	1040	801	..	...	..	..	716	610	27
28	2·67	1306†	..	..	..	..	..	..	..	..	..	28
29	2·74	1300†	1139†	..	..	..	..	..	..	..	..	29
30	2·85	1292†	1139†	1058	..	merged	..	merged	merged	716 (715)	613	30
31	3·03	1277†	1139†	..	777	”	..	”	”	702 (717)	610	31
32	3·29	..	1141†	..	..	..	..	..	..	..	..	32
33	3·42	1238†	1114†	1058	790	merged	..	merged	merged	703 (714)	610	33
34	3·51	1230†	1136†	..	..	..	..	..	..	..	..	34
35	3·87	1190†	1144†	1090	770	merged	..	merged	merged	(716) 716	600	35
36	3·98	1171*	1138*	1087	..	..	..	..	..	713	604	36
37	4·37	1136*	1136*	..	..	..	..	..	..	(714)	..	37
38	4·50	1146*	1146*	1087	777	merged	..	merged	merged	715	616	38

his diagram still upon the hypothesis that both a stable and meta-stable system existed; and it will be seen that the eutectic freezing lines of the two systems are still held to be distinct, the solubility of graphite in this range being considered less than that of the carbide.

C. B. Upton[1] has also evolved another diagram, but his modifications are based upon theoretical considerations of small practical significance.

To Goerens we are indebted for a very distinct advance in the development of the diagram. From his experiments, that worker came to the following conclusions:—

(1) *The carbon in molten iron is in solution as carbide.*

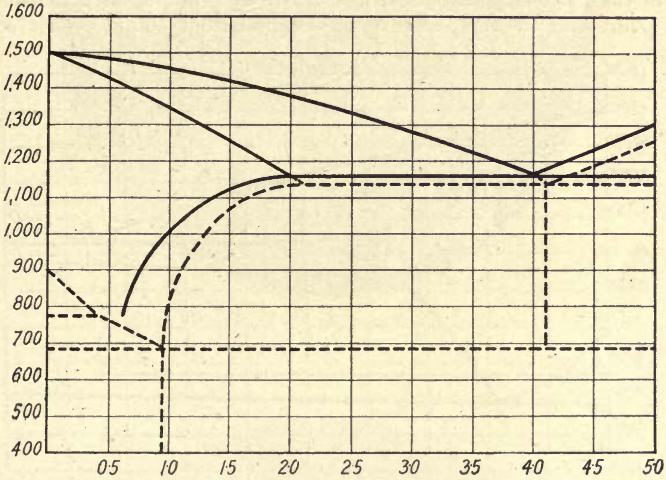

FIG. 9.

(2) *The system must be considered strictly to be one of iron-iron-carbide*, as the iron-iron-graphite lines do not hold after due appreciation of his observations.

He considers that the line B–D (fig. 10, equilibrium diagram, based upon Carpenter and Keeling's observations) represents the temperatures at which the carbide and molten metal are in equilibrium. A further cooling results in the precipitation of free carbide, which under such conditions is decomposed, with the resulting formation of "kish." Following along these lines, he proves, in the writer's opinion, that it is only after the resolution of the eutectic at about 1130° C. into free carbide and "austenite" that the free carbon found in pig irons is formed. It will further be understood that the degree of rapidity with which the cooling of the iron both before and after freezing takes place is the factor which mainly determines the ratio of free to combined carbon in the finished product.

The author has proved to his own satisfaction that this view is correct, and that it is indeed *absolutely necessary in iron-carbon alloys to have had present free carbide before free carbon can be obtained.*

H. M. Howe[2] discusses the evidence for and against the stability of the

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[1] *Jour. Phys. Chem.*, May 1909.

[2] *American Institution of Mining Engineers*, July 1908.

carbon in the free state as against stability in the combined state. This work is voluminous and merits a careful perusal, although the writer unfortunately opens with further modifications of the nomenclature of the subject, which is to be deplored. It is pointed out that as the dissociation of the carbide is accompanied by an evolution of heat, *i.e.* is exothermic, it would appear that the latter phase is the stable one.

In the treatise by Wüst, to which reference has already been made, will be found an admirable account of his conception of the phenomena of solidification and cooling of pig iron, based upon both his own work and that of his pupils, and it is of sufficient importance to be presented somewhat fully.

One of the most important features of the diagram is the position of the eutectic point and its temperature of solidification. This, Wüst considers, may safely be taken as occurring at about 1130° C., with allowance for experimental error. He gives two micrographs illustrating the structure of this eutectic alloy.

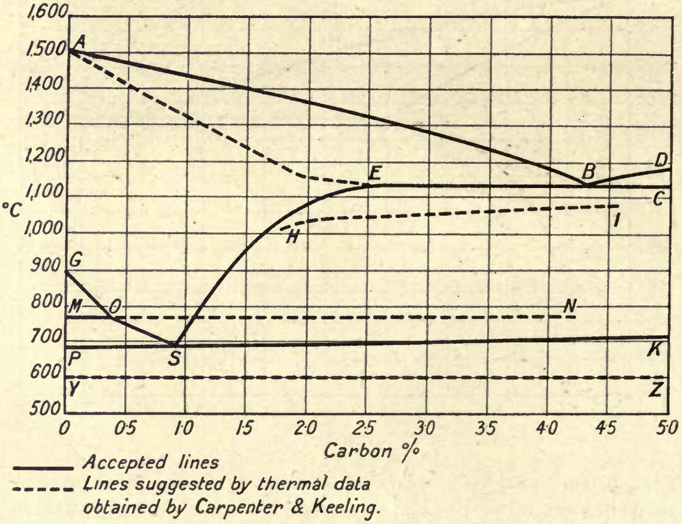

FIG. 10.

Fig. 11 is a micrograph of × 5 magnification of a sample of eutectic composition quenched in water, whilst fig. 12 is of the same section magnified 100 times. This well-known structure, presented by the solidified eutectic, Wüst proposes to christen "Ledeburite," after his distinguished compatriot; and since it has not yet been given a distinctive name, it would be courteous to accept the suggestion. He describes a most interesting set of experiments made to determine the manner in which the separation of graphite takes place.

The micrographs in figs. 13 and 14 represent the structure of a 200 grm. specimen of eutectic pig iron (the complete analysis is not given) which, after occupying a period of 350 seconds during freezing, was immediately quenched. They will be seen to indicate the presence of graphite in austenite, accompanied by traces of the still remaining patches of "Ledeburite."

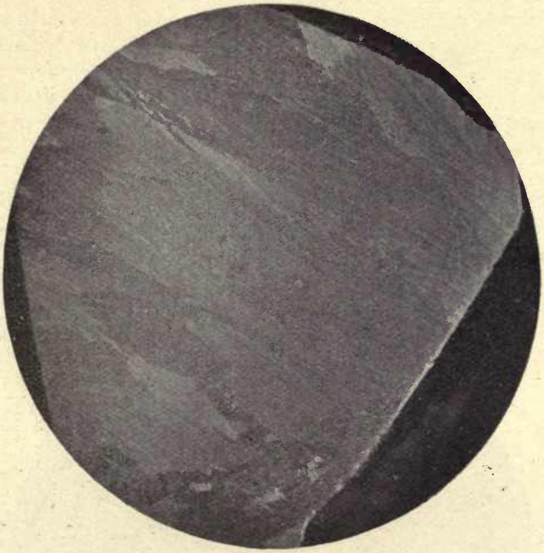

FIG. 11.—Etched. Magnified 5 diameters.

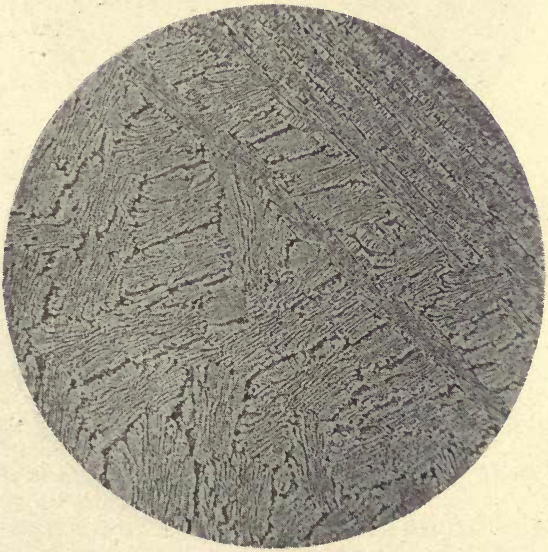

FIG. 12.—Etched. Magnified 100 diameters.

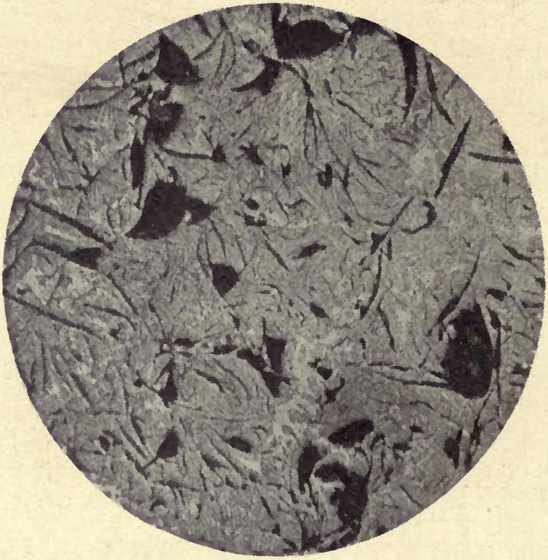

Fig. 13.—Etched. Magnified 50 diameters.

Fig. 14.—Etched. Magnified 200 diameters.

A similar mass of the same material was then quenched after remaining 200 seconds at the same temperature, and the striking result was obtained indicated in figs. 15 and 16. It will be seen that whilst much graphite is seen to be surrounded as before by the constituent austenite, much larger areas of the "Ledeburite" have persisted. These experiments undoubtedly prove that the production of the graphite takes place progressively during the recalescence observed at about 1130° C. Experiments also published[1] by Heyn and Bauer point to the truth of this data.

A series of pyrometric observations made by Wüst's pupil, Spieker, are then described, with a view to deciding as to the accuracy of the lines which are suggested by the phenomena observed by Carpenter and Keeling at the temperature of 1050°, 800°, and 600° C. (lines H–I, O–N, and Y–Z respectively, fig. 10). The readings were carefully taken of the cooling curves presented by a range of alloys containing ·10 to 4·30 per cent. of carbon cooled *in vacuo*, and the results may be given as follows:—

Fig. 15.—Unetched. Magnified 5 diameters.

The eutectic change at 1135° C. is noted in all the alloys of and above 2·45 per cent. C. No evidence was obtained of any evolution of heat at either 1050°, 800°, or 600° C., and he therefore considers that Carpenter and Keeling's observations are not substantiated, and that these lines in the diagram may be eliminated.

The pearlite change was observed at 700° C. in the whole range of the alloys from ·4 to 4·3 per cent. carbon.

Having already stated that the thermal methods do not sharply define the exact point at which the eutectic ceases to occur, Wüst proceeds to describe a most interesting set of experiments performed by Gutowsky. This

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[1] *Stahl und Eisen*, xxvii. pp. 1565–1571.

worker's method consisted of heating the various specimens slowly to the required temperature and then quenching. "In this way it is possible to observe the change from the homogeneous mixed crystals to that of the partly melted alloy, *i.e.* the temperature at which the solidus line is overstepped." It is claimed by Gutowsky that it is invariably found in such experiments "that the fluid portion contains more carbon than the solid portion with which it is in equilibrium." This method is of interest, and it is stated that if the solidus curve A–E, fig. 10, is overstepped, small rounded nodules or drops of supposed Ledeburite are to be observed through the section, whereas if the line has not been reached, the normal structure for the particular temperature at which the bars have been quenched will be observed. Hence it is claimed that the exact position of the solidus line can be determined by careful experiment. The experiments will now be described, but the author considers that further support should be obtained before the results are accepted.

FIG. 16.—Etched. Magnified 100 diameters.

Gutowsky's experiments were performed on alloys containing from ·50 to 1·74 per cent. of carbon. Quenchings below the line A–E are reported to have produced microsections containing no evidence of fusion, whilst it is claimed that after the line is overstepped microscopic evidence is obtained of local fusion.

Fig. 17 illustrates the structure of the 1·76 per cent. carbon alloy quenched at 1130°, *i.e.* just below the eutectic change point. It will be seen to present the austenitic structure usual after such quenchings. Fig. 18 illustrates the development in the structure upon quenching at 1167° C. Evidence would appear to be presented of the solidus line having been overstepped. The author would like here to call attention to the excellence of these micrographs, for which he is indebted to Dr Wüst. Fig. 19 illustrates the appearance

FIG. 17.—Etched. Magnified 200 diameters.

FIG. 18.—Etched. Magnified 200 diameters.

under a magnification of 1200 diameters of the local fusion zones occurring in the same section quenched at 1154° C. They are claimed to compare with the well-known eutectic structure.

Wüst considers that the alloys are in the molten state above ABD (fig. 10), and further that, whether in the molten or solid iron, the carbon exists in the combined state (at any rate, previously to dissociation after separation). On cooling, the carbide freezes out along BD, and it is by the dissociation of this carbide that, as suggested by Goerens, kish is produced.

Aachen first discovered that grey and white irons of similar composition freeze at the same temperature, and this fact, followed up and confirmed by Wüst, Heyn, and Goerens, has finally resulted in the now accepted theory that in either case it is primarily the cementite-austenite eutectic that is formed.

Fig. 19.—Etched. Magnified 1200 diameters.

It depends, therefore, upon the composition and conditions of cooling as to whether the carbide persists or not, and whether white or grey iron is produced. Wüst has shown that even in a purely iron-carbon alloy, allowed to cool very slowly, the whole of the carbon will be found in the free state.

Conclusions.—As a result, therefore, of a due appreciation of existing data, it is clear that the material collecting in the bath at the bottom of the blast furnace consists of a saturated solution of carbon in iron. As this cools down to the freezing range, carbide is thrown out of solution which simultaneously dissociates into iron and carbon, with the production of kish. The iron then freezes, the eutectic splitting up into austenite (solid solution) and carbide, which latter constituent, controlled by the prevailing conditions of rate of cooling and composition, either persists or dissociates. Further cooling causes the gradual precipitation of further free carbide, which behaves in a similar manner to the carbide separated at the eutectic change point. When we arrive at the temperature of the pearlite change point we still have the solid solution corresponding in composition to hardenite, which now resolves itself into carbide and free iron. The carbide will, again, either dissociate, with the production of perfectly soft pig iron, free from combined carbon, or will persist, and be recognised as the pearlite in the final iron.

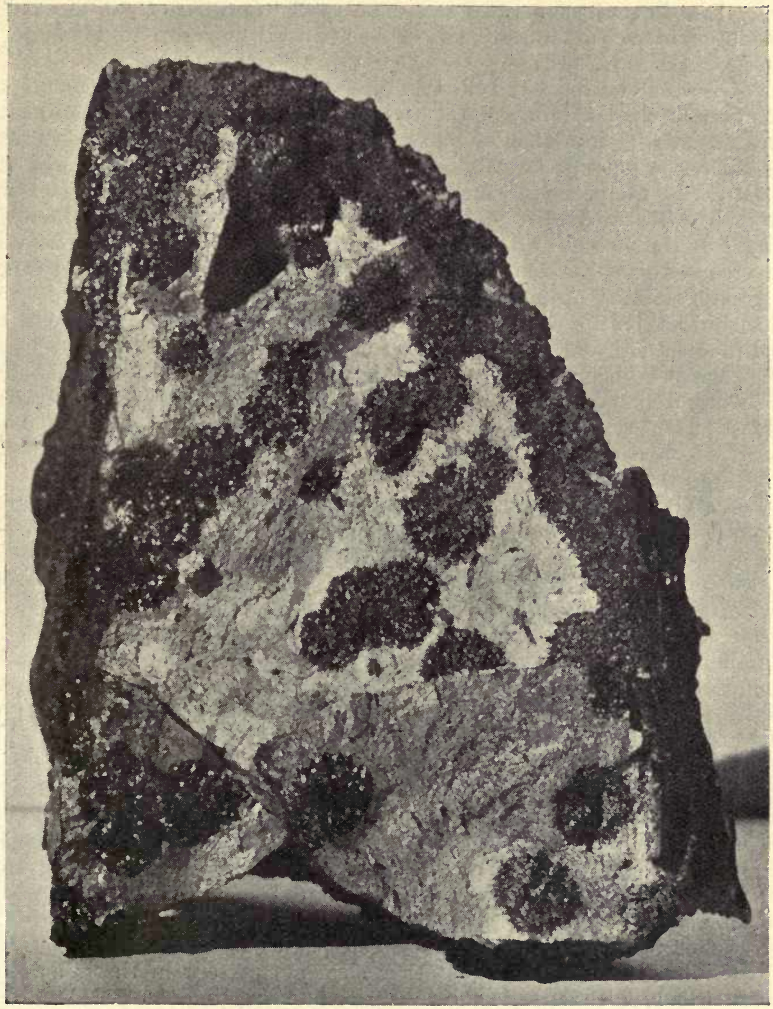

Fig. 20.—Fracture of white Swedish iron.

The black patches represent spherical graphitic formation shown in transverse section.

Consideration of Mottled Pig-iron Fractures.—In fig. 20 is shown a type of fracture which has from time to time been the subject of much discussion. This particular illustration is from a contribution by Sir R. Hadfield to a discussion upon Mr Saniter's paper upon Carbon and

Iron, read before the Iron and Steel Institute in 1897. It will be seen that it affords an instance of the fracture presenting the features both of white and grey iron. The question which then naturally arose was whether the white iron or the grey iron is the earlier formation.

H. M. Howe discusses this question in a recent paper upon the iron-carbon diagram, and gives a résumé of the arguments put forward in explanation of such fractures. His explanation will probably be found to be correct, and is as follows :—

"It is a well-established rule that pressure in and by itself favours the formation of the less bulky of the two phases. Now, the change from the state of cementite into that of bulky graphite implies much expansion, but this expansion must necessarily set up stress within the solid metal, and thus be resisted by the pressure which it itself sets up. Thus the very fact that this change from cementite to graphite does take place in spite of its being opposed by the pressure which it creates, argues that there is a force at work to overcome this opposition, and that force is a manifestation or symptom of the greater stability of the graphitic than the cementite state."

Such fractures are only found in irons containing a certain balance of the constituents; and, as Howe says, dissociation of the carbide on the outer edge takes place previous to the pressure being set up, both by the contraction of the cooling iron and also by the commencement of the dissociation at various centres. The pressure due to these causes is evidently sufficient to retain the carbon in combination in the white areas of the fracture seen in the photograph.

Does Graphite change to Cementite?—Under certain circumstances this action takes place, and always according to the following rule. Pure cast iron, perfectly cooled over a sufficiently long period, will be found to consist of the two phases, iron (ferrite) and graphite. If, however, the iron be cooled quickly from any temperature between 1135° C. and 700° it will be found to contain some of the carbon in the combined state and in varying degree. The diagram in fig. 10 will give an idea of the amount of carbon as carbide retained in solution in the iron by absolute quenching from various temperatures, and it will be seen to vary from over 2·0 per cent. down to ·89 per cent. If we, therefore, take the graphitic iron under discussion and maintain it at high temperatures, the carbon recombines with the iron and diffuses through the mass, and this action continues until equilibrium for the particular temperature is reached. Should the temperature be one of, say, 1050° C., it will be seen that more carbon is in solution than is necessary to form pearlite; and hence, if the iron is cooled fairly quickly, the carbon of supersaturation will separate as cementite. Thus is graphite converted into cementite; but it must be remembered that cementite is the meta-stable phase, which, given the necessary slow cooling, will again revert to the stable phases, iron and free carbon.

The influence of the various other elements present in the iron will be found treated under separate subsequent chapter headings.

CHAPTER II.

INFLUENCE OF SILICON.

After carbon, silicon is undoubtedly the most important constituent of cast iron. Although Gautier and C. Wood had previously indicated its influence, T. Turner's researches, published in 1885–6,[1] were apparently the first systematic investigations in this field.

The grey foundry irons of commerce, whether annealed or not (figs. 21 and 22), generally consist microscopically of a ferritic matrix, in which is observed free carbon along with varying amounts of pearlite. It is therefore essential that the influence of silicon on iron in the absence of carbon should be appreciated before passing to a consideration of the somewhat more complex subject in hand.

The Iron-Silicon Alloys.—Guertler and Tammann[2] describe the systematic investigation of an iron-silicon series of alloys. They also give an interesting epitome of the previous work done by other workers. The authors prepared a set of alloys varying from 5·0 to 88·0 per cent. of silicon, and carefully determined the freezing and other thermal data upon which the equilibrium diagram of the series is built (see fig. 23).

If reference be made to the diagram (fig. 23), it will be seen that up to 30 atoms per cent. (18 per cent. by weight) the silicon would seem to be present as Fe_2Si in solid solution (mixed crystals). The reason for this conclusion is that all the mixed crystals lying in this area of the diagram, on being treated with acids, give a residue corresponding to the formula Fe_2Si. The authors contend that had the silicon been present in simple solution, a residue much richer in silicon would, under these conditions, result. Further, they point out that the microstructures presented within this range, after etching with hydrochloric acid, are found to consist of a single constituent.

Figs. 24 and 25 typify the structures obtained with 31·2 and 42·4 per cent. (atoms) of silicon; and if studied in conjunction with the diagram, fig. 23, will be found of considerable interest.

It will be seen by the diagram that up to 31·0 per cent. (atoms) of silicon, which alloy constitutes the compound Fe_2Si, there is a progressively rapid lowering of the primary freezing points of the alloys, and then an equally rapid rise until the composition of 50 atoms per cent. (equal to the compound FeSi) is reached. Guertler and Tammann deduced from this that the compound FeSi is of a fixed chemical nature, and assert that such an alloy (50·2 atoms per cent., or 33·7 per cent. by weight) presents no break in its cooling curve in the eutectic ranges. If either more iron or silicon be added,

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[1] *Jour. Chem. Soc.*, vols. xlvii. and xlix.

[2] *Zeitschrift für anorg. Chemie*, vol. xlvii. p. 163.

FIG. 21.—Grey cast iron. Etched HNO_3. Magnified 52 diameters.

FIG. 22.—Annealed white cast iron. Etched HNO_3. Magnified 52 diameters.

the eutectic break in the curve becomes apparent. It is also stated that whilst it might have been expected that alloys between 33·0 and 50 atoms per cent. would consist of the FeSi crystals in a matrix of Fe_2Si, this was not so, the matrix in this range proving to be an eutectic containing 34·7 per cent. of Si.

Discussing the physical properties of these alloys, they found that the latent heat of fusion decreases greatly from silicon on the one hand to iron on the other. It was found that all the alloys containing up to 47·5 atoms per cent. Si exercised a strong influence upon a magnetic needle, but that the influence gradually decreased with further increase in silicon, until, with 50 atoms per cent., no attraction was noticed. Jouve found that the magnetic permeability became less with the increase in silicon, but not in a continuous manner, breaks being observed at 33·3 and 50 atoms per cent. Si. Curiously, the authors state that the presence of silicon does not materially influence the *Ar*2 point,[1] and give the following figures in support:—

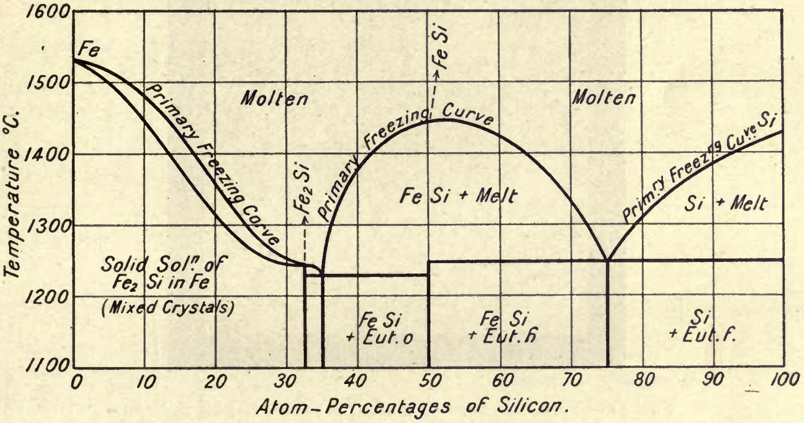

FIG. 23.—Atom-percentages of silicon.

Atoms per cent. Si.	Ar_2 recalescence °C.
0·06	760° ± 5°
10·40	750° ± 10°
20·00	745° ± 10°
29·10	735° ± 10°
38·60	770° ± 10°
47·50	720° ± 20°

Hadfield and also Baker found that the mechanical properties of the iron were not materially influenced with up to between 2 and 3 per cent. of silicon, such alloys of iron and silicon being quite ductile, and really indistinguishable from soft commercial wrought iron.

---

[1] If this is the transformation point of beta to alpha iron as described by allotropists, it is rather strange that it should persist in definite chemical compounds of iron and silicon.

FIG. 24.—Ferro-silicon. 31·2 atom per cent. silicon = Fe_2Si.

FIG. 25.—Ferro-silicon. 42·4 atom per cent. silicon showing Fe_2Si in eutectic matrix.

Baker gives the results of a most careful research, and the results of his analytical and accompanying mechanical tests are given in following tables.

Ingot No. . .	691.	728.	722.	745.	731.	723.	730.	782.	749.	729.
Silicon charged .	...	1·1	2·2	3.2	4·2	5·6	6·3	7·8	8·6	...
Combined carbon.	0·044	0·038	0·039	0·038	0·038	0·040	0·038	...	0·030	0·036
Silicon . .	0·024	1·020	2·125	2·903	4·026	4·885	5·998	7·470	7·952	10·955
Manganese . .	0·036	0·079	0·040	0·061	0·062	0·072	0·061	0·210	0·046	0·122
Aluminium . .	0·010	0·016	0·048	0·069	0·091	0·141	0·098	0·050	not determined	
Sulphur . .	0·030	0·038	0·029	0·041	0·033	0·027	0·032	0·011	0·025	0·025
Phosphorus . .	0·014	0·019	0·020	0·018	0·018	0·021	0·020	0·019	0·30	0·044
Iron (by difference)	99·842	98·790	97·689	96·870	95·733	94·814	93·753	...	..	...
Total impurities.	0·134	0·190	0·176	0·227	0·242	0·301	0·249	...	...	...

Ingot No.	Silicon per cent.	Condition.	Elastic limit, tons per sq. in.	Maximum stress, tons per sq. in.	Elongation per cent. on 2 in.	Reduction of area per cent.	Remarks on Fracture, etc.
691	0·024	Rolled	?	23·94	37·5	68·6	Grey granular.
,,	,,	,,	20·09	25·11	43·0	68·0	,,
,,	,,	Normal	11·48	22·41	42·5	66·3	,,
,,	,,	,,	11·73	22 71	43·5	67·7	,,
,,	,,	Annealed	?	23·29	44·0	74·1	,,
,,	,,	,,	19·87	21·96	50·0	68·9	,,
728	1·020	Rolled	27·18	30·62	36·0	69·2	Grey granular.
,,	,,	,,	26·99	30·93	37·5	65·6	,,
,,	,,	Normal	23·93	30·66	35·5	67·0	,,
,,	,,	,,	25·33	30·59	35·5	66·6	,,
,,	,,	Annealed	21·33	28·26	41·5	77 1	Grey granular, bordering on crystalline.
,,	,,	,,	18·76	26·11	39·0	75·4	,, ,, ,,
722	2·123	Rolled	27·97	35·32	27·5	46·4	20 per cent. crystalline, 80 per cent. grey granular.
,,	,,	,,	27·74	35·46	28·5	44·4	50 ,, ,, 50 ,, ,,
,,	,,	Normal	21·05	32·30	25·5	31·4	Finely crystalline.
,,	,,	,,	21·80	32·90	24·5	26·1	,,
,,	,,	Annealed	19·45	29·78	38·5	65·7	Grey granular, bordering on crystalline.
,,	,,	,,	20·23	30·22	40·0	66·1	,, ,, ,,
745	2·903	Rolled	30·20	37·56	30·0?	52·7?	Finely crystalline, flaw in piece.
,,	,,	,,	29·28	37·24	15·5	14 6	,,
,,	,,	Normal	27·88	30·40	3·0	3·1	Coarsely crystalline.
,,	,,	,,	26·84	32·28	5·5	5·2	,,
,,	,,	Annealed	19·08	33·48	35·5	59·5	Very finely crystalline, with small grey granular area in centre.
,,	,,	,,	24·76	34·32	35·5	60·6	
731	4·026	Rolled	Coincides with Maximum Stress.	40·10	Nil	Nil	Coarsely crystalline.
,,	,,	,,		43·43	,,	,,	,,
,,	,,	Normal		36·56	,,	,,	,,
,,	,,	,,		36·50	,,	,,	,,
,,	,,	Annealed		43·57	3·0	4·0	,,
,,	,,	,,		43·55	1·5	1·7	,,

Ingot No.	Silicon per cent.	Condition.	Elastic limit, tons per sq. in.	Maximum stress, tons per sq. in.	Elongation per cent. on 2 in.	Reduction of area per cent.	Remarks on Fracture, etc.
723	4·885	Rolled	Coincides with Maximum Stress.	40·81	Nil	Nil	Coarsely crystalline.
,,	,,	,,		42·54	,,	,,	,,
,,	,,	Normal		36·27	,,	,,	,,
,,	,,	,,		36·42	,,	,,	,,
,,	,,	Annealed		41·46	,,	,,	,,
,,	,,	,,		41·46	,,	,,	,,
730	5·998	Rolled	Coincides with Maximum Stress.	21·36	Nil	Nil	Coarsely crystalline.
,,	,,	,,		18·70	,,	,,	,,
,,	,,	Normal		16·14	,,	,,	,,
,,	,,	,,		16·09	,,	,,	,,
,,	,,	Annealed		26·16	,,	,,	,,
,,	,,	,,		27·00	,,	,,	,,
782	7·47	Rolled	Coincides with Maximum Stress.	26·26	Nil	Nil	Coarsely crystalline, broke in shoulder.
,,	,,	,,		21·54	,,	,,	,, ,,
,,	,,	Normal		24·00	,,	,,	,,
,,	,,	,,		17·38	,,	,,	,,
,,	,,	Annealed		21·06	,,	,,	,, broke in shoulder.
,,	,,	,,		,,	,,	,,	,,

It will be seen that up to 2·0 per cent. of Si the ductility of the iron is not materially affected. One interesting feature which this work brought out was that the *Ar*2 recalescence point was lowered on the average 8° C. for each unit percentage increase of silicon, and yet, as will be shown later, in the presence of large percentages of carbon the contrary is the effect.

To prove that the ferritic matrix of soft grey or annealed white iron is no more affected by the presence of silicon than pure iron, the author[1] presents a set of heat-treated white irons of varying silicon percentages, which microscopically consisted only of ferrite and annealing carbon nodules. They all gave a good bending angle of about 90°, and the static tests failed to reveal any influence exerted by the silicon present upon the character of the ferritic matrix. The analyses and bending angles are given in the following table:—

	Si per cent.	CC per cent.	Gr per cent.	Mn per cent.	S per cent.	P per cent.	Bending Angles.
A	0·45	0·05	3·10	0·20	0·05	0·05	95
B	0·90	0·06	3·11	0·21	0·05	0·05	98
C	1·10	0·05	3·11	0·20	0·05	0·05	94
D	1·88	0·07	3·05	0·19	0·05	0·05	89

It may therefore be concluded that normal percentages of silicon do not materially affect the properties of the iron by direct influence.

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[1] *Jour. Iron and Steel Inst.*, 1906.

The Influence of Silicon upon the Solubility of Carbon in Iron. —Silicon, when added to iron in the presence of carbon, materially affects it by reducing the solubility of carbon, and this phase has been very carefully investigated by Wüst and Petersen.[1] Their results are tabulated below, and it will be seen that the eutectic alloy containing 4·3 per cent. of carbon is considerably modified, and that at what is a frequent commercial percentage of silicon, viz. 3·0 per cent., the carbon percentage of the eutectic is reduced to 3·4 from 4·3 per cent.

No. of Test.	Si per cent.	Total Carbon.	Freezing point °C.
1	·13	4·29	1138
2	·21	4·23	1131
3	·66	4·05	1152
4	1·14	3·96	1155
5	1·41	3·88	1160
6	2·07	3·79	1175
7	2·68	3·56	1185
8	3·25	3·41	1187
9	3·69	3·32	1197
10	3·96	3·24	1205
11	4·86	3·08	1210
12	5·06	2·86	1215
13	13·54	1·94	1233
14	18·76	1·19	1240
15	26·93	0·87	1255

It will be found that the pig irons of commerce generally contain about the eutectic percentage of carbon for the given composition. This is explained by the fact that the normal conditions prevalent in the blast furnace facilitate the absorption of carbon up to saturation for the particular temperature, and during cooling to the freezing point the excess carbon is thrown off as kish (as discussed upon page 22), until at the eutectic composition freezing takes place. Taking this fact into consideration with the results of Wüst and Petersen, it will be seen that the presence of silicon slightly raises the freezing point. This action is obviously due to the reduction of the total carbon content. (See diagram, page 16.)

The Influence of Silicon upon the Properties of Cast Iron.—Percy emphasised the importance of the presence of silicon, and Lowthian Bell went so far as to say that, whilst in excess it was detrimental, "still in moderate quantities it should be sought after." It was, however, left to T. Turner to define and to explain the actual influence and the considerable advantages to be obtained by the scientific control of this useful element. Turner prepared a series of test bars of varying silicon content by melting siliceous pig iron and wrought iron with an excess of carbon. The total carbon was kept in the region of 2·0 per cent., so that the whole of the series might be comparative, as it would naturally, with the higher percentages of silicon, have been impracticable to run the carbon at the normal percentage found in the foundry pig iron of commerce. The alloys were cast into ingots, which were subsequently broken up, remelted, and cast into the test bars used in the experiments. The test bars were 1⅛ of an inch

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[1] *Metallurgie*, vol. iii. pp. 811–820.

in diameter, with a parallel of 16 inches. After exhaustive analyses, the bars were broken on the Mason College testing machine by Professor Kennedy. The results, both of the analytical and mechanical tests, will be found in the following table :—

EFFECT OF SILICON ON THE PROPERTIES OF CAST IRON.

Silicon per cent. (calculated).	Relative density at 20° C. (Water at 20°=1).		Relative hardness.	Tensile Strength= per sq. in.		Modulus of Elasticity.	Crushing Strength per sq. in.		Calculated transverse Strength. Bars 1 foot long, 1 in. square, loaded in the centre.		Chemical Analysis.						
	Cylinders.	Turnings.									Total Carbon.	Graphite.	Combined Carbon.	Silicon.	Phosphorus.	Manganese.	Sulphur.
				lbs.	tons.		lbs.	tons.	lbs.	tons.							
0	7·560	7·719	72	22,720	10·14	25,790,000	168,700	75·30	2702	1·206	1·98	0·38	1·60	0·19	0·32	0·14	0·05
0·5	7·510*	7·670	52	27,580	12·31	28,670,000	204,800	91·42	3280	1·464	2·00	0·10	1·90	0·45	0·33	0·21	0·05
1	7·641	7·630	42	28,490	12·72	31,180,000	207,300	92·54	3370	1·504	2·09	0·24	1·85	0·96	0·33	0·26	0·04
1·4	7·555	7·473	..	31,440	14·04	23,500,000	183,900	82·08	3498	1·561	2·21	0·50	1·71	1·37	0·30	..	0·05
2	7·518	7·350	22	35,180	15·70	23,560,000	137,300	61·29	3446	1·538	2·18	1·62	0·56	1·96	0·28	0·60	0·03
2·5	7·422	7·388	22	32,760	14·62	25,450,000	172,900†	77·18†	3534†	1·577†	1·87	1·19	0·68	2·51	0·26	0·75	0·05
3	7·258	7·279	22	27,390	12·23	21,150,000	128,700	57·45	2850	1·272	2·23	1·43	0·80	2·96	0·34	0·70	0·04
4	7·183	7·218	27	25,280	11·28	15,640,000	106,900	47·74	2543	1·135	2·01	1·81	0·20	3·92	0·33	0·84	0·03
5	7·167	7·170	32	22,750	10·16	18,720,000	103,400	46·16	2342	1·046	2·03	1·66	0·37	4·74	0·30	0·95	0·05
7·5	7·128	7·138	42	11,950	5·34	14,750,000	111,000	49·55	1505	0·672	1·86	1·48	0·38	7·33	0·29	1·36	0·03
10	6·978	6·924	57	10,630	4·75	13,930,000	76,380	34·10	1252	0·559	1·81	1·12	0·69	9·80	0·21	1·95	0·04

* This number is rather low, as the specimen afterwards proved to be somewhat faulty.

† The value in this case is probably exceptionally high ; a crushing strength of about 60 tons might be anticipated from its position in the series.

The fractures are carefully described by Turner, and should be considered along with the results in the foregoing table.

8807. Crystalline silvery, not sound, rough edges.
8448. Silvery, a blowhole $\frac{1}{4}$ dia.
8447. Silvery with some large facets, irregular, and discoloured in centre.
8446. Close-grained blue-grey, somewhat unsound, and lighter in colour than 8444.
7867. Ordinary close-grained cast iron, small blowhole.
8445. Similar 8446.
8444. Close-grained blue-grey, somewhat unsound.
8894. Close-grained grey, granular fracture, face unsound.
7866. Sound, close-grained, silvery fracture, without large facets.
7865. Large crystalline, with silvery facets, colour very light.

Upon an examination of the analyses of these bars it will be seen that, apart from a gradual rise in the manganese percentage due to the composition of the siliceous iron used, the analyses are comparative, but, in drawing deductions, the reader should, as Turner states, bear in mind that the results are for certain definite conditions. The results are given diagrammatically in fig. 26.

It will be seen that the maximum tensile is obtained with 1·96 per cent.

of silicon and 0·56 per cent. combined carbon; the best crushing strengths were obtained when the silicon did not exceed 1·00 per cent., and the combined carbon approximated to 2·0 per cent. The importance of these results lay chiefly in the fact that they systematically demonstrated that it was by controlling the condition of the carbon that the mechanical properties of the alloys were influenced by the silicon content.

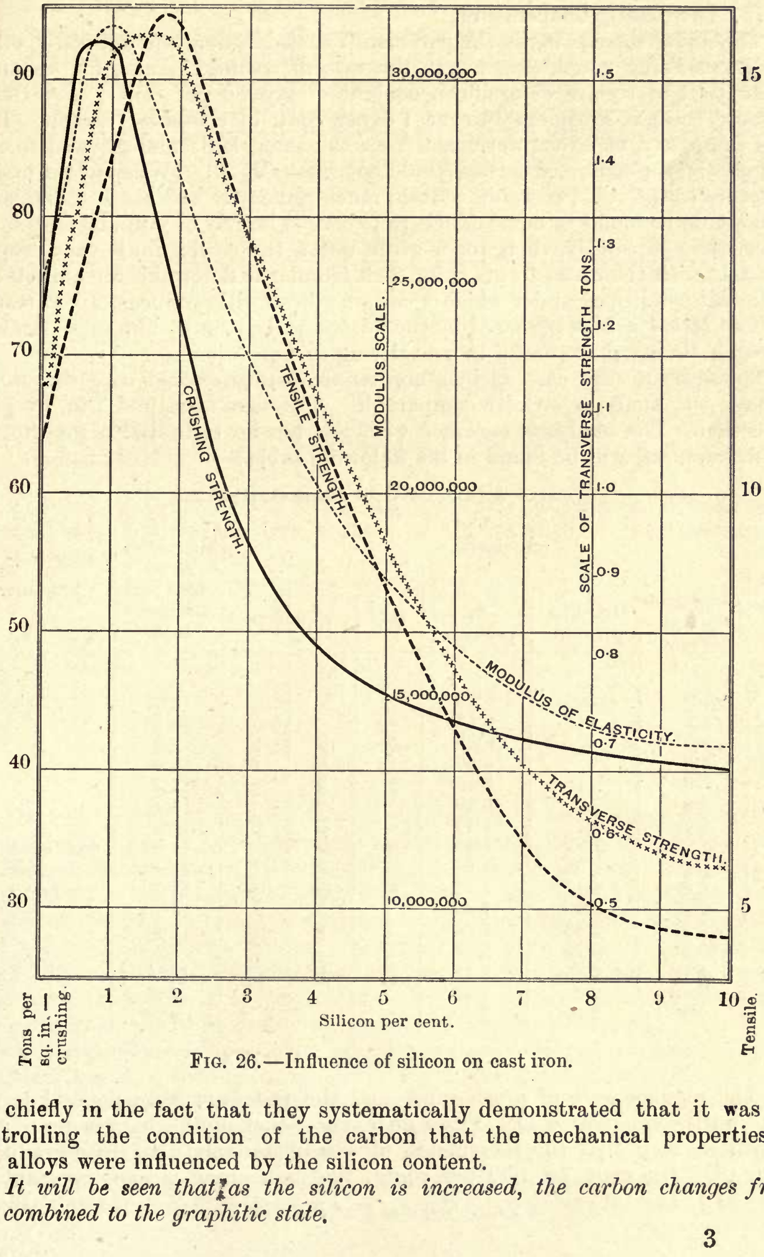

FIG. 26.—Influence of silicon on cast iron.

It will be seen that as the silicon is increased, the carbon changes from the combined to the graphitic state.

Conditions which modify the Influence of Silicon.—The influence of silicon is greatly modified by varying conditions, the chief of which are—

(1) The size of the casting.
(2) The rate of cooling.
(3) The casting temperature.

The size of the casting is the paramount consideration, and naturally, other conditions being equal, determines the rate of cooling. Take, for instance, a test bar 1 in. square of a silicon content of say ·80 per cent.; most likely it would contain considerably over 1·0 per cent. of combined carbon. If a solid lump, say, of 2 tons were cast from the same ladle and allowed to cool very slowly, the combined carbon would be practically nil. Whereas the microstructure of the test bar would contain much cementite and pearlite, the large mass would be found in microstructure to consist largely of graphite embedded in ferrite. Obviously, then, for a given effect, the silicon must vary proportionately with the mass, and it is for each founder to determine for himself the particular conditions under which a certain silicon will produce a given result.

Two series of bars prepared by the author, and given by him in a Carnegie Research Memoir,[1] are useful in considering this question.

The first set were cast at just normal temperatures, and care was taken to have the analyses strictly comparable. The bars measured 1 in. by $\frac{3}{8}$ in. in section. The analyses, together with the tensile tests and a description of the fractures, will be found in the following table:—

SERIES A (ALL CAST AT NORMAL HEAT).

Test No.	Analysis.						Maximum stress tons per square inch.	Fracture.
	Combined Carbon per cent.	Graphite per cent.	Si per cent.	Mn.	S.	P.		
7	2·9	trace	0·28	Not exceeding 0·20 per cent.	Not exceeding 0·05 per cent.	Not exceeding 0·05 per cent.	18·0*	white.
8	2·9	,,	0·53				22·8	,,
9	2·9	,,	0·63				14·5	,,
10	2·9	,,	0·66				13·4	,,
11	2·9	,,	0·88				17·4	,,
12	2·9	,,	0·99				18·1	,,
13	3·0	,,	1·10				16·0	,,
14	2·7	0·28	1·43				11·22	trace mottled.
15	2·3	0·65	1·68				11·40	mottled.
16	0·6	2·47	1·72				12·70	grey.
17	0·55	2·6	1·80				10·70	,,
18	0·55	2·68	1·96				14·9	,,
19	0·5	2·75	2·07				8·5	,,
20	0·5	2·75	2·19				15·6	,,
21	0·49	2·8	2·36				9·8	,,
22	0·48	2·85	2·50				9·06	,,

* ? unsound.

The moulds were of green sand, and the test bars were not "knocked out" until completely cold. From an examination of the figures presented, it will be seen that the increments of silicon are small, and rise gradually from 0·28 per cent. to 2·50 per cent.; the manganese is kept constant at

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[1] *Jour. Iron and Steel Inst.*, 1906.

slightly under ·20 per cent.; the sulphur and phosphorus are constant with ·05 per cent.

The remarkable feature is the very rapid change of the carbon from the combined to the free state (see diagram, fig. 27).

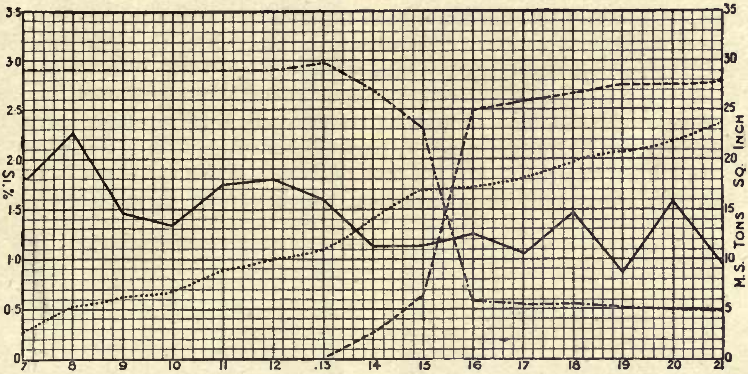

FIG. 27.—(Test Nos., series "A.")—Curve II.

It was to be expected that the gradually increasing silicon would gradually precipitate the free carbon, as for instance in the case recorded by Longmuir:—

	Combined Carbon.	Graphite.	Si.	Mn.	S.	P.
A	3·4	...	0·04	0·03	0·03	0·02
B	3·4	0·06	0·11	0·10	0·02	0·02
C	3·3	0·21	0·35	0·18	0·04	0·013
D	3·0	0·35	0·45	0·04	0·04	0·017

It will, however, be seen that in this instance no gradual precipitation was obtained, and it would certainly appear that 3·0 per cent. of carbon was held in combination in spite of the presence of 1·43 per cent. of silicon, and then that the further addition of silicon seems rapidly to have decreased the power of the iron to retain the carbon in combination, with the result that 1·7 per cent. of silicon produced a completely grey bar. It must here be distinctly understood that the bars were of the small section already stated, but even then it will be seen that it needed only a comparatively small increase in silicon completely to overcome the chill of the mould.

If comparison of the mechanical tests is made with the results of Professor Turner, it will be seen that, instead of a gradual rise and fall to and from a maximum, there is in this instance a quite irregular curve (fig. 28).

In test 8, with 0·53 per cent. of silicon, a tensile stress of 22·8 tons per sq. in. is obtained, the whole of the carbon being in the combined state. It will also be seen that a tensile stress of 15·6 tons was obtained with a silicon content of 2·19 and 2·75 per cent. of graphite. The results would certainly indicate that low silicon and high combined carbon give the best results when the bars are tested in tension.

The noticeable irregularities in the mechanical results were carefully investigated, and generally the microstructure accounted in part for the variations. For instance, Nos. 8 and 9 varied by 8·3 tons. Judging by the fracture, both would be considered good samples of white iron, No. 9, however, having a somewhat coarser crystallisation than No. 8. The microscope revealed the normal cementite-pearlite structure of white iron in each case, but there was a distinctly different arrangement of the micro-constituents.

Photomicrographs, figs. 29 and 30, respectively illustrate this. No. 8 has a well-mixed structure showing no particular arrangement, the whole mass being well knit together; in the case of No. 9, however, there is a definite orientation of the cementite membranes, which run in distinct lines, and no doubt cause planes of weakness. This variation is most likely due to some elusive condition prevailing during the casting operations.

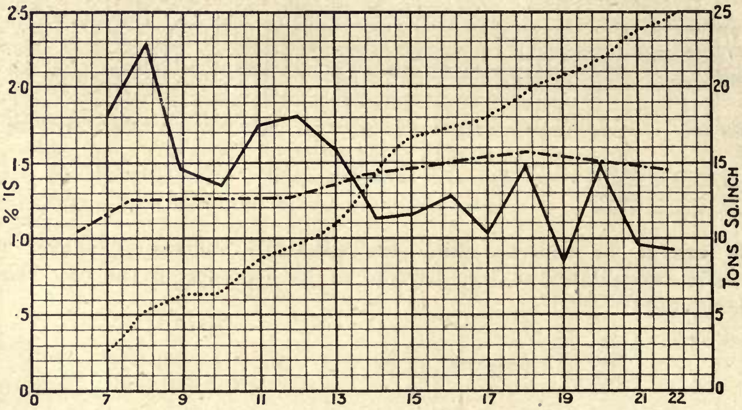

Fig. 28.—(Test Nos., series "A.")—Curve III.

To take a case of variation in the grey iron bars, it will be seen that whilst No. 19 possesses a tensile strength of 8·5 tons per sq. in., No. 20 gave 15·6 tons. Here it is curious to relate that the only distinction was in the fact that, after etching, the sections were seen macroscopically to be split up by thin membranes of a non-etching constituent, afterwards proved to be cementite. It was noticed that the 15·6 ton bar had a larger and more distinct crystallisation than the bar giving the lower test. This phenomenon has since been confirmed by Messrs Cook and Hailstone, although the author considers those workers are mistaken when they attribute the appearance to the phosphide eutectic. They give two bars, one with a tensile strength of 9·1 tons per sq. in., and the other with a tensile of 18·3 tons, with a constant silicon of 1·32 per cent., with combined carbon recorded as 0·85 and 0·90 per cent. respectively. These figures are interesting as an instance in which other influences were of greater importance than the silicon content.

It was stated earlier that the casting temperature considerably modified the influence of silicon. The second series published by the author in the paper already referred to illustrate this phase. This second series were made comparable with the former, and the only variable influence, to the author's knowledge, was the temperature at which the bars were cast. The casting temperature is uniformly higher in the later than in the earlier set. The analyses and mechanical results are set forth in the curve, fig. 31, and following table.

Fig. 29.

Fig. 30.

White Cast Irons, similar in composition. Fig. 29 gave 22·8 tons per square inch. Fig. 30 gave 14·5 tons. Magnification, 45 diameters. Both etched with nitric acid. It will be seen that both these sections consist of cementite filled in with granular pearlite.

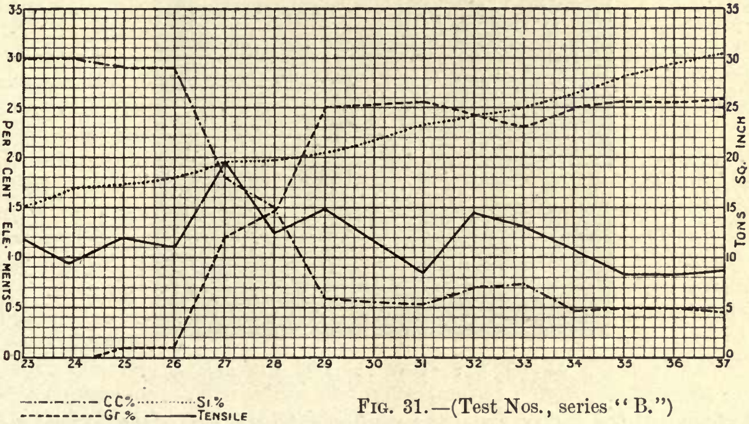

Fig. 31.—(Test Nos., series "B.")

SERIES B (CAST HOTTER THAN SERIES A).

Test No.	Analysis.						Maximum stress tons per square inch.	Fracture.
	Combined Carbon.	Graphite.	Si.	Mn.	S.	P.		
	per cent.	per cent.	per cent.					
23	3·00	trace	1·51	Not exceeding 0·20 per cent.	Not exceeding 0·05 per cent.	Not exceeding 0·05 per cent.	11·6	white.
24	3·00	,,	1·71				9·4	,,
25	2·90	0·10	1·73				12·0	slightly mottled.
26	2·91	0·11	1·80				11·0	,,
27	1·78	1·20	1·95				19·6	mottled.
28	1·50	1·47	1·97				12·4	,,
29	0·62	2·50	2·05				15·0	grey.
31	0·55	2·55	2·31				8·4	,,
32	0·73	2·40	2·41				14·4	,,
33	0·75	2·30	2·50				13·1	,,
34	0·49	2·50	2·67				10·60	,,
35	0·51	2·55	2·82				8·19	,,
36	0·52	2·55	2·94				8·21	,,
37	0·47	2·60	3·05				8·66	,,

It will be noticed, in regard to the tensile results, that the two series are only consistent in their inconsistency. The main point, however, is that the rapid change of the carbon from the combined to the free state is confirmed; the change, however, owing to the much higher casting temperature, takes place with a higher silicon content. As a result of these experiments, the author

FIG. 32.—Etched HNO_3. Magnified 52 diameters.

made further observations[1] upon this feature, and one experiment in particular is worthy of being described.

Two bars, 2 in. by 1 in. by 12 in., from the same ladle of iron, were cast of the following composition:—

Carbon	3·20 per cent.
Silicon	1·10 ,,
Sulphur	0·02 ,,
Phosphorus	0·20 ,,
Manganese	8·41 ,,

The first was cast at 180° C. higher temperature than the other. Upon breaking the bars, the higher temperature one was found to be mottled white, whilst the low temperature one was found to be grey. The microstructure in the white areas of the first corresponded with the normal white iron cementite-pearlite structure (see fig. 34), whilst that cast at the lower temperature, upon examination, proved to have the microstructure as illustrated in figs. 32 and 33. The author considers sufficient evidence has now been given as to the influence of casting temperature upon the effect of a given silicon.

The general Influence of Silicon further discussed.—It will be of interest to here include some of the results of a recent research published by Haigh and Turner. A series of iron-carbon-silicon alloys were prepared by these workers, and the analytical and thermal data are now presented (page 41).

It will be observed that in each alloy of this series three temperature arrests are noticed. The first, varying from 1195° C. to 1247° C., is obviously due to the separation of the primary austenite, the irons, as will be seen from the table, containing considerably less carbon than is necessary to produce the eutectic composition. The second arrest, which is very distinct, is due to the freezing of the iron-carbide eutectic: it is of interest to note that the temperature of this arrest increases with the addition of silicon. The third arrest, also very distinct through the whole of the series, is due to the resolution of the solid solution into pearlite. The position of this point is profoundly affected by the increase of the silicon content, the temperature of the change being progressively increased until with 4·83 per cent. Si it has risen from 700° C. to 795° C. This series of iron contained no manganese, and it is interesting to record that in a comparable alloy to which 0·50 per cent. manganese had been introduced the freezing point of the iron-iron-carbide eutectic was lowered 15° C., whilst that of the pearlite change dropped 87° C. This action of manganese is, however, discussed under another heading (see p. 80).

The results obtained with Turner's extensometer (p. 116) are typified in fig. 35.

Whilst with the pure washed iron a practically uniform contraction takes place, it was found that with the addition of silicon, without any change in the condition of the carbon, a very different cooling curve was obtained. Whereas in the washed iron only slight expansions were noticed whilst passing the eutectic freezing and pearlite change point, in the silicon white iron a considerable expansion took place immediately upon solidification, and also upon passing the pearlite change.

With the alloy containing 1·19 per cent. of silicon there is the first considerable appearance of graphite, and consequently a marked increase in the expansion both in period and magnitude.

Haigh and Turner, in discussing the combined carbon retained in the

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[1] *Royal Society* (*Proceedings of*), A, vol. lxxxv., 1911.

samples, confirm that with the increase in silicon the carbon required to form

Fig. 33.—Unetched. Magnified 52 diameters.

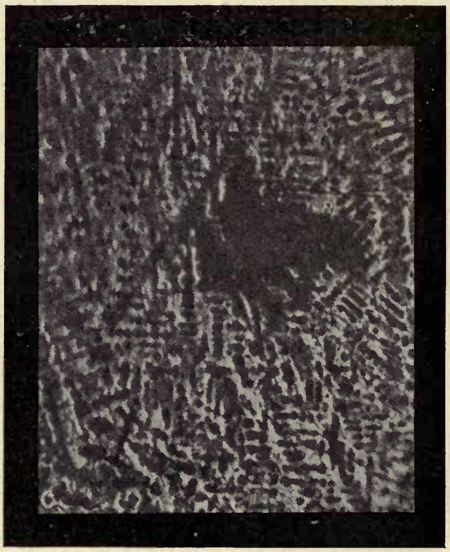

Fig. 34.—Etched HNO_3. Magnified 52 diameters.

a saturated solid solution is less. They further state that whereas with pure iron saturation is reached at 0·90 per cent. carbon, with 4·8 per cent. silicon it is reached at 0·64 per cent.

The hardness tests were performed upon this series with the scleroscope, and the results are indicated in fig. 36. It would appear that when free carbon does not result, the addition of silicon hardens the iron.

SILICON AND CARBON CONTENTS AND TEMPERATURE ARRESTS.

No. of bar.	Fracture.	Silicon.	Total Carbon.	Graphitic Carbon.	Combined Carbon (by diff.).	Temperature Arrests.			Other Arrests.
						H_1(°C.).	H_2(°C.).	H_3(°C.).	
		per cent.	per cent.	per cent.	per cent.				
1	White	0·03	2·71	0·16	2·55	1245	1138	700	Indications in most cooling curves between the temperatures 800° C. to 900° C. of a slight arrest corresponding to bend out in extensometer curve before the bending corresponding to H_3.
2	,,	0·23	2·61	0·17	2·44	1217	1138	714	
3	,,	0·66	2·95	0·13	2·82	1244	1136	726	
4	,,	0·97	2·56	0·23	2·33	1247	1136	730	
5	Grey	1·19	2·70	1·32	1·38	1244	1136	734	
6	,,	1·50	2·48	1·29	1·19	1230	1137	739	
7	,,	1·95	2·47	1·50	0·97	1246	1141	746	
8	,,	2·18	2·54	1·50	1·04	1213	1146	752	
9	,,	2·43	2·54	1·51	1·03	1243	1146	752	
10	,,	2·77	2·67	1·47	1·20	1238	1148	754	
11	,,	2·80	2·51	1·48	1·03	1245	1153	764	
12	,,	3·06	2·77	1·93	0·84	1202	1154	774	
13	,,	3·47	2·79	1·87	0·92	1195	1158	780	
14	,,	4·03	2·34	1·55	0·79	1220	1160	774	
15	,,	4·43	2·41	1·75	0·66	1201	1160	786	
16	,,	4·83	2·26	1·62	0·64	1211	1161	795	
17	,,	*3·00	2·62	2·40	0·22	1210	1146	687	

*Manganese = 0·5 per cent.

Summing up, therefore, it must always be understood that the influence of silicon is always conditional, and is exerted indirectly by its influence upon the condition of the carbon. The author remembers, through the courtesy of H. E. Field, once seeing a 90-ton iron casting made in Pittsburg. The prolonged cooling of such a mass would discount to a large extent any other influence, and undoubtedly the material in such a case would show an unquestionably graphitic structure, even with a very low silicon content.

It has now been shown that the influence of silicon is conditional, but, nevertheless, the author would be the last person to detract from the practical utility of the control of this element in works practice. If any particular quality is desired in cast iron, it can generally be obtained by suitably regulating the percentage of silicon. As a general rule, the figures given by McWilliam and Longmuir[1] represent safe practice, and are here reproduced.

Type of Casting.	Silicon per cent.
Chilled grey iron castings . .	·75 to 1·00
High pressure cylinders . .	1·30%
General machinery . . .	1·50%
Soft iron castings . . .	2·50%
Stove grate, etc.	2·5% to 3·0%
Hollow ware	3·0% to 3·5%

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[1] *General Foundry Practice.*

The above figures are only tentative, and are much influenced by the

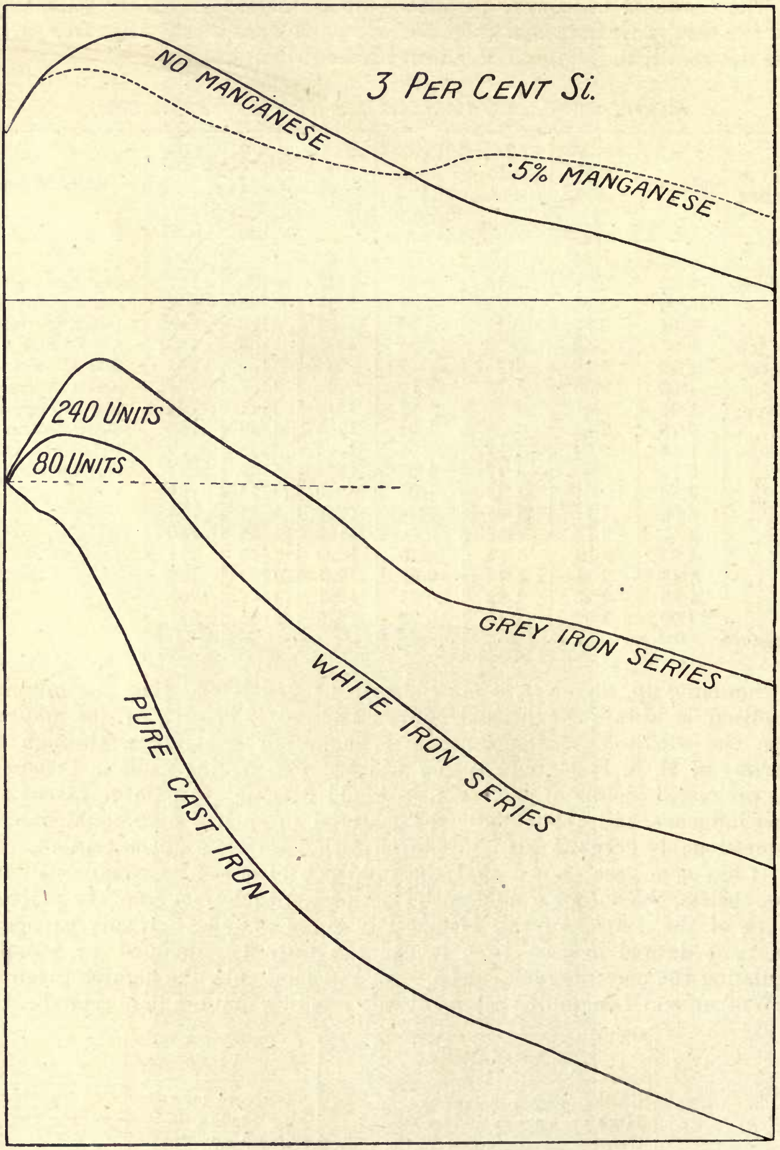

Fig. 35.

conditions before described. Still, if the iron in a foundry is running hard or soft, or is showing too much shrinkage, it will be found that an investigation of the silicon content, other conditions being equal, will satisfactorily provide a solution of the trouble.

It may not here be out of place to discuss the influence of remelting. From the interesting early experiments of Fairburn down to the latest published data, the modification of the properties of cast iron by remelting is emphasised in importance. The one essential fact is that with each remelt the silicon is reduced, and thus the iron is rendered harder. This tendency is also usually accentuated by small increments of sulphur derived from the fuel, which incidentally assists in producing similar results.

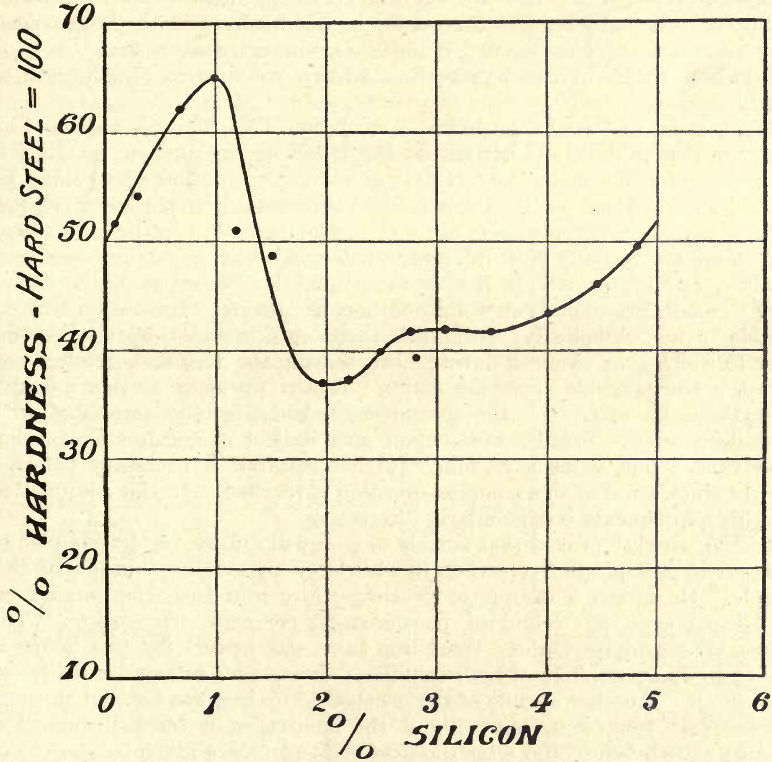

FIG. 36.

The influence of varying percentages of silicon in modifying the properties of cast irons under heat treatment will be found separately treated under another heading in Chapter XII. p. 154.

How does the Silicon cause the Precipitation of Free Carbon?—Before this question can be discussed, it is necessary first to determine in which of the constituents the silicon exists, not only in the final product, but also during the whole of the period following upon solidification.

It was shown in the previous chapter that all pig irons immediately after solidification carry their carbon primarily as carbide, which either persists or dissociates into iron and carbon, with the production of graphite. To take, then, an iron of eutectic composition. Previous to solidification, the silicon, whatever elements it may be combined with, is in solution. Upon solidification, the eutectic breaks up into the cementite carbide and austenite (solid solution), and the question naturally suggests itself, Where, then, is the silicon—in the carbide or in the austenite? It is to be deduced that it must be in solid solution as silicide in either or both the carbide and austenite. There is, of course, always the possibility that it may, under some conditions, form other compounds.

Several investigations have of late been conducted with a view to throwing light upon this subject. Gontermann, in his work upon the iron-carbon-silicon system, to which reference is made elsewhere, considers that it is to be found in both the carbide and austenite, and this would seem to be proved by recently published work.

Stead, in his address to the British Association, 1910, describes some of his work upon this subject, and arrives at the following conclusions, *i.e.* that in low silicon irons the austenite retains the silicon in solution as silicide; he, however, considers that as the silicon content is increased, some must crystallise with the carbide as carbo-silicide of iron; and he finds that in the high silicon alloys there are actually two different cementites which crystallise out from the alloy, one comparatively free from silicon, the other containing much of the element, presumably in solid solution as silicide. He claims that he was able to microscopically distinguish these two carbides by the varying degree to which they oxidised during heat tinting, the former becoming red, whilst the silico-carbide remained white. To the presence of this unstable silico-carbide he attributes the graphitic condition usually associated with high silicon irons. Stead's work upon this subject constitutes a considerable advance; but, as he says, much further research is necessary before a complete elucidation of this complex question is reached. In this conjunction one of his experiments is particularly interesting.

It being already proved that silicide of iron will diffuse, he determined to endeavour to precipitate free carbon in white iron by availing himself of this principle. He mixed a sample of crushed white iron free from impurities, with 10 per cent. by weight of powdered 20 per cent. ferro-silicon. The mixture, after compression in a short iron tube, was heated for two hours at 1000° C. in an atmosphere of hydrogen gas. It was then removed and allowed to cool in air. Another sample of the crushed white iron was also put through the same heat treatment, but without the admixture of ferro-silicon. The combined carbon before and after the heat treatments are given below:—

	Before.	After.
White iron heat treated alone	3·50	3·44
,, ,, with silicide . .	3·20	0·60

He considers that this experiment conclusively demonstrates that the carbon in the carbide may also be precipitated by the diffusion of the silicide from the austenite of the alloys at high temperatures.

The present author has done some research work upon this question, and also finds that some of the silicon does actually crystallise with the carbide, and further finds that this proportion in the carbide increases somewhat in ratio with the increase in silicon in the alloy. He, however, finds that when the iron-iron-carbide eutectic containing this element solidifies, the greater portion is retained in solid solution in the austenite.

Heat treatment experiments, described elsewhere (page 169), taken into consideration with chemical investigations, in the author's mind certainly point to the silicon content of the carbide being responsible for the varying degree of stability of that constituent.

Further, to discuss the precipitation of the free carbon. In high silicon irons, during the further cooling down of the solid solution (austenite) remaining after the separation of the primary graphite, more cementite carbide is liberated. This carbide will, it is to be presumed, have more or less silicide associated with it, and will also be less likely to persist the higher the silicon content of the iron. As we reach the temperature of the pearlite change we have still remaining the solid solution of carbide of iron, which also contains much silicide; during the resolution of this solid solution into pearlite, if the silicon is high, the whole of the pearlite carbide thus produced dissociates, and we then find that the ferritic matrix thus produced contains the whole of the silicon, presumably in solid solution as silicide.

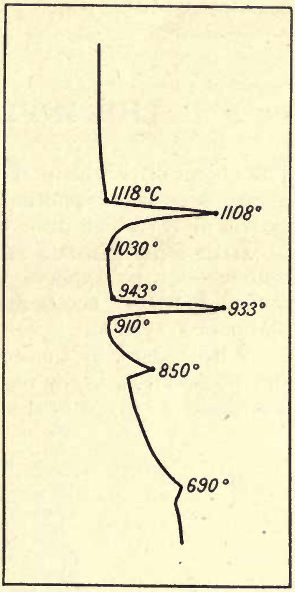

FIG. 37.—Cooling curve of grey siliceous iron.

Fig. 37 is a cooling curve of a grey siliceous iron given by Stead.[1] The composition is as follows:—

Combined carbon	trace	
Graphite	3·30	per cent.
Manganese	0·676	,,
Silicon	4·321	,,
Sulphur	0·025	,,
Phosphorus	1·660	,,

The arrest at 1118° C. marks the primary freezing point; but whilst it is mainly due to the freezing of the iron-carbide eutectic (containing the bulk of the silicon), the period is increased by the dissociation of the carbide liberated during the freezing of the eutectic. The second arrest at 945° is due to the freezing of the iron-phosphorus-carbon eutectic. The arrest at 850° is due to the formation of pearlite, and corresponds closely with the arrest in a similar alloy examined by Gontermann. "The arrest at 690° is probably due to the formation of pearlite in the eutectic of iron and phosphorus, and is of great interest, for it points to the conclusion that silicon is not a constituent of the austenite of the ternary eutectic." This example of the thermal phenomena to be observed during the cooling down of such an iron is typical in degree of ordinary foundry irons.

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[1] Brit. Assoc., Sheffield, 1910.

CHAPTER III.

THE INFLUENCE OF PHOSPHORUS.

THE object of this chapter is to determine, if possible, the influence of varying percentages of phosphorus upon the constitution and properties of those iron-carbon alloys which come within the category of the cast irons.

Iron-Phosphorus Alloys.—To enable one properly to understand the influence of phosphorus upon iron in the presence of large quantities of carbon, it will be better first to study the phenomena presented by the iron-phosphorus system.

With regard to the actual combinations which take place between iron and phosphorus, Percy recorded[1] at least seven definite chemical compounds, and these are given in the following table:—

	Fe_6P.	Fe_3P.	Fe_2P.	Fe_4P_3.	Fe_5P_4.	FeP.	Fe_3P_4.
	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.
Iron	91·54	84·42	78·32	70·67	69·31	64·37	57·54
Phosphorus . .	8·46	15·58	21·68	29·33	30·69	35·63	42·46

This subject had been practically left as it was in Percy's time down to the publication of Stead's research. The latter author, by systematic investigation, discovered that iron retained in solid solution about 1·70 per cent. of phosphorus (as phosphide Fe_3P), and it is to him, indeed, that we are indebted for much of our present knowledge of the influence of phosphorus, both in iron and in the iron-carbon alloys. In 1900, at the September meeting of the Iron and Steel Institute, he presented the now classical paper[2] in which his researches were first published.

It was Stead who determined that the solid solution was of the phosphide Fe_3P, and not of the element phosphorus; and he further demonstrated that larger additions of the element resulted in the appearance of the phosphide as a definite micro-constituent between the crystals of the solid solution. This micro-constituent was shown to have a hardness of about 5·5 on Mohr's scale, and it will be appreciated how much its presence must influence the mechanical properties of the material.

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[1] Percy's *Metallurgy of Iron and Steel.*

[2] *Jour. Iron and Steel Inst.*, vol. ii., 1900.

The addition of 10·2 per cent. of phosphorus was found to result in the production of a definite eutectic of iron and phosphide (Fe_3P), with a melting point of 980° C. This eutectic was shown to consist of 61 per cent. of Fe_3P and 39 per cent. of the saturated solution of Fe_3P in iron.

When the percentage is still further increased, crystals of pure Fe_3P appear in the eutectic, until at 15·58 per cent. Stead was able to demonstrate that the whole mass consisted of the phosphide Fe_3P. With a further excess it was found that Fe_2P appeared, until at a percentage of 21·68 it constituted the whole mass.

In 1908 Saklatwalla published[1] a research which, while confirming Stead's observations of the chemical constitution of the iron-phosphorus system, supplemented his thermal data. Saklatwalla carefully prepared a fairly complete set of pure alloys, and recorded his readings of the thermal phenomena observed during the complete range of freezing of the whole of the series. His results are shown in the following table, and are graphically indicated in the subsequent freezing diagram, fig. 38.

No. melt.	P per cent.	Solidifying points °C.	
1	0·50	1510	...
2	1·40	1410	...
3	2·38	1384	886
4	5·31	1343	886
5	6·57	1262	921
6	6·90	1231	957
7	8·30	1150	1007
8	9·11	1104	1009
9	9·66	1050	991
10	9·93	1025	1000
11	11·70	1030	1005
12	13·51	1052	1008
13	14·06	1072	999
14	15·22	1104	1001
15	15·85	1004	957
16	16·81	970	965
17	17·10	1036	967
18	17·92	1090	956
19	18·60	1121	965
20	20·50	1207	965
21	20·78	1241	1078
22	24·5	1295	1218

It will be seen how completely this research confirms Stead's work.

The author considers he cannot do better than here introduce a selection of the latter worker's photomicrographs.

Fig. 39 typifies the structure obtained from the solid solutions (under 1·7 per cent. of phosphorus) of this iron-phosphorus system. These "polygonal crystalline grains" increase with the percentage of phosphorus, until when the point of saturation is passed we obtain microstructure similar to that shown in fig. 40. Here it will be seen that the structurally free phosphide appears as a definite constituent.

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[1] *Jour. Iron and Steel Inst.*, vol. ii., 1908.

Fig. 41 is of the 10·2 per cent. of the series, and shows the microstructure of the solidified Fe_3P solid solution eutectic.

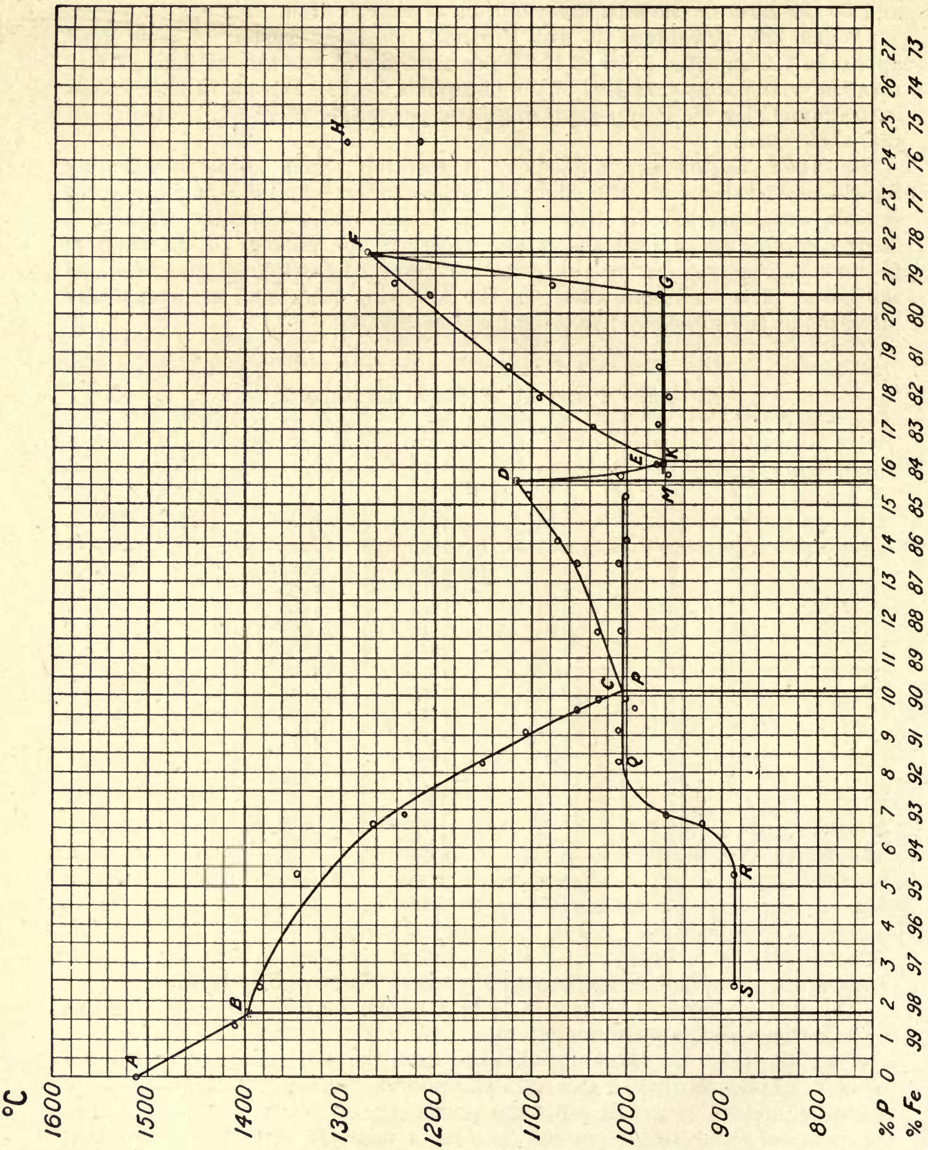

Fig. 38.

The structure illustrated in fig. 42 typifies those obtained when, with the still higher percentage, the phosphide is seen structurally free in a eutectic matrix.

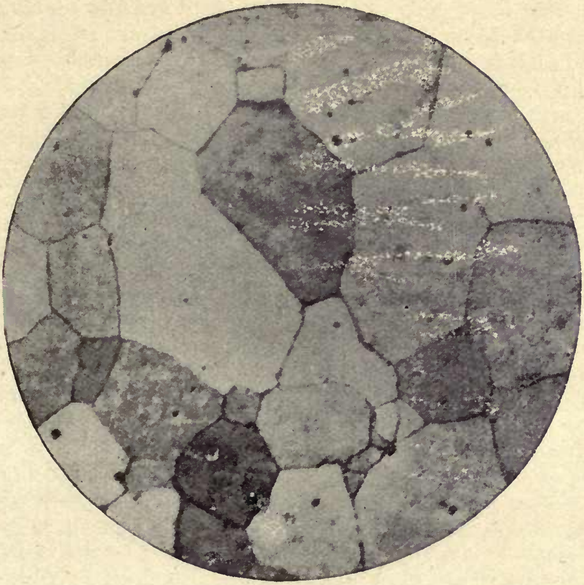

FIG. 39.—Type of all the metals in Class I. Polygonal crystalline grains. Solid solutions of Fe_3P in iron. The grains, under like conditions of heating and cooling, increase in size with the increase of phosphorus. Magnified 50 diameters.

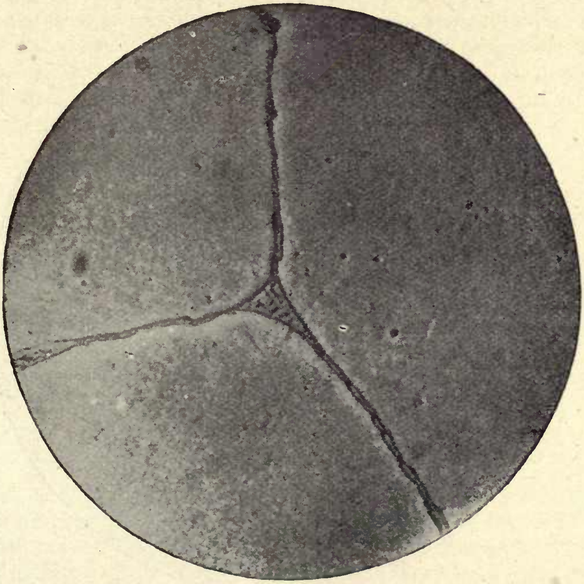

FIG. 40.—Metal ingot with 1·8 per cent. phosphorus, showing portions of three contiguous grains surrounded by a cellular envelope of Fe_3P with a little of the eutectic at the part where the three grains meet. Magnified 350 diameters.

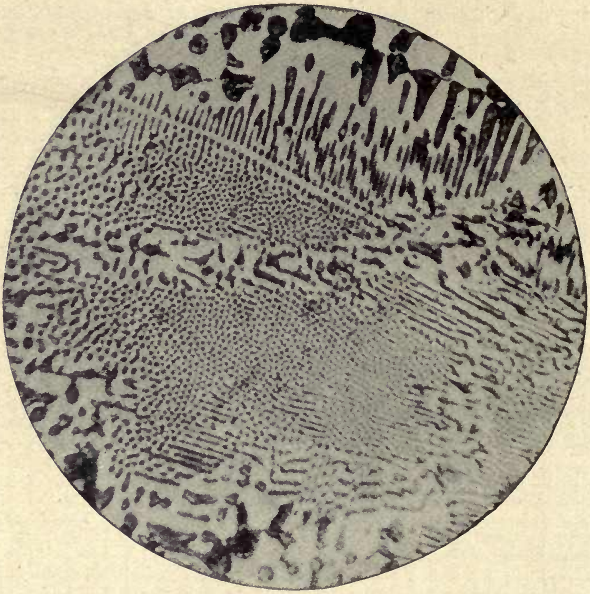

FIG. 41.—Ingot containing 10·2 per cent. phosphorus and 89·8 per cent. iron. It is the eutectic of phosphorus and iron. It has only one critical point at about 980° C. Etched with nitric acid. Magnified 350 diameters.

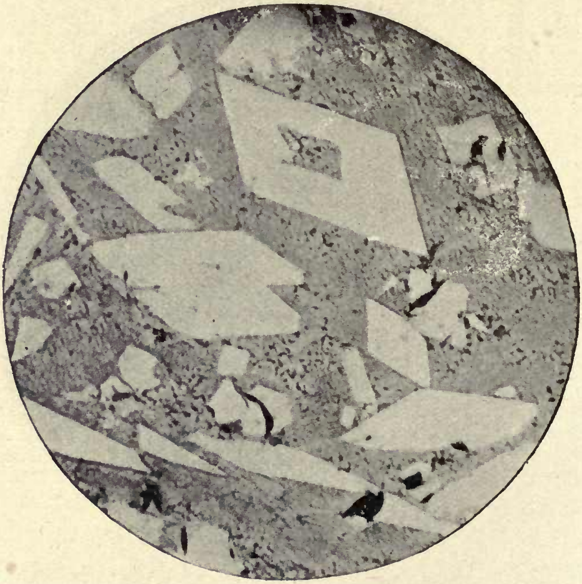

FIG. 42.—Ingot containing 11·07 per cent. phosphorus and 88·9 per cent. iron, showing sections of rhombic or oblique idiomorphic crystals of Fe_3P embedded in a ground mass of the eutectic. Magnified 60 diameters.

Unfortunately we have little data as to the mechanical properties of these alloys. Arnold, in his paper[1] upon the "Influence of Elements on Iron," gives the results obtained from an alloy containing 1·36 per cent. of the element, otherwise it contained only comparative traces of other impurities. This bar is interesting as containing about the percentage of phosphorus contained in irons produced from foundries working on the well-known Lincolnshire and Derbyshire irons. It gave upon the testing machine a maximum stress of 28·98 tons per sq. in., but presented no indication whatever of ductility, its elongation and reduction of area being recorded as nil. The microstructure was presumably similar to that shown in fig. 39, with the crystals very well developed, there being no evidence of free phosphide.

Influence of Phosphorus in Presence of Carbon.—Having now presented the iron-phosphorus system, the influence of phosphorus upon the iron-carbon system will now be considered. It has been shown that above, say, 1·70 per cent. of phosphorus in a Fe–P alloy, the free phosphide makes its appearance, and (in Chapter I.) that above 0·89 per cent. of carbon in an Fe–C alloy free carbide makes itself evident in the microstructure. If we now turn to the "ternary" alloy, if it may so be called, of iron, carbon, and phosphorus, we shall find that an increase in either carbon or phosphorus results in the throwing out of more phosphide or carbide, as the case may be. The addition of carbon to the saturated solid solution of phosphorus throws out of solution some of the phosphide; the addition of phosphorus to the 0·89 per cent. of carbon steel (saturated solid solution) results in the throwing out of solution of some of the carbide. This is explained by the appropriation, by the added element, of some of the iron belonging to the original alloy, thus rendering the original alloy supersaturated with the premier element.

Dr Stead's work is again the authority for the foregoing observations.

To a saturated solution of phosphorus he added progressively increasing quantities of carbon, and the experiments indicated in a beautiful manner the influence of this element in throwing the phosphide out of solution. The results are given in the following table:—

Nos.	Carbon.	Phosphorus.		
		Free as Fe_3P.	In solution.	Total.
1	nil	nil	1·75	1·75
2	0·125	·18	1·37	1·55
3	0·180	·59	1·18	1·77
4	0·70	1·00	0·75	1·75
5	0·80	1·06	0·70	1·76
6	1·40	1·16	0·60	1·76
7	2·00	1·18	0·55	1·73
8	3·50	1·40	0·31	1·71

It will be seen that free phosphide is thrown out in increasing proportions with each increment of carbon. Even, however, with the 3·50 per cent. of carbon, which is really a cast iron, we find that as much as ·31 per cent. of phosphorus remained in solution. It will be noticed that with only 0·18 per cent. of carbon some free phosphide is seen to be present. Fig. 43 illustrates

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[1] *Jour. Iron and Steel Inst.*, 1894.

this, and the fact that the phosphide is seen to be surrounded by the pearlite at this early stage gives some indication of chemical physics governing the precipitation.

When the carbon "is increased to 1·4 per cent., the eutectic phosphide becomes surrounded by a solid layer of cementite or carbide of iron, which increases in thickness as the carbon is increased. The envelopes of carbide are solid and do not consist of two constituents, whereas the enclosed matter has the usual broken-up duplex character of a solidified eutectic. The white carbide and phosphide appear to run into one another." "On reheating the sample to 900° C. and allowing it to cool moderately rapidly, the greater mass of cementite was no longer found as an envelope to the phosphide eutectic areas, but now existed as independent cells, cutting up the original large grains of pearlite into a number of smaller grains. The phosphide eutectic retained its original position." This was a neat little experiment, and threw much light on the temperatures at which phosphide and carbide diffuse in iron. Obviously, whilst the carbon as carbide diffused at 900° C., the phosphorus did not. This question of the diffusion of the phosphorus is, however, somewhat obscured by the presence of the carbon, which would resist any attempt of the phosphide to re-enter into solution; it therefore does not necessarily follow that, in the absence of carbon, the phosphide would not have commenced to diffuse.

FIG. 43.—Ingot containing 1·74 per cent. phosphorus and 0·18 per cent. carbon. The mottled portions surrounded by dark borders are the eutectic of phosphide of iron. The borders are pearlite. The white ground mass is the solid solution of phosphide of iron in iron. Magnified 60 diameters.

When the carbon had passed the 2·0 per cent. limit, Dr Stead found very definite evidence of a carbide-phosphide eutectic, which contained, as subsequently confirmed by Wüst, about 6·7 per cent. of phosphorus and 2·0 per cent. of carbon.

Stead first isolated this particular eutectic in 1875 by squeezing a sample of Cleveland pig iron during freezing. The eutectic in this first instance was found to contain 0·79 per cent. of silicon, but this fact will be again referred to.

Influence of Phosphorus on the total Carbon Content.—It will be inferred that since both the phosphorus and carbon required their quota of iron, the presence of either will decrease the amount of the other, which can simultaneously be present in the pig iron. This is a question of importance, when we consider the very considerable quantities of phosphorus found in our foundry pig irons. Stead, in the paper at present under consideration, gave interesting complete analyses of a hematite and phosphoric pig respectively :—

	Hematite.	Cleveland.
	per cent.	per cent.
Combined Carbon .	0·15	0·12
Graphite . .	3·95	3·63
Manganese . .	0·85	0·75
Silicon . . .	2·80	2·80
Sulphur . . .	0·03	0·03
Phosphorus . .	0·04	1·56

It will be noticed that 1·56 per cent. of phosphorus appears to be responsible for lowering the carbon content from 4·10 to 3·75 per cent., which is a very appreciable reduction.

Working upon this hypothesis, our incomparable investigator melted under conditions which made possible the presence of high percentages of carbon, and obtained the following conclusive results :—

Analysis of Mixture.		Carbon in melted Metals.	Fracture.
Iron.	Phosphorus.		
per cent.	per cent.	per cent.	
100	none	4·15	white
96	4·10	3·25	,,
93	7·90	2·00	,,
87	13·00	0·70	,,
83	16·00	nil	,,

The heat employed was as far as possible in each case made to approximate that of the blast furnace, and it was found in a subsequent series that the lowering of the temperatures lowered the percentage of carbon present in the alloys.

Does Phosphorus affect the Condition of the Carbon?—The absence of graphite in any of these alloys was a notable feature, and this brings us to the often debated question, Does phosphorus tend to influence the condition of the carbon? It is a well-known fact that normal foundry irons containing 1 to 1¼ per cent. of phosphorus and 2 to 3 per cent. of silicon generally, upon analysis, show very little indication of combined carbon, although their fracture is generally lighter in appearance. The difference in fracture is attributable, no doubt, to the presence of the free phosphide. Dr Stead came to the conclusion, after careful investigation, that phosphorus was without influence upon the actual condition of the carbon in the pig iron, and supports his view with the results of the following experiment.

A series of melts were made, in charcoal-lined crucibles, with varying proportions of silico-phosphide and iron. It is recorded that the temperature was very intense, "certainly higher than that of the blast furnace." The results, which are of considerable interest, are here appended:—

	1.	2.	3.	4.	5.
	per cent.	per cent.	per cent.	per cent.	per cent.
Combined Carbon	1·10	0·56	0·11	nil	nil
Graphite	2·62	1·73	1·88	1·69	0·83
Silicon	0·92	1·96	1·96	2·84	3·36
Manganese	traces	traces	traces	traces	traces
Phosphorus	0·21	4·95	6·85	8·35	12·86

In considering the influence of phosphorus upon the condition of the carbon, it will be seen that in these experiments the issues were not clear, since there is a gradually increasing percentage of silicon, apart from the unavoidable gradually decreasing percentage of total carbon. Stead observes that the graphite progressively increased in size from sample 1 to 5, and it is also obvious that the ratio of graphite to combined carbon also increased. It should, in these experiments, be understood that the phosphorus practically occurs as free phosphide, and hence we must consider the remainder of the alloy on its own merits, and then it will be seen that in each case there is sufficient silicon present adequately to account for the absence of much combined carbon.

Since, however, there is seldom more than 1½ per cent. of phosphorus present in pig irons used in foundry work, it may be considered that the influence of such percentages upon the condition of the carbon is negligible.

Influence of Phosphorus in Foundry Irons.—What, then, are the advantages or disadvantages resulting from the amounts of phosphorus frequently present in pig iron?

The distinctive advantage is the low melting points of such irons. To anyone who has melted phosphoric foundry iron and hematite grey iron in a cupola this feature is well known. Small intricate castings can successfully be cast at distinctly lower temperatures; and with a lower coke consumption in the case of the irons containing over 1·0 per cent. of phosphorus than in the case of the almost phosphorus-free irons. Wüst has demonstrated, in this connection, that the initial freezing temperature of saturated iron-carbon alloys is actually lowered 27° C. by the addition of 1·0 per cent. of phosphorus, and that subsequently further additions continue to depress the freezing point until 6·7 per cent. is reached, after which further additions of phosphorus progressively tend again to raise it.

The disadvantage of the presence of phosphorus in pig irons is that the cast irons produced from them are more brittle and have less strength. This is accounted for by the structurally free phosphide invariably present in such material, and it will readily be appreciated that this is due in great measure to the variation in the coefficient of contraction, which thus sets up planes of weakness wherever the constituent occurs. The already weakened condition of foundry irons, owing to the weakening effect of the numerous graphitic plates, somewhat obscures this action; and indeed it is a fact that very fair results (for cast irons) are obtained when such material, properly made, is put into the testing machine.

With regard to foundry irons, it must be pointed out that even with under 0·10 per cent. of phosphorus the phosphide is seen under the microscope structurally free, and this is due to the fact that the percentage of carbon is sufficient to throw it out of solution.

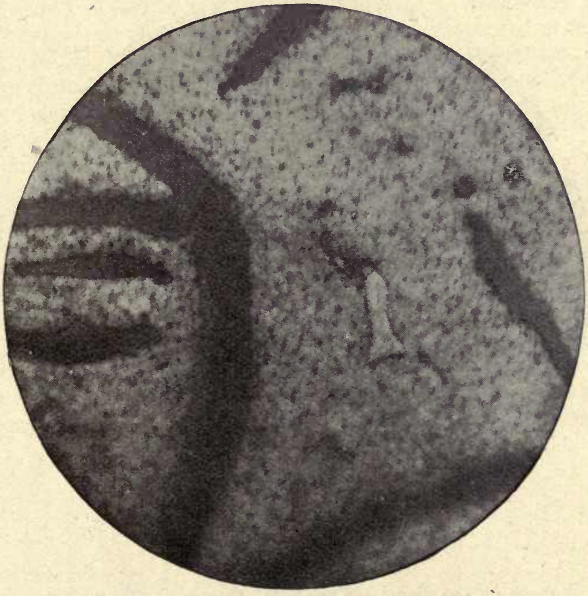

FIG. 44.—East Coast hematite, showing small phosphide area in centre, the section of the graphite plates surrounding it. Magnified 250 diameters.

Fig. 44 is a micrograph which gives a fair idea of the microstructure of such iron.

It may be of advantage if we now consider generally the structure of phosphoric irons. The irons which have to be considered cover the whole range from white to grey, and the condition and environment of the phosphide is very different in the normal grey irons to that occurring in the white varieties.

In all pig irons the phosphide eutectic invariably solidifies at about 950° C., and at the higher temperatures is practically the same; the important factor, however, to consider is the presence of silicon, which has a considerable influence upon this eutectic during the subsequent cooling down. The result is that whilst the silicon causes the breakdown of the carbide, it is incidentally the means of destroying the carbide content of the eutectic. Hence, whilst in white irons we find the carbide and phosphide which form the eutectic lying micrographically in juxtapositition, we find the phosphide of the eutectic occurring in grey irons by itself. Judging from the data available, one would consider that the higher the silicon content of the iron the more rapid would be this reaction, as the silicon would seem to be actually present in the eutectic in percentages much less than that of the whole iron, still increasing with its silicon content.

Fig. 45 gives an excellent idea of the general microstructure of grey phosphoric irons, and incidentally enables one to comprehend the influence of the phosphorus upon the mechanical properties of the material.

Fig. 45.—No. 3 Cargo Fleet Cleveland pig iron, showing dark sections of the graphite plates, the broken-up structure of the phosphide eutectic, and the ground mass of iron with silicon and manganese. Magnified 250 diameters.

With regard to shrinkage, Keep made a number of practical experiments, with the result that he concluded that, if anything, phosphorus had a tendency to decrease shrinkage. The condition of the carbon, however, is such an overwhelmingly important factor in determining shrinkage that it would be unwise to generalise upon the experiments performed by Keep and others. It would seem that only so far as phosphorus influences the condition of the carbon could it have any effect, and this phase of its influence has already been discussed. Most likely the expansion noticed by Turner and Keep at about 950° C. was really due to the dissociation of that portion of the carbide which down to that temperature had formed an integral part of the eutectic (and also probably partially to the actual splitting up of the carbide phosphide eutectic).

There is at present no real evidence that this element materially influences either the degree of hardness or the depth of chill obtainable from the iron.

Heat-tinting Method of detecting Free Phosphide micrographically.—In concluding this chapter, it may be of service to describe the method used to prepare microsections in a suitable manner for the detection of the presence of phosphide, and this cannot be done better than by giving Stead's own description.

In his paper upon "Iron Phosphorus" he states: "In studying the compounds containing both separated massive carbide and phosphide of iron existing, as they often do, side by side, it has been found that the etching methods will not develop indications sufficient to enable the microscopist to tell one from the other. Mr Osmond and I have independently discovered that the very beautiful method employed first by Professors Behrens and Martens, which consists of simply heating the polished metals till they are more or less coloured by oxidation, enabled them to do so. Carbide of iron, on heating, takes the oxidation tints of straw-yellow, yellow, brown, red, purple, blue, and silver-grey, in sequential order. Phosphide of iron passes through the several ranges of colour, but not so rapidly as the carbide.

"When a piece of metal which contains carbide and phosphide of iron is heated (by placing it on an iron plate which is heated) until the section assumes an orange colour to the naked eye, and is then rapidly cooled by placing it on a bath of mercury to check further oxidation, on examination under the microscope the carbide will be seen to be red and the phosphide a pale yellow colour; or if heated till the carbide is blue, the phosphide will be brown or red-salmon in colour."

The above method, after a little practice, will be found to be a very simple and effective manner of detecting the presence of even very small percentages of free phosphide.

CHAPTER IV.

INFLUENCE OF SULPHUR.

THE actual influence of varying proportions of sulphur upon the physical properties of the final iron casting is still a much debated question; it depends so much upon the balance of the other constituents that no really definite statement is advisable. In the absence of manganese, it certainly assists in retaining the carbon as carbide, thus producing hard iron, whilst if the iron be very high in manganese, MnS will be formed and the hardening action be neutralised.

Caron[1] discovered that when manganese was added to sulphurous cast iron some of the sulphur was eliminated, and upon this chemical action Massenez[2] worked out his desulphurisation process. The sulphide of iron is attacked by the manganese, with the formation of MnS, most of which rises through the metal and joins the slag. The sulphide of manganese remaining in the metal is easily identified microscopically by its colour: as stated by J. O. Arnold, it usually exists as dove-coloured globules, easily detected in the unetched microsection. Saniter's[3] method of eliminating the sulphur consists of adding calcium chloride or fluor spar, and is most effective, removing the sulphur as CaS. Stead[4] has also demonstrated that sulphur is removed during the puddling process by the highly basic iron slag. According to the latter authority, when much sulphur is introduced into molten cast iron, the sulphur combines with its quota of iron and floats to the top as sulphide; it is claimed that in this way white iron may be rendered grey, since the remainder of the melt is richer in carbon, and the precipitation of that element is made much less difficult. The question, however, is whether the percentage of sulphur remaining in solution is not sufficient to prevent the precipitation even in rich carbon alloys, particularly if silicon, which considerably modifies such action, is not present in any quantity.

Generally speaking, in ordinary foundry practice it will be found that the sulphur is present in such small quantities and under such conditions that it is without marked influence upon the iron.

Keep considers that such a percentage as ·05 per cent. found in foundry iron will have no deleterious influence, any such influence being simultaneously corrected by the silicon present.

In illumination of this point, Wüst has recorded that in irons containing 3·15 per cent. of carbon and about 1 per cent. of silicon, on an average ·01 per

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[1] *Comptes Rendus*, lvi. p. 828, April 1863.

[2] *Jour. Iron and Steel Inst.*, 1891, i. p. 11.

[3] *Ibid.*, 1892, ii. p. 216.

[4] *Ibid.*, 1893, i. p. 48.

cent. of sulphur prevents the separation of 0·02 per cent. of graphite, but that with 2 per cent. of silicon its effect is less. It will therefore be seen that the action of sulphur is largely dependent upon the other constituents, and silicon in particular, present in the iron.

The reason for the small percentage of sulphur in foundry iron, rarely over 0·08 per cent., is found in the conditions governing the blast furnace during the production of such material. The temperatures, the composition of the burden, and the resulting slags, in the foundry iron blast furnace practice, are conducive to the reduction of silicon, but not conducive to the absorption of sulphur. The actual presence of such silicon percentage in the molten iron would appear to be, from data published, a partial explanation of the comparative absence of sulphur; and it is a matter of considerable interest that only a very small proportion of the sulphur in the charge is actually found in the molten product.

Turner[1] has demonstrated this point. His experiments are of considerable interest. He melted an alloy containing 10·34 per cent. silicon and 10·15 per cent. sulphur (he does not, however, state the percentage of carbon present), and found that the solidified melt consisted of two layers of the following composition:—

	S per cent.	Si per cent.	Fe per cent.
Metal separated . .	1·46	13·45	...
Sulphide separated . .	22·14	5·55	72·27

It is thus clear, however, that the sulphide, in its exit, carried with it some of the silicon (most likely as iron silicide in solution in the sulphide).

J. E. Stead[2] published an interesting experiment in further support of Turner's data. He experimented with iron of the following composition:—

Carbon	3·164 per cent.
Silicon	0·28 ,,
Sulphur	3·23 ,,

This was crushed with the same weight of 50 per cent. ferro-silicon, and the mixture was then melted in a clay crucible. The crucible was afterwards found to contain "well-fused white iron covered with grey powder and a matted felt-like layer of perfectly pure silica. The grey powder yielded sulphuretted hydrogen gas on treating with acid; it was a mixture of sulphide and silica." The composition of the metal mixings before and after melting were as follows:—

	C per cent.	Si per cent.	S per cent.
Before . . .	1·58	25·14	1·62
After . .	nil	21·84	0·08

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[1] *Jour. Iron and Steel Inst.*, 1888, i. p. 28.

[2] *Jour. Staff. Iron and Steel Inst.*, March 1908.

This, whilst confirming Turner's observations, also proves that sulphur and carbon cannot be present in a composition equal to Fe_2Si.

These experiments are considered to illustrate the reason why high silicon irons are found comparatively free from sulphur.

It will be remembered, bearing upon this matter, that the sulphurous irons used in the malleable casting industry contain comparatively little silicon, and the author considers it useful here to include the series of analyses of the range of irons produced from blast furnaces working upon hematite and ironstone respectively. It will be seen that as the silicon content increases the sulphur content decreases, and *vice versa.*

HEMATITE.

	GC.	CC.	Si.	S.	P.	Mn.
No. 1	3·65	·20	3·0	·02	·04	·5
,, 2	3·40	·40	2·5	·03	·04	·5
,, 3	3·10	·60	2·1	·04	·04	·5
,, 4	2·6	1·00	1·7	·11	·04	·5
,, 5	2·0	1·50	1·15	·18	·04	·5
Mottled	1·4	2·00	·9	·24	·04	·1
White	trace	3·30	·6	·29	·04	traces

LINCOLNSHIRE.

	GC.	CC.	Si.	S.	P.	Mn.
No. 3 Foundry . . .	3·20	·45	3·00	·035	1·30	1·70
,, 4 ,, ...	2·8	·70	2·60	·045	1·30	1·60
Grey Forge	2·6	·85	2·40	·055	1·30	1·43
No. 4 Close	2·3	1·0	2.30	·06	1·30	1·30
Mottled	1·4	1·5	1·25	·09	1·30	1·10
White	·10	2·8	·50	·16	1·30	1·05

Influence of Sulphur upon Iron in the Absence of Carbon.— Having indicated the percentages of sulphur with which we are likely to meet, it may now be of advantage to discuss the position it holds in the constitution of cast iron.

In the first place, it must be recorded that iron readily combines with sulphur, with the production of sulphide. Treitschke and Tammann have done some excellent work upon the equilibrium of the Iron-Sulphur System, and the diagram in fig. 46 clearly summarises the results of their investigations.

It will be seen that the system must be regarded as one of iron-iron-sulphide (FeS). It is unnecessary to give a detailed description of this diagram, since it is so explicit. One point of exceptional interest, however, is the final separation of the remaining FeS from the solid solution at so low a temperature as 130° C., and this fact alone indicates the advisability of more attention being given to the low temperature regions of phase rule diagrams.

K. Friedrich points out that his recent work does not entirely confirm the diagram given by Treitschke and Tammann. He finds the melting point of iron to be 1527° C. and that of FeS to be 1171° C., and determines the eutectic as a concentration of 85 per cent. FeS, with a melting point of 983° C. He finds the arrest points of pure iron, whilst being lowered by the addition of FeS, at no time coincide.

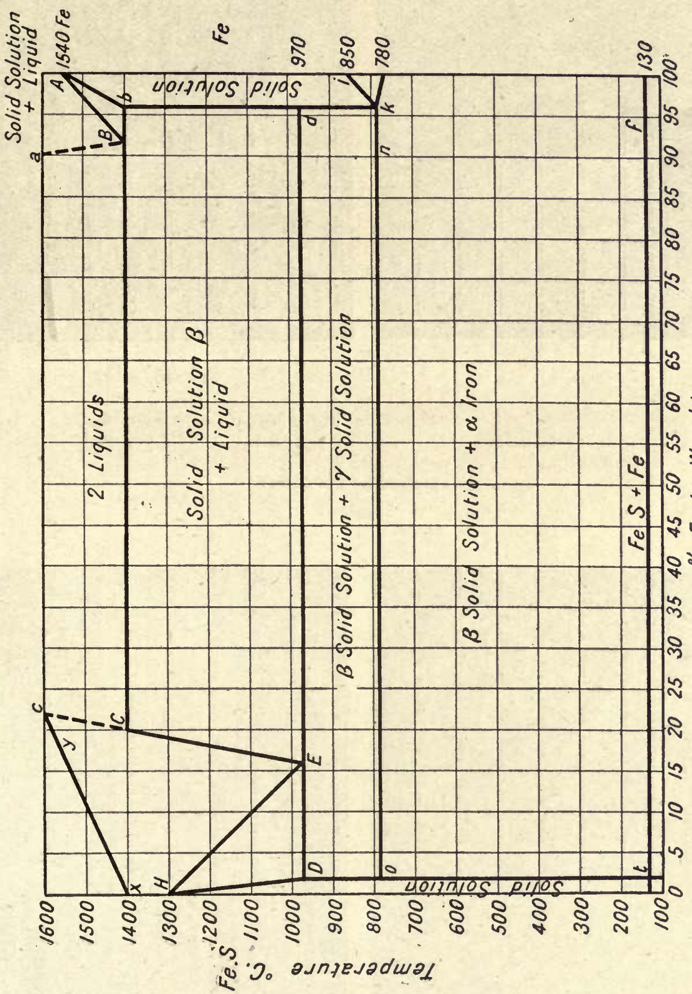

FIG. 46.

Stead, in a most interesting lecture,[1] has described the structure obtained from iron-sulphur melts of varying percentages. The four photo-micrographs, figs. 47, 48, 49, and 50, indicate the ultimate position of the constituents iron and iron-sulphide.

Fig. 49 is of an alloy containing 76·9 per cent. iron and 23·1 per cent. of sulphide. The iron of supersaturation gradually falls out of solution after

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[1] *Jour. Staff. Iron and Steel Inst.*, March 1908.

FIG. 47.

FIG. 48.

	Fig. 47.	Fig. 48.
Iron crystallites . .	10·0 per cent.	52·7 per cent.
Iron sulphide . . .	90·0 ,,	47·3 ,,

Magnified 50 diameters.

FIG. 49.

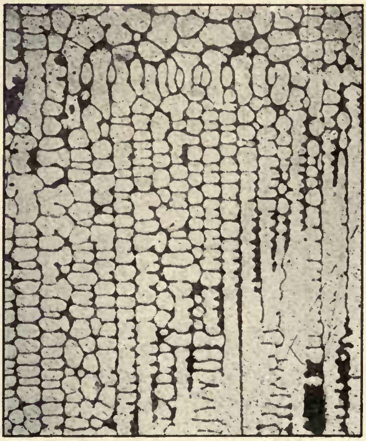


FIG. 50.

	Fig. 49.	Fig. 50.
Iron crystallites . .	76·9 per cent.	88·45 per cent.
Iron sulphide . . .	23·1 ,,	11·55 ,,

Magnified 50 diameters.

solidification, until at about 960° C. the eutectic, consisting of 85 per cent. FeS and 15 per cent. Fe, separates into FeS and iron containing 3 per cent. of FeS. The solid solution, consisting of iron and 3 per cent. of FeS, deposits the remaining FeS on passing through the change point at 130° C.

The other micrographs, figs. 47, 48, and 50, indicate the ultimate structure of alloys containing the sulphide in decreasing amount, the sample micrograph shown in fig. 50 only containing 11·55 per cent.

It must here be recorded that Zeigler has shown the existence of an eutectic of the second order, constituted of FeS and Fe, and FeO and Fe, and to this he attributes the redshortness of steels. This phase, however, is somewhat outside the scope of this work.

Experiments to decide upon the Action of Sulphur in the Presence of Carbon.—Donald M. Levy has published a most interesting research, which, whilst in the author's opinion it does not satisfactorily clear up the question as to what is the action of sulphur in cast iron, still contains much experimental data which will do much finally to provide an explanation.

Levy melted white iron with varying proportions of sulphide in carbon crucibles under good conditions, and obtained the series of alloys the analyses of which are given in the following table:—

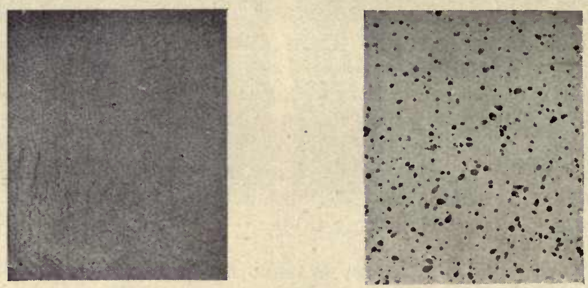
COMPOSITION OF MELTS OF WASHED IRON AND IRON SULPHIDE.

Mark.	Combined Carbon.	Graphite.	Silicon.	Sulphur in Melt.	Sulphur added to Charge.	Appearances.	Remarks.
	per cent.	per cent.	per cent.	per cent.	per cent.		
A	2·73	...	0·010	0·005	...	White	Original material.
B	1·00	1·71	0·019	0·005	...	Grey	A, melted and cooled normally, curve B.
C	1·23	1·43	0·032	0·035	...	Mottled	A, melted in unlined pot. Quick cool.
D	1·50	1·20	0·010	0·030	...	...	A, melted in lined pot. Slow cool.
E	1·20	1·49	0·025	0·081	0·125	...	Normal cool, curve E.
F	2·68	...	0·012	0·328	0·250	White	,, ,, ,, F.
G	2·65	...	0·025	0·274	0·30	,,	Rapid cool.
H	2·76	...	0·013	0·356	0·50	,,	Slower cool.
I	2·76	...	0·019	0·408	0·50	,,	Rapid cool.
J	2·68	...	0·030	0·43	0·63	,,	Normal cool, curve J.
K	2·52	...	0·021	0·65	0·75	,,	,, ,, ,, K.
L	2·65	...	0·016	0·80	1·00	,,	,, ,, ,, L.
M	2·48	...	0·020	0·86	1·00	,,	,, ,, ,, M.
N	2·65	...	0·019	1·14	3·00	,,	,, ,, ,, N.
O	2·44	...	0·016	1·37	2·50	,,	Crystalline crust on surface. Couple shorted.
P	2·37	...	0·018	1·31	3·00	,,	Normal cool, curve P.
Q	2·55	...	0·023	1·25	5·00	,,	Normal cool, curve Q.

The manganese and phosphorus, after careful analysis, were found to be present only in traces, and were therefore not recorded. The fracture of alloys free from sulphur were close grey; up to 0·081 they were mottled, but the other alloys were quite white in fracture.

Polished microsections of each were obtained, and the interesting fact is noted that, practically up to 1·0 per cent. of sulphur (see fig. 51), the surface of each presented a bright even appearance, only "marked all over by the delicate dendritic pattern of the pearlite." When over 1·0 per cent. of sulphur was present the sections were pitted all over according to the amount of excess sulphide present in the alloy.

Levy deduces from his own observations, here recorded, that the saturation point for sulphur in iron-carbon alloys containing 2·73 per cent. carbon is slightly less than 0·9 per cent., and this deduction is apparently well founded. With sulphur not exceeding 0·9 per cent., the sulphide was found by analysis to be uniformly distributed through the mass, but when higher percentages were present more sulphide was found in the upper than the lower part of the melt. This feature became accentuated as the percentage increased. Experiments made to determine the influence of the varying quantities of sulphur upon the hardness and brittleness of the alloys were not attended with really conclusive results.



a. *b.*

Fig. 51.—Showing appearance of polished sections. (*a*) Ingot K (unsaturated with sulphur, 0·65 per cent.). (*b*) Ingot Q (sulphur, 1·25 per cent.); in charge, 5 per cent. sulphur. Magnified 6 diameters.

Cooling curves of each of the alloys were carefully taken, and the various arrests observed are recorded in the following table :—

Melt.	Sulphur Contents per cent.		Arrests.			
AB	0·005	...	1279°	1138°	... (887)	695°
E	0·081	...	1277°	1133°	... (887)	696°
F	0·23	...	1239°	1132°	.. (856)	695°
J	0·43	...	1247°	1128°	... (863)	696°
K	0·65	...	1239°	1118°	... (859)	693°
L	0·85	...	1236°	1128°	... (865)	698°
M	0·86	...	1204°	1121°	... 870	694°
N	1·14	...	1189°	1122°	(972) (870)	692°
P	1·31	1204	1189°	1133°	982 872	697°
Q	1·25	1223 (1204)	1190°	1127°	980 866	695°
R	34·8	1206	...	...	977 ...	...
S	...	1187	...	...	972 ...	...

It is interesting here to record that T. Liesching,[1] during his researches upon the influence of sulphur upon the iron-carbon system, found that the addition of the element lowers the freezing temperature of the eutectic, without, however, affecting the pearlite change.

To return to Levy's research, the sample R is the sulphide used in the experiments.

The melt AB resulted in an iron containing 1·71 per cent. graphite. The first arrest at 1279° C. is described as the "solidification of the iron holding carbon to the extent of 1·5 per cent.," *i.e.* austenite. Levy here states that "with fall of temperature, and probably below 1000° C.," the carbide falls out of solid solution. The author considers this somewhat incorrect since, immediately after passing the eutectic change point, the carbide is progressively thrown out. The second arrest at 1138° C. indicates the splitting up of the eutectic (4·3 per cent. carbon) into cementite (Fe_3C) and austenite. The third arrest, indicated at 887° C., is attributed to the separation of cementite from the austenite, but this the author does not consider a satisfactory explanation, since the cementite, as previously mentioned, progressively separates from higher down to lower temperatures than that in question. A satisfactory explanation of this phenomena, which is also recorded by Carpenter and Keeling, does not at present seem forthcoming.

The precipitation of the free carbon finally found in the resulting alloy probably took place immediately upon the separation of the free carbide at the second arrest (1130°).

The curve R of the sulphide used in the experiments showed two arrests, the first indicating the solidification of the FeS, the second indicating the splitting up of the eutectic of iron and iron sulphide.

The general features of the curves are given as follows:—

(*a*) A considerable lowering of the upper solidifying points, *i.e.* the primary austenite separation.

The author would suggest that this is due to the sulphur taking its quota of iron from the melt, and thus raising the carbon content of the iron, which naturally results in a lower primary freezing point.

(*b*) A lowering of the 4·3 per cent. eutectic point.

This is not considered to be sufficiently conclusive, since whilst in the 0·86 per cent. S alloy it is given 1121° C., in the 0·65 per cent. it is 1118° C.

(*c*) The continuity of the eutectic freezing point and also of the *Ar* 1.2.3, and the absence of an arrest in the neighbourhood of 970° C. on the curves of the melts within the saturation limits of about 0·8 per cent. sulphur.

Levy considers that the depression of the eutectic (iron-carbide) freezing point must be considered as having some bearing upon the influence of sulphur in retaining the carbon in the combined state; taking this along with the fact that he found no further arrest which he could attribute to the presence of sulphur, he considers that it solidified as a component of the 4·3 per cent. carbon eutectic at 1120° to 1130° C.

It will be noted that in the samples in which free sulphide was observed in the polished section the arrest at 950° to 970° was observed.

If we now pass to the microstructure of these alloys we find most valuable records. The structure, form, and the position of the sulphide is found entirely to depend upon the proportion of sulphur present in the iron.

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[1] *Metallurgie*, vii. pp. 565–571, Sept. 22, 1902.

In alloys containing less than 0·8 per cent. S no sulphide is found in the pearlitic areas which represent the primary austenite; it is all found in, and as a distinct component of, the eutectic separating at 1120° to 1130° C. Stead also noticed this $Fe_3C + Fe - FeS + Fe$ eutectic. Figs. 52 and 53 typify such structures at low and high magnification (M, ·86 per cent. S). Mr Levy suggests that the rectilinear structure observed owes its persistency to the presence of the sulphide, and claims that this appearance is evidence which tends to illustrate the action of sulphur in preserving the combined form of the carbon. This theory will be discussed later. No doubt the sulphide films tend to influence the structure of the solidified eutectic, but it is distinctly another question as to whether the particular structure has any decided influence upon the stability of the carbide. It is stated by Levy that "as the percentage of sulphur decreases, the amount of rectilinear eutectic diminishes; and, in an increasing proportion of the matrix, the components commence to assume a more or less balled-up character," which is shown in figs. 54 and 55 (F, ·23 per cent. S) at low and high magnification.

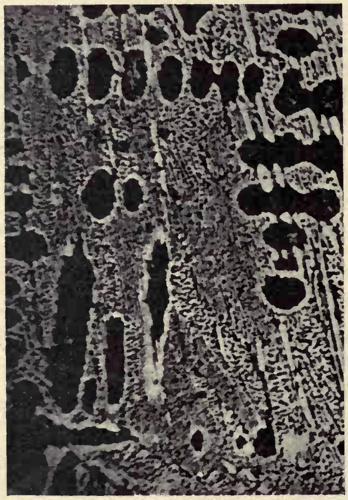

Fig. 52.—Showing marked rectilinear character of the eutectic in white iron containing and preserved by sulphur (sample M, 0·86 per cent. sulphur). Magnified 120 diameters.

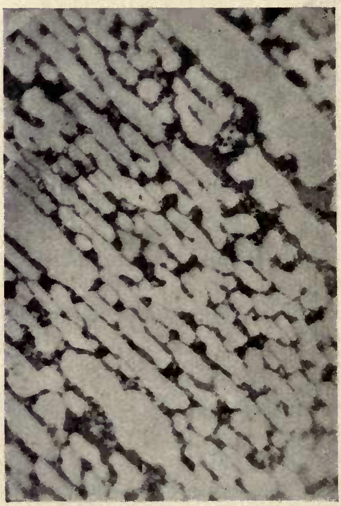

Fig. 53.—Area of Cementite-pearlite-sulphide eutectic of fig. 1, highly magnified. Sulphide, half-tone, joining up pearlite (mottled). Cementite white. Magnified 600 diameters.

Although the author cannot quite agree with Levy that it is actually necessary for the carbide to ball up before dissociation, it is only just to quote his observation to the effect "that the lower the sulphur contents the more is the running up of the eutectic constituents noticeable, until eventually, with very low sulphur in the alloy, the components ball up so quickly that there is sufficient time for the decomposition to set in, in the aggregated cementite areas, with the formation of grey on mottled iron." Figs. 56 and 57 are given to illustrate the manner in which the action is brought about. They are microstructures of melt E (a mottled iron). The sulphide

FIG. 54.—Showing process of balling-up of constituents of eutectic (sample F, 0·23 per cent. sulphur). Magnified 120 diameters.

FIG. 55.—Showing eutectic area of fig. 54, highly magnified. Magnified 600 diameters.

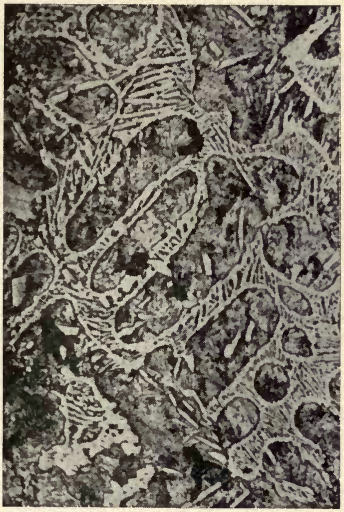

FIG. 56.—Showing white area of a mottled iron through preservation of cementite eutectic, containing and by means of sulphur. Areas of fine graphite in surrounding grey portion also shown. Melt E (sulphur 0·081 per cent.). Magnified 120 diameters.

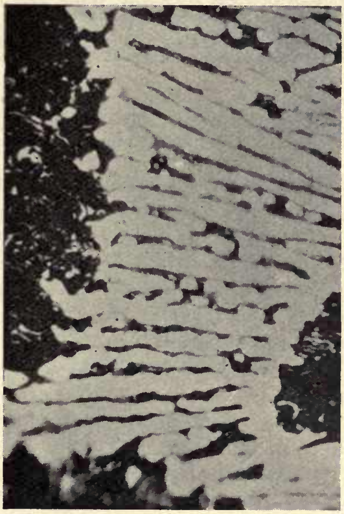

FIG. 57.—Showing eutectic areas of fig. 56, highly magnified. Sulphide links joining up pearlite, marked. Magnified 600 diameters.

is considered to be associated with the cementite, and it is stated that the graphite grows in size in proportion to its distance from the sulphide.

In fig. 51 will be seen the photomicrographs of the ingot containing 0·65 per cent. sulphur and of the one containing 1·25 per cent. sulphur. The magnification is only 6 diameters, and they illustrate very well indeed, as before pointed out, the sulphide of supersaturation.

Fig. 58, a photomicrograph of 200 diameters magnification, illustrates in a beautiful manner the structural position of this excess sulphide.

Levy made careful experiments with a view to ascertain whether there was any chemical evidence as to in what form sulphur was present in these alloys. His results seem to indicate that the whole of the sulphur came off as H_2S. When the samples were dissolved in HCl, no evidence was obtained in support of the theory that the sulphur was in chemical union with the carbon and iron.

The deduction which was drawn from the experiments here mentioned was that there is "no evidence to support the view that sulphur exerts its influence by a chemical union with the carbon; and the research indicates, in Levy's opinion, that the purely physical, or rather mechanical, effects of the sulphide, and its resultant films, offer a satisfactory explanation of the action exercised even by very small proportions."

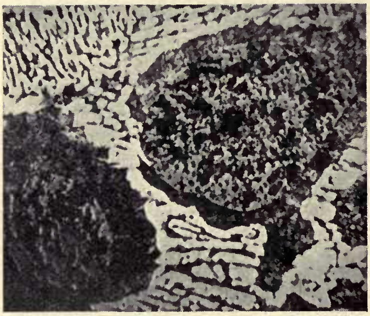

FIG. 58.—Excess sulphide surrounded by pearlite fringe (figs. 1*b* and 2). Magnified 200 diameters.

The author's own experiments would make him believe that even in the presence of fair quantities of sulphur the free carbide can with ease be broken down by heat treatment. He has, however, found that the pearlite matrix is generally retained. In some manner the sulphide would seem to retard the separation and dissociation of the carbide of saturation at the *Ar* 1 critical point. This phase of the action would point to a chemical or physico-chemical influence being brought to bear. The author has indeed obtained, by electrolysis, a fair amount of carbide from a white iron containing 0·45 per cent. of sulphur, and failed to find any of the element present in it; but since the HCl used for the separation of the carbide is so active with sulphur compounds, this fact does not actually preclude the possibility of its having been there. It is of interest to note that silicon was not present in such carbide to the same extent as in a similar iron with the sulphur absent.

Stead has recently given[1] the results of some of his recent work undertaken to determine the manner in which sulphur actually assists the carbon in persisting in the combined state.

The iron selected for experiment was of the following composition:—

CC.	2·98
Gn.	nil
Mn	·29
Silicon	1·89
Sulphur	·27
Phosphorus	1·62

[1] *British Association for Advance of Science*, 1910.

Obviously the iron was white owing to its sulphur content. It is stated that the microstructure was of interest, there being very little of the iron-iron-carbide eutectic; this was accounted for by the action of the phosphorus content in substituting the ternary eutectic of iron-phosphorus and carbon, found by Wüst to contain Fe 91 per cent., P 7 per cent., C 2 per cent.

In fig. 59 will be found the cooling curve of this iron, taken at Dr Stead's request by Carpenter and Edwards.

The first arrest, at 1149° C., indicates the primary freezing point, the austenite here beginning to separate.

The second arrest, at 1074°, is due to the solidification and breaking up of the iron-iron-carbon eutectic into cementite and austenite.

The third arrest, at 945°, is the freezing point of the ternary eutectic (Fe, P and C).

The fourth arrest indicates the resolution of the solid solution into pearlite (Fe_3CFe).

It is stated that both manganese sulphide and iron sulphide were to be observed in the section, but Stead states that he found in this instance no indication of striations of sulphide in the carbide plates, such as Levy had noticed.

Stead's first experiment was to melt the iron with sufficient manganese to give 1·0 per cent. in the finished iron, and the resulting fracture was perfectly grey, the 3·0 per cent. of combined carbon being reduced to ·6 per cent. Obviously, then, the carbon is retained in the combined state by that portion of the sulphur not associated with the manganese.

It is next recorded how the carbides were very carefully separated from the original hard white iron, with a view to determining whether sulphur crystallised with the carbides. After careful analysis the following results were obtained:—

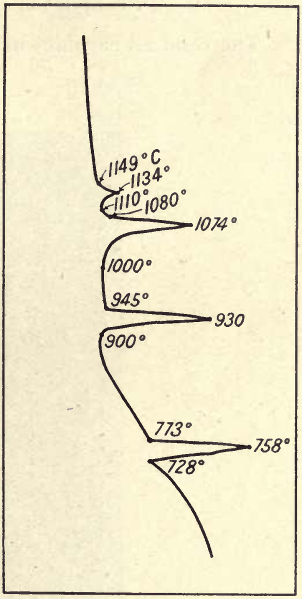

Fig. 59.—Cooling curve of white cast iron.

Iron	92·43 per cent.
Carbon	6·06 „
Silicon	0·12 „
Sulphur	0·12 „
Phosphorus	0·97 „
Water, etc.	0·30 „
	100·00

After further attempting to purify this carbide, it was still found to contain as much as 0·10 per cent. of sulphur.

Stead's next experiment was to determine whether the sulphur would crystallise with the carbide if more than sufficient manganese was present to form MnS.

In the following experiment the chilled portion of a crushing roll was experimented upon :—

Combined Carbon	3·75 per cent.
Graphitic Carbon	trace
Manganese	0·65 per cent.
Silicon	0·70 ,,
Sulphur	0·10 ,,
Phosphorus	0·23 ,,

The residual carbides in this instance were found to contain—

Silicon	0·028 per cent.
Sulphur	0·016 ,,

Fig. 60.—Iron-carbon-sulphur alloy (4·37 per cent. carbon).

White thick bands = massive carbide of iron.
Complex structure = iron-iron-carbide-sulphide-pearlite eutectic.
(By permission of the British Association.)

Stead now considered that he had established the fact that, in the absence of manganese, some of the sulphur did crystallise with the carbide, and his next experiments were consequently made to determine the maximum sulphur which would behave thus under the most favourable conditions. A pure white iron, containing only traces of silicon, sulphur, and phosphorus, and 3·5 per cent. of carbon, was melted in a plumbago crucible. To the molten metal sulphur was added in the form of sticks. The resulting alloy presented a white fracture with large cleavage faces, and under the microscope revealed a structure as shown in fig. 60.

It will be seen that carbide-sulphide eutectic is cut up by large plates of carbide. These plates of carbide are stated to contain inclusions of sulphide of iron, and Mr Stead gives a very interesting micrograph, fig. 61, illustrating this point; the section has been heat-tinted, and the sulphide is seen as the white specks.

A portion of this sulphurous material was again melted and treated with a second quantity of sulphur, with a view to confirming the saturation of the alloy.

The analyses, after both the first and second meltings, were found to be as follows:—

	1st Melt.	2nd Melt.
Carbon . . .	4·37	4·39
Sulphur . . .	1·00	1·00
Silicon . . .	0·03	0·05

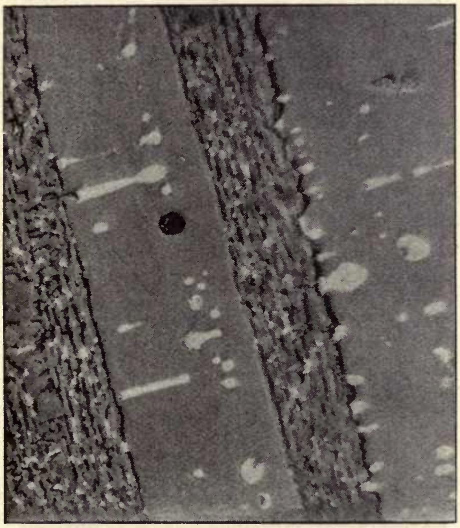

Fig. 61.—Same as fig. 60, heat-tinted and more highly magnified.

Broad bands = massive carbide of iron with inclusion of sulphide of iron.
Complex structure = jointed eutectic of Fe—Fe_3C—FeS. The white specks are all FeS.

(By permission of the British Association.)

Dr Stead separated the carbides in each melt, and found the sulphur content to be ·08 and ·09 respectively; and he therefore states, "from this it would appear that carbides will not carry in solid solution more than about 0·1 per cent. of sulphur."

Since it was found that even drastic annealing would not precipitate free carbon in these alloys, it was concluded that, whatever other influence the sulphur may have, it is that portion which crystallises with the carbide which is mainly responsible in preventing the separation of graphite by making the carbide stable.

Auto-sulphur Printing.—Sulphur is one of the elements found in cast irons and steels which have a great tendency both to liquate and segregate. An ingenious method of determining the manner of distribution of the sulphurous constituents has been devised by R. Baumann,[1] and has been used with great success by Stead and others.

No. 3 Foundry. A.

No. 4 Foundry. B.

No. 6 Forge. C.

FIG. 62.—Sections of Staffordshire Pig Iron, from auto-sulphur prints, showing that the tints are proportional to the sulphur present. Half natural size.

Stead takes a smooth surface bromide paper, soaks it in 3 per cent. solution of strong sulphuric acid, and then squeezes the dripping paper upon the

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[1] *Metallurgie*, 1906, p. 416.

well-polished surface of the metal which is to be examined. The print is then carefully removed, washed with water to remove the acid, and is then

Fig. 63.—Sections of Cleveland Pig Iron. Ormesby brand. From auto-sulphur prints. Half natural size.

immersed in sodium hyposulphite to remove the excess silver salt. After further washing and drying it is ready for mounting.

In a paper to which reference has already been made,[1] Stead publishes some very interesting autoprints of pig-iron sections which are here reproduced. When the sulphur is very low it would appear to be evenly distributed, but on reaching ·05 per cent., brown stains are obtained corresponding to MnS. The structural position of this constituent would suggest that it crystallised in advance of the Fe, Fe_3C eutectic.

A, B, and C, fig. 62, are of the following analyses respectively :—

	No. 3.	No. 4.	No. 6.
CC per cent. .	0·365	0·05	0·910
Gr ,, . .	3·435	3·39	2·335
Mn ,, . .	0·677	0·49	0·403
Si ,, . .	2·586	2·613	1·605
S ,, . .	0·040	0·113	0·218
P ,, . .	0·325	0·39	0·353

Section B, fig. 62, which is obtained from a No. 4 Darlaston pig iron (·113 per cent. S). It will be seen how the MnS takes the imperfect skeleton octahedral form. The figures A and C are explained by the analyses, A containing only ·04 per cent. of sulphur, whilst C contains ·218 per cent.

Sections D, E, F, fig. 63, were obtained from a set of Cleveland pig irons of varying sulphur content, and are equally interesting.

Section E is considered by Stead to be particularly interesting. He says "that this particular pig was evidently run into the mould at a comparatively low temperature; that the manganese sulphide had crystallised out in the metal when it was still passing along the mould in a plastic state; that the crystallites were also plastic and joined each other, and were rolled into the round particles actually present."

Enough data has now been given to show the considerable practical utility of this method of investigation, and the author can only state that he has personally found the method of service, whether investigating pig iron, cast iron, malleable castings, or steel.

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[1] *Jour. Staff. Iron and Steel Inst.*, March 1908.

CHAPTER V.

INFLUENCE OF MANGANESE IN CAST IRON.

Manganese is one of the important elements usually present in cast iron. Its actual influence is as yet, however, not quite understood. One result of its action is certainly determined, and that is, that if manganese and sulphur are both present, they unite to form the chemical compound MnS. This action of the element is, as before explained, used for the elimination of sulphur in the huge mixers now in operation in many steel works. The manganese sulphide rises to the surface, and some of the sulphur is eliminated from the iron; that portion of the sulphide remaining in the material upon solidification can be discerned under the microscope as a separate constituent. By this action the well-known influence of sulphur in assisting in the retention of the combined carbon is neutralised. H. Souther[1] records the fact that by raising the manganese from 0·16 to 0·50 per cent. the trouble he had been having from local hardness disappeared. Probably this influence was due to the manganese neutralising a somewhat high sulphur percentage.

The Influence of Manganese in neutralising the Action of Sulphur.—An interesting memoir upon the influence of manganese in this direction was recently published by D. Levy.[2] Under another heading the influence of sulphur has been discussed; and although it may be suggested that this subject also comes under the heading of the influence of sulphur, it is decided to treat with it here, since the action of manganese in neutralising the influence of sulphur is one of the most important features connected with its presence in iron or steel.

As previously shown, sulphur, in some manner as yet imperfectly understood, prevents the dissociation of the carbide in iron containing comparatively little silicon. Not only is this noticeable in the iron as cast, but also in the heat-treated condition; the presence of the sulphur preventing the last portions of the carbon present in the combined state from being precipitated as free carbon, even after the most drastic annealing. Manganese, when present, combines with the sulphur as before stated, and produces manganese sulphide, which is entirely without influence upon the reactions concerned in the separation of this free carbon. The result is that the microstructure reveals under such condition numerous globules of this constituent, and it may be worth while carefully to study its properties.

Brinell, and also Arnold and Waterhouse, have shown that a steel may contain considerable sulphur (over 0·50 per cent.), and yet, if a suitable manganese addition be made, work well and produce excellent results on

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[1] *Iron Age*, vol. xxvi. p. 283.

[2] *Jour. Staff. Iron and Steel Inst.*, 1909–10.

the testing machine, the manganese sulphide present appearing to behave in a distinctly neutral way, after the manner of the slag in wrought iron. It must not, of course, be taken for granted that it is entirely without action. The globules during the working down are drawn into threads; and whereas in a longitudinal direction they are of little moment, if a test bar be taken transversely the influence of the presence of such foreign matter becomes apparent in the decreasing ductility. This aspect may be considered to be somewhat irrelevant, but is worth considering in the production of malleable cast iron, such material having points of similarity with the steel under discussion. Without, however, pursuing the matter further, the author would recommend the student to give careful attention to the research conducted by Arnold and Waterhouse. Levy, in the paper before referred to, discusses the reaction by which manganese sulphide is formed, and indicates that to ensure the complete conversion of sulphide of iron into sulphide of manganese an excess over the actual amount of manganese indicated by the equation is necessary. In molten steel the action may be regarded as follows:—

$$\mathrm{FeS} + \mathrm{Mn} = \mathrm{MnS} + \mathrm{Fe}.$$

Levy points out that Schutz found that when manganese and iron sulphide were heated together in proportions represented by the above equation at a temperature of 1500° C., instead of the products being wholly iron and manganese sulphide, two distinct products resulted, *i.e.* (1) a button of metallic iron containing manganese; (2) a layer of manganese sulphide containing 11·5 per cent. of iron.

Even when manganese sulphide and iron were heated together they did not remain distinct, the iron taking up 10 per cent. of manganese and the manganese sulphide 4 per cent. of iron. This naturally could only have resulted from the following equation:—

$$\mathrm{MnS} + \mathrm{Fe} = \mathrm{FeS} + \mathrm{Mn}.$$

It will be seen that a most interesting problem is here presented, which no doubt requires, as Levy suggests, further investigation. It is, however, obvious that an excess of manganese is necessary completely to transform the sulphide of iron into sulphide of manganese. Levy points out that the lower the carbon the more free iron will be present in the alloy, and consequently it may be inferred that greater excess of manganese is necessary to complete the reactions in steels than in the higher carbon alloys falling under the category of cast irons.

It may be assumed that, in the presence of a fair percentage of manganese, sulphide of manganese is formed, and tends to rise towards the surface of the molten metal. This sulphide has a melting point of about 1400° C. (Levy), and its comparative infusibility and insolubility, combined with its low specific gravity and its active assimilation by silicates, assist in its separation from the molten iron. If, however, the iron be rapidly cooled it will be entrapped, and will be observed, as before described, as the dove-coloured globules (Arnold) to be viewed through the microscope. Levy found that owing to its early freezing this constituent exists primarily between the austenite crystals, and is therefore joined in supersaturated alloys by the cementite thrown out during the cooling of the solid solution, and consequently is mainly found in juxtaposition with the cementite.

Evidence in favour of the insolubility of manganese sulphide in the solid solution will be found in the behaviour of cast iron of comparatively low silicon content, *i.e.* if no manganese is present the sulphur is in some manner able to cause the pearlite carbide to persist even under drastic heat treatment;

hence iron sulphide would appear, in some degree, to be in combination or solution. If, however, the manganese is present in the correct proportions, this action is neutralised, and the dissociation of the pearlite carbide is allowed to take place in the same manner as in the absence of sulphur; hence the author's opinion that the manganese sulphide is not in combination or in solution in the solid solution down to the pearlite change.

If the manganese is not present in the alloys in sufficient excess, manganese sulphide and iron sulphide are found in juxtaposition, and are easily distinguishable from each other by their distinctive colours.

It must be remembered that in the foundry irons containing 2 to 3 per cent. silicon the sulphur usually present has little action, and it will be seen that the influence of manganese upon cast iron must also be studied from other standpoints. What, for instance, is the influence directly attributable to the manganese upon the mechanical properties of the resulting castings? What influence has it upon the condition of the carbon? Until recently the accepted idea was that the element "toughened" the iron, and incidentally had a tendency to cause the carbon to remain in the combined state.

Influence of Manganese upon the Iron-Carbon System.—F. Wüst[1] describes a most interesting research conducted to determine the effect of manganese upon the iron-carbon system. The alloys of the series studied varied in carbon from 4·0 to 6·9 per cent., and in manganese from 0 to 80 per cent.

His main deductions are as follows:—

(1) The presence of manganese raises the degree of solubility of carbon in iron.

(2) The addition of the element lowers the pearlite change point, so much so that with 5 per cent. Mn in high carbon alloys it is completely absent. The condition of the pearlite is considerably modified with the increasing percentages, becoming more emulsified, until with the highest percentages of manganese the resolution of the solid solution into carbide and iron—of which the pearlite consists—possibly does not take place.

(3) The primary freezing point is slightly depressed by the addition of manganese up to 13 per cent., after which it is again gradually raised until with content of 80 per cent. it has reached 1250° C.

H. Lütke,[2] as a result of his researches into the influence of Mn upon the iron-*carbon* system, arrived, curiously, at the conclusion that the carbon percentage in the solid solution is not appreciably affected until the Mn content exceeds 49 per cent.

Relation of Mn to the Iron Carbide.—In the absence of sulphur, or when the manganese is present in sufficiently large excess, it is found in the supersaturated alloys to crystallise largely with the carbide of iron, and most probably exists as double carbide. This has been demonstrated by the author, who abstracted the carbide from a highly manganiferous white iron. The analysis of the iron and carbide respectively is shown in the following table:—

	Iron.	Carbides.
Carbon	3·40	7·20
Silicon	0·85	0·15
Manganese	2·66	3·74
Sulphur	0·012	...
Phosphorus	0·041	...

Arnold and Read have shown that even in steels not exceeding the saturation

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[1] *Metallurgie*, vi. pp. 3–14, Jan. 8, 1909.

[2] *Ibid.*, vi. pp. 268–273, May 8, 1910.

limit the manganese is in combination with the carbide of iron, and separates out along with the pearlite carbide as double carbide of iron and manganese.

H. I. Coe presented a paper[1] in September 1910 before the Iron and Steel Institute which deserves careful consideration, since it throws quite a new light upon the question.

Two series of alloys were prepared. The first consisted of white irons containing varying percentages of the element. In each series the whole of the thermal phenomena was carefully studied, and from the data thus derived much is to be learnt.

Influence of Manganese upon White Cast Iron.—He prepared his white iron series by melting American washed iron with varying weights of high-grade ferro-manganese. Test bars were cast, and the thermal data recorded by means of a thermo-couple pyrometer; and by means of Turner's extensometer, described elsewhere (p. 116), the expansion phenomena was simultaneously carefully recorded. The composition of the resulting series of alloys is given in the following table:—

No. of Bar.	Carbon.	Manganese.	Silicon.	Inches Expansion.	Remarks.
	per cent.	per cent.	per cent.		
	3·80	40·20	0·14	...	Manganese alloy used.
	3·05	0·035	0·01	...	White iron used.
1	3·15	0·03	0·040	0·0000	Casting full of blowholes. Spongy gate.
1A	...	...	...	0·0000	,, ,, ,,
2	3·19	0·43	0·053	0·002675	Full of blowholes. Slight depression in gate.
3	3·24	0·82	..	0·003838	Full of blowholes. Spongy gate.
4	3·28	1·48	...	0·006978	Much sounder bar.
5	3·05	1·67	0·055	0·008141	Blowholes still present. Large depression.
6	3·09	2·37	...	0·007908	Smaller depression in gate.
7	3·19	2·82	...	0·005848	Some blowholes. Similar depression.
8	3·12	3·50	0·050	0·004071	Sound bar. Large depression in gate.
28	3·14	4·42	...	0·002326	Smaller depression and scoriaceous gate.
9	3·19	5·25	0·061	0·001745	Sound bar. Fairly large depression.
23	3·45	5·40	0·083	0·004652	Sound sharp casting.
10	3·43	6·30	...	0·006978	
19	3·39	7·20	0·081	0·009886	Small depression in gate.
11	3·36	9·00	0·068	0·006978	Hollow gate.
29	3·45	9·12	...	0·008141	,,
26	3·50	10·40	...	0·006978	Moderately hollow gate.
12	3·46	10·67	0·072	0·009304	Large depression in gate.
22	3·50	12·35	...	0·010467	,, ,,
20	3·49	13·50	...	0·008141	,, ,,
24	3·65	13·70	0·085	0·006397	Small depression.
13	3·41	14·84	...	0·002906	Small depression in gate.
25*	3 80	16·00	...	0·008141	Fairly large depression.
21	3·45	16·20	0·100	0·006978	Small depression
31*	3·76	17·05	...	0·004071	Fairly large depression.
30*	3·91	18·65	...	0·000930	Large depression.
14	3·38	18·92	0·103	0·00000	Small ,,
27	3·81	19·65	...	0·003489	Large hollow in gate under surface.
15	3·85	23·30	0·120	0·011630	Do. Grey skin with green slag.
16	3·95	30·50	0·173	0·011630	,, ,,
17	3·85	34·10	0·156	0·011630	Do. Hollow in gate filled with crystals.
18	3·93	38·55	0·155	0·012211	,, ,, ,,

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[1] *Jour. Iron and Steel Inst.*, vol. ii., 1910.

The sulphur and phosphorus were exceeding low, and the silicon, it will be seen, never exceeded 0·17 per cent. The total carbon content was well maintained above 3·0 per cent., whilst the manganese was gradually raised from ·03 to 38·55 per cent.

It is rather unfortunate that no mechanical tests were performed upon the bars. It is stated, however, that all the bars were brittle and intensely hard, the carbon all being present in the combined state. "The addition of the first 5 per cent. of manganese to the white iron produced no appreciable difference in brittleness, but further increase up to 13 per cent. seemed to give a more brittle bar. Above this amount the bar appeared again stronger, until with 19 per cent. of manganese there was quite a considerable increase in the toughness of the specimen. With 30 per cent. and above, the metal partook of the nature of a spiegel, and became very weak and brittle."

FIG. 64.—Bar 1. Magnified 1000 diameters. 0·03 per cent. Mn, 3·15 per cent. C. Pearlite + eutectic.

FIG. 65.—Bar 10. Magnified 1000 diameters. 6·30 per cent. Mn, 3·43 per cent. C. Rectilinear cementite needles, through solid solution. Sorbitic fringe.

Microstructures presented by the White Iron Series.—The structures presented by sections of these materials consisted of cementite (carbide), and pearlite, and the influence of the manganese, according to Coe, materially influenced the structure of the latter constituent. He found that the addition of manganese modified the appearance of this product, usually known as pearlite, which results from the resolution of the "hardenite" solid solution. The lamellar form found in the earlier members of the series had become, on passing 3·0 per cent. manganese, a distinctly sorbitic or granular pearlite, and with the increase of the element was seen, at high power, to be veined with cementite, whilst with still increasing manganese the solid solution practically persisted as such. It is also recorded that instead of the carbide separating from the austenite during cooling, and joining the primary cementite bands, it was found scattered through the areas originally composed of the solid solution. The main influence of the manganese is therefore seen to be the modification of the resulting solid solution, and this change is well illustrated by the micrographs in figs. 64, 65, culled from Mr Coe's selection.

Pyrometric Results.—Besides the original determination of the thermal data, small quantities of each of the alloys were remelted and the determinations remade. The results obtained are given in the following table and diagram, fig. 66.

No. of Bar.	Total Carbon.	Manganese.	Silicon.	First Arrest.	Second Arrest.	Pearlite Point.
	per cent.	per cent.	per cent.			
1	3·14 { gr. 1·87 c.c. 1·27 }	0·025	0·01	1285	1139	700
28	3·15	3·75	0·27	1270	1141	645
11	3·37	7·95	0·17	1247	1140	525
13	3·47	13·60	0·22	1204	1140	...
14	3·84	16·80	0·26	1160	1141	...
15	4·00	21·63	0·33	1140	1130	...
16	4·05	28·80	0·41	...	1125	...
17	4·45	32·42	0·42	1133	1125	...

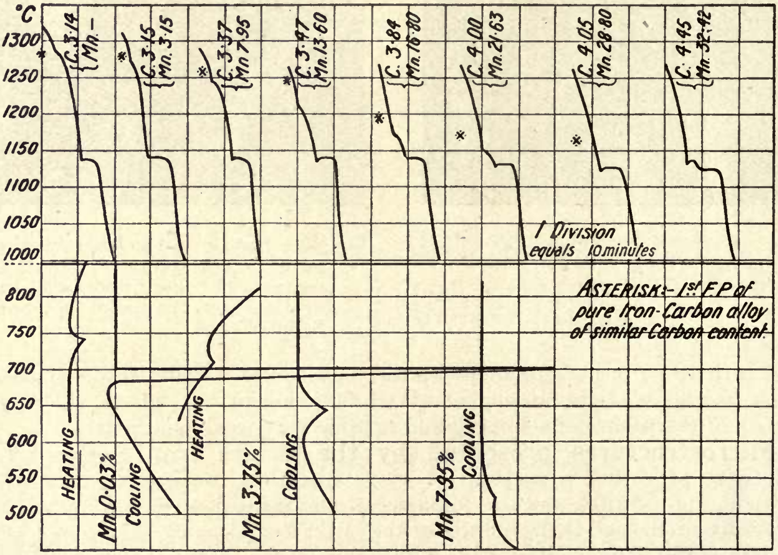

Fig. 66.

The asterisks in the diagram denote the temperatures at which the primary austenite (most of the alloys being under the eutectic composition) would have begun to freeze in a pure iron-carbon series. It will be seen that the manganese assists the carbon in lowering this primary freezing point to such an extent that, with 13 per cent. of manganese, freezing actually occurs 40° lower than in the corresponding pure iron-carbon alloy.

As pointed out by Wüst, the pearlite change point is very materially affected; and here we have the explanation of the changes in the structure of that constituent when observed under the microscope. It will be seen that the change point is materially depressed, and the author records that the intensity also diminished at the same time, with the result that 8·0 per cent. of manganese it was hardly to be detected.

Hardness and Changes in Volume.—It is of considerable interest to note that specimens when tested with the scleroscope revealed varying degrees of hardness, and also distinctly varying amounts of ultimate expansion, and the figures obtained from these two sets of observations are diagrammatically illustrated, in conjunction with the fall in the pearlite change point, in the following diagram, fig. 67.

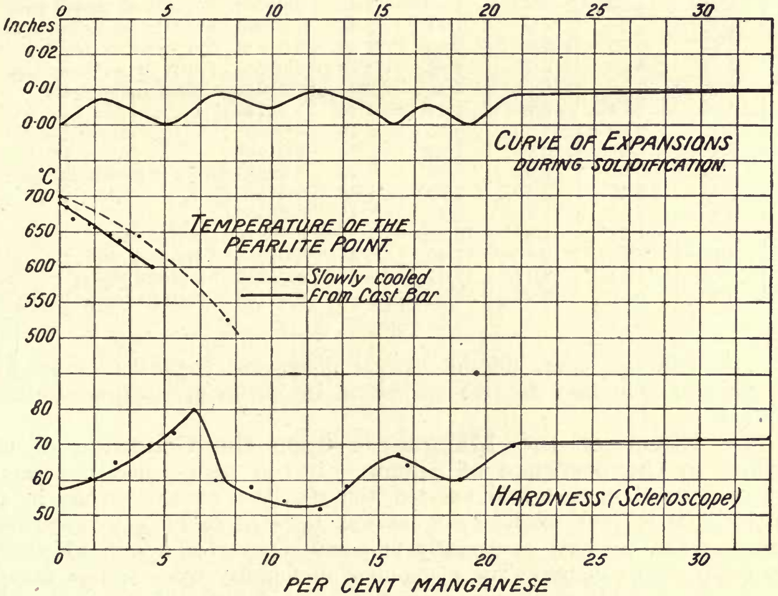

FIG. 67.

With regard to the expansion phenomena, it will be observed that minima are obtained in the American washed iron, and the 5 per cent., 15·3 per cent., and 19 per cent. alloys.

This curious variation in the shrinkage Coe attributes to the formation of the carbides, Fe_3C; $8\ Fe_3CMn_3C$; $2\ Fe_3C$, Mn_3C and $3\ Fe_3C\ 2\ Mn_3C$ respectively, and possibly that is the correct explanation. The variations in the hardness indicated are of interest, but not easy to explain. The increase in hardness up to 6·3 per cent. is no doubt explained by the previously recorded modification of the pearlite, but the subsequent variations are not so readily accounted for.

The Effect of the Addition of Manganese to Grey Irons.—This is the most important point to be considered, as silicon is invariably present in foundry iron in fair quantity.

Coe prepared a very good series of test bars containing percentages of manganese varying from 0·55 per cent. to 30·30 per cent., with a silicon content approximating to 2·5 per cent. His analyses of this series are recorded in the following table:—

Bar.	Total Carbon.	Graphitic Carbon.	Combined Carbon.	Manganese.	Silicon.	Inches Expansion.	Remarks.
	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.	
	4·01	..	4·01	31·50	2·80	...	Original manganese alloy.
	3·71	3·45	0·26	1·07	2·45	...	Original pig iron.
A	3·56	2·87	0·79	0·55	2·45	0·01931	S=0·08 %, P=0·06 %.
B	3·70	3·39	0·31	1·00	2·46	0·02628	Slightly depressed gate.
C	3·63	3·16	0·47	1·61	2·35	0·01396	Slightly large depression.
D	3·60	3·25	0·35	2·23	2·35	0·01826	Very small depression.
E	3·60	3·33	0·27	2·65	2·39	0·01907	Fairly larger depression.
F	3·70	3·12	0·58	3·45	2·48	0·01942	Considerable piping.
G	3·80	2·94	0·86	4·19	2·44	0·02140	,, ,,
H	3·12	2·69	0·43	5·15	2·40	0·01861	,, ,,
K	3·40	2·65	0·75	5·83	2·34	0·01931	,, ,,
M	3·24	2·60	0·64	6·62	2·40	0·02280	Even depression in gate.
N	3·85	2·15	1·70	8·35	2·38	0·01977	,, ,, ,,
O	3·85	2·10	1·73	9·89	2·45	0·03082	,, ,, ,,
P	3·95	1·98	1·97	10·30	2·41	0·02884	Deep piping.
R	4·00	1·85	2·15	11·15	2·48	0·02256	Very deep piping.
T	4·25	1·14	3·11	17·57	2·54	0·03373	Moderate piping.
U	3·89	nil	3·89	30·30	2·96	0·01163	White fracture. Deep pipe.

In the following figure, 68, the thermal phenomena, expansion figures, and the ratio of combined to free carbon in the series are diagrammatically recorded.

The Effect of the Manganese upon the Condition of the Carbon in the presence of Silicon.—It had been generally accepted that manganese in cast iron assisted the retention of the carbon in the combined state, thus producing what was believed to be a tougher iron. Here, however, we have a carefully prepared series of alloys in which this view receives no support. The manganese in foundry irons seldom exceeds 2·0 per cent.; and if we examine Coe's figures we shall find that, whereas with 0·55 per cent. of Mn he records the presence of 0·79 per cent. of combined carbon, the percentage recorded in the presence of 2·23 per cent. of Mn is only 0·35 per cent. It would therefore be deduced that manganese under such conditions does not stiffen cast iron by its influence upon the condition of the carbon. With, however, 8·0 per cent. and over of manganese the carbon persists in the combined state, but then we come upon the alloys which belong to the "spiegel" family, and may no longer be considered as true cast irons. The occasional irregularities to be noticed in the combined carbon, in almost all experiments, upon the influence of various elements in cast iron, are no doubt due to variation in the casting temperatures. This influence the author has found to be of great importance, it having the effect of assisting the production of the phenomena of super-cooling, and no doubt the somewhat high result in bar G may be attributed to this cause.

The Thermal Phenomena of the Series.—The freezing point is not materially affected by the percentages of manganese found in cast iron, but with high percentages the general tendency is to lower it. It will, however, be seen on reference to fig. 68 that the influence is irregular, but we shall require further data before this variation can be thoroughly explained.

The pearlite change point in the neighbourhood of 700° C. is very materially influenced, and in a similar manner to that observed in the series free from silicon, *but with greater effect*. Whereas in the non-silicon iron with 4·45 per cent. of Mn the change point is distinctly recorded between 620 and 587° C., in the silicon series with 4·19 per cent. of Mn the phenomena was not observed down to so low a temperature as 350° C. The author has found that whereas in the non-silicon series the point gradually disappears, in the silicon series it disappears "abruptly with less than 4·0 per cent. of manganese." It might be deduced from these facts that manganese in large percentages, even in the presence of silicon, assists the combined carbon in the solid solution in persisting in that state, and hence one possible explanation of the influence of *large* percentage of manganese in producing the hard white iron of the higher members of the series. The microstructures entirely confirmed the thermal data.

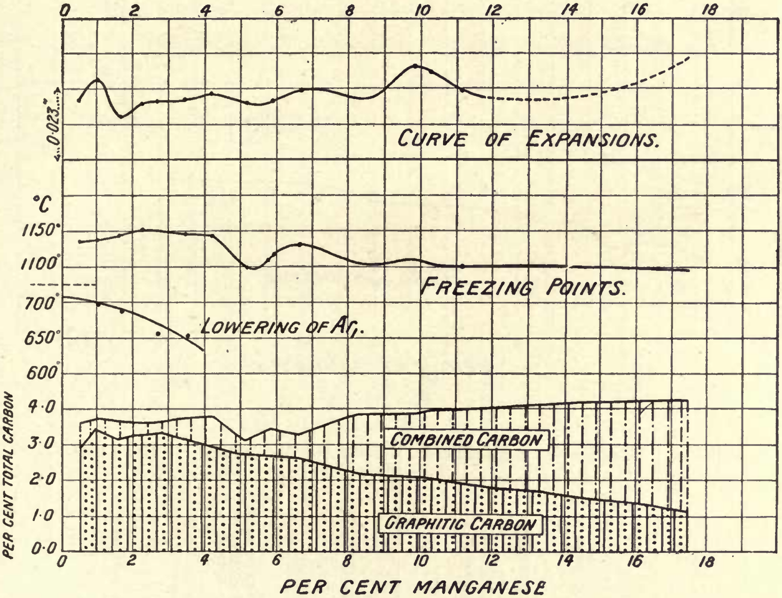

FIG. 68.

Shrinkage and Hardness.—The shrinkage of these grey irons gradually increased with the addition of manganese, as did also the hardness as determined by the scleroscope, and the data from these two sets of observations will be found in the following diagram, fig. 69, and tables.

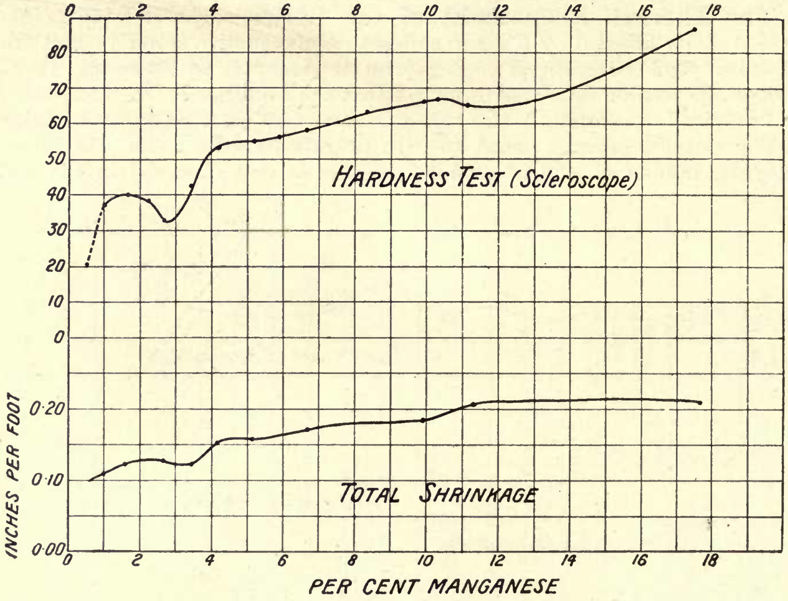

FIG. 69.

Bar.	Manganese.	Hardness.	Bar.	Manganese.	Hardness.
	per cent.			per cent.	
A	0·55	20	K	5·89	56
B	1·00	37	M	6·62	58
C	1·61	40	N	8·35	63
D	2·23	38	O	9·89	66
E	2·65	33	P	10·30	67
F	3·45	42	R	11·15	65
G	4·19	53	T	17·51	87
H	5·15	55			

Bar.	Manganese.	Shrinkage.	Bar.	Manganese.	Shrinkage.
	per cent	inches.		per cent.	inches.
B	1·00	0·108	H	5·15	0·157
C	1·61	0·122	M	6·62	0·170
E	2·65	0·128	O	9·89	0·182
F	3·45	0·121	R	11·15	0·209
G	4·19	0·151	T	17·51	0·209
			U	30·30	0·235

General Remarks.—Keep[1] has published an interesting set of experiments made to determine the influence of manganese upon cast iron. The

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[1] *Cast Iron.*

figures he gives with regard to composition are not the direct result of analysis, but rather of calculation; hence comparison is hardly possible with other work on the subject. The experiments, however, are of great practical value and his observations sound.

With regard to the influence of manganese upon the condition of the carbon, he gives instances in which grey fractures have been obtained with high percentages of the element, and comes to the conclusion that in ordinary foundry irons the percentages present have little influence. He also considers that the strength and chill are little affected. It is interesting to note that, according to him, both the shrinkage and hardness of cast iron are influenced by the addition of normal quantities.

T. D. West gives the result of a research conducted under works conditions, with a view to determining the influence of manganese. The results are given in table.

	No. of test	Iron used.	Breaking Strength.	Deflection.	Contraction.	Chill.	Hardness.	Sil.	Sul.	Mang.	Phos.	CC.	G.C.	Total C.	No. of test.
Heat No. 1.	1	Foundry pig	lbs. 2169	″ ·107	″ ·180	none	·572	4·53	·025	·52	·194	·06	2·98	3·04	1
	2	Mn in cupola	2268	·110	·231	none	?	4·40	·018	6·12	·178	·28	2·61	2·89	2
Heat No. 2.	3	Foundry pig	1715	·101	·198	none	·625	4·51	0·31	·48	·203	·07	3·19	3·26	3
	4	Mn in cupola	1808	·082	·237	slight	·415	4·41	0·23	2·62	·198	·23	3·01	3·24	4
Heat No. 3.	5	Charcoal pig	1510	·075	·276	none	·438	4·45	·110	·41	·213	·03	3·06	3·09	5
	6	Mn in cupola	1822	·090	·291	none	·410	4·31	·067	1·09	·210	·05	3·10	3·15	6
	7	Mn in cupola	1654	·072	·315	·025	·248	4·30	·032	4·09	·192	·16	3·09	3·25	7
	8	Mn in ladle.	1577	·077	·284	none	·506	4·52	·108	·51	·211	·03	3·05	3·08	8
Heat No. 4.	9	Foundry pig	1428	·101	·125	none	·730	3·92	·034	·44	·164	·06	3·35	3·41	9
	10	Mn in cupola	1690	·102	·204	slight	·600	3·88	·029	1·08	156	·19	3·16	3·25	10
	11	Mn in cupola	1763	·083	·161	none	·705	3·88	·029	·76	·162	·08	3·29	3·37	11
Heat No. 5.	12	Foundry pig	1652	·105	·216	none	·553	3·88	·031	·49	·194	·09	3·06	3·15	12
	13	Mn in cupola	2269	·130	·260	slight	·107	3·53	·020	3·53	·152	·30	2·87	3·17	13
	14	Mn in ladle	1995	·100	·229	none	·532	3·82	·026	·68	·193	·11	3·22	3·33	14
	15	Mn in ladle	2016	·100	·246	none	·578	3·62	·025	·87	·191	·11	3·39	3·50	15
	16	Mn in ladle	2122	·095	·279	slight	·490	3·74	·025	1·18	·192	·10	3·03	3·13	16
Heat No. 6.	17	Foundry pig	1888	·100	·309	none	·347	2·47	·030	·97	·255	·42	3·44	3·86	17
	18	Mn in cupola	1794	·097	·320	none	·282	2·40	·022	2·26	·250	·45	3·38	3·83	18
	19	Mn in cupola	1845	·080	·330	·062	·204	2·41	·022	3·71	·231	·47	3·25	3·72	19
	20	Mn in ladle	1970	·102	·309	none	·314	2·56	·038	1·16	·254	·40	3·44	3·84	20
Heat No. 7.	21	Charcoal pig	2355	·095	·339	·128	·385	1·88	·039	·26	·458	·61	2·92	3·53	21
	22	Mn in cupola	2331	·090	·348	·166	·244	1·69	·036	2·43	·435	·64	2·82	3·46	22
	23	Mn in ladle	2394	·100	·341	·055	·450	1·89	·035	·67	·455	·50	3·02	3·52	23
	24	Mn in ladle	2310	·102	·340	·040	·328	2·06	·033	·78	·457	·47	3·11	3·58	24
Heat No. 8.	25	Bessemer pig	1701	·125	·226	·300	·420	1·34	·076	·54	·087	·61	3·28	3·89	25
	26	Bessemer pig	1497	·055	·242	all	white	1·30	·061	5·11	·076	3·41	·17	3·58	26
Heat No. 9.	27	Charcoal iron	1570	·052	·401	1·375	·040	·53	·070	·34	·407	1·14	2·66	3·80	27
	28	Mn in cupola	1082	·046	·427	all	white	·63	·042	2·84	·365	3·53	·15	3·68	28
	29	Mn in ladle	1772	·100	·326	1·100	·242	·69	·068	·69	·420	·49	3·41	3·90	29
	30	Mn in ladle	2066	·095	·322	·230	·222	·74	·060	·74	·424	·62	3·28	3·90	30

The breaking strength and deflection given are in each case the average of four tests, two being $1\frac{1}{8}$-in. round bars cast on end, and the other two being the 1-in. sq. bars cast flat, and used for obtaining the contraction and chill.

The hardness number is a relative one obtained by West with the drill press. The figures in the table are of considerable interest, and it is to be regretted that, as the temperature at which such test bars are poured greatly affects the proportion of combined carbon, the temperatures were not recorded. The results, however, give an excellent idea of the effects likely to be obtained in the foundry by the addition of manganese.

CHAPTER VI.

THE INFLUENCE OF OTHER ELEMENTS UPON THE PHYSICAL PROPERTIES OF CAST IRON.

Vanadium.—Of late years the metallurgy of cast iron has received considerably more attention than previously, and much research has been directed towards making cast iron more consistent in its behaviour under physical tests, both in the cast and annealed condition. One feature of this development is the introduction of some of the elements such as have, with advantage, been employed in steelmaking. Vanadium is now suggested as a valuable addition in increasing the strength of cast iron; and as there is at present considerable disagreement as to exactly what the influence of this element is, the results of the following experiments conducted in the works laboratories under the author's supervision might be of interest, and they were therefore presented to the Iron and Steel Institute in the form of a paper.[1] The results of several sets of experiments published of late by various workers are more or less conclusive in showing the advantage of the addition of the element in small quantities.

G. L. Norris[2] gives an instance where vanadium increased the life of locomotive cylinders. Cylinders made of cast iron not treated with vanadium showed a wear of $\frac{1}{32}$ in. per 100,000 miles, whereas vanadium cast-iron cylinders showed only microscopical wear after running 200,000 miles. Average tests upon such irons gave the following results:—

	Transverse strength.	Tensile strength.
Plain cast iron . . .	2130 lb.	24,225 lb.
Vanadium cast iron . .	2318 ,,	28,728 ,,

The New York Central Railway Co. have already ordered a considerable number of engines equipped with vanadium cast-iron cylinders.

J. Kent Smith gives interesting figures in an article in the *American Foundry* of February 1909.

He considers that the action of vanadium is threefold:—

(*a*) It acts as a scavenger, clearing out the oxygen and nitrogen which he considers exist under certain conditions in cast iron; and,

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[1] *Jour. Iron and Steel Inst.*, vol. i., 1911.

[2] New England Foundrymen's Association, May 1910.

(*b*) It "somewhat strengthens the iron by its solid solution in the carbonless constituent of that iron, rendering the molecules of its constituents more coherent than ever, and their crystals more resistant to abrasive wear and less susceptible to breakage on disintegration along the cleavage lines."

(*c*) It acts upon the carbides.

The author does not agree with Kent Smith as to the first claim made above, since he does not consider that oxygen is present in properly melted iron of high silicon and manganese content. The second and third claims deserve consideration, however. Kent Smith proceeds to substantiate his observations with experimental results, and shows that he has increased the tensile strength of cylinder and other cast irons 50 per cent. by the addition of 0·2 to 0·25 per cent. of vanadium. He also gives instances of similarly increased figures under the transverse tests, and further demonstrates that these results are not at the expense of deflection by recording figures obtained from the standard American bars as high as ·145°. He also records improvement under the compression and hardness tests.

It is also claimed that parts subject to much wear are improved by the addition of small quantities of the element, and in this matter support is obtained from theoretical considerations.

Dr R. Moldenke[1] describes some interesting experiments made to determine the influence of this element upon the properties of cast iron.

The iron was melted in the cupola, and the additions of manganese and vanadium were made to the metal when in the ladle. The test bars were cast to the standard size of the American Society for Testing Materials, *i.e.* 1¼ in. in diameter, cast on end, in dried moulds. The testing was done upon a 5000 lb. Riehle testing machine, and some of the results are given in the following table:—

Iron melted.	Analysis.					Broke at lbs.	Deflection in ins.	Modulus of rupture.
	Va per cent.	Mn per cent.	S per cent.	P per cent.	Si per cent.			
Machinery	...	0·54	·065	0·66	2·72	1·980	0·105	38·680
Iron	0·27	0·56	...	...	...	2·360	0·100	46·070
,,	0·33	0·54	...	...	...	1·980	0·100	38·700
,,	0·36	0·59	...	...	...	2·372	0·09	46·320
Remelted White Iron car wheels	...	0·4	0·13	0·38	0·58	1·470	0·05	28·100
,,	0·21	0·54	0·08	0·37	0·50	3·920	0·095	76·650
,,	0·25	1·15	0·11	0·59	0·65	2·970	0·09	58·040
,,	0·27	0·74	0·08	0·43	0·53	3·030	0·09	59·220
,,	0·31	0·45	0·119	0·41	0·45	2·800	0·055	54·890
,,	0·36	0·40	0·09	0·42	0·45	3·020	0·060	59·030
,,	0·45	0·40	0·11	0·41	0·42	2·950	0·070	59·230
Burnt Grey	...	0·35	0·09	0·63	2·13	1·310	0·090	25·500
Iron	0·05	0·35	0·09	0·63	2·13	2·220	0·100	43·380
Burnt White	...	0·43	0·14	0·42	0·41	1·440	0·050	28·170
Iron	0·05	0·65	...	...	...	1·910	0·055	37·400

The author, however, wishes to point out, without detracting from the value of Moldenke's work, one or two considerations which must not be

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[1] American Foundry Association, 1907.

overlooked when deductions are being drawn from the foregoing experiments. Better results were undoubtedly obtained with vanadium present than without it: it is, however, difficult to obtain any distinct rule, since the influence of 0·22 per cent. of the element would seem to be as great as that of 0·45 per cent. In the case of burnt metal, either white or grey, a distinct advantage would appear to be obtained by the addition of so low a percentage as 0·05. It is, however, important that we should take into consideration the somewhat variable analyses, and it is to be regretted that the condition of the carbon is not recorded.

It will be seen from the foregoing data that vanadium strengthens cast iron, and the author has himself, under certain conditions, found such to be the case. The observations he has made, however, point to the view that this action was merely due to the influence of that element upon the condition of the carbon, *i.e.* it assisted the carbon to persist in the combined state. By scientific working, as is appreciated, the condition of the carbon can be completely controlled without reference to any special elements, and it was therefore decided to determine whether any additional advantage over the ordinary procedure was to be gained by the addition of the expensive metal vanadium. To sum up, the question to be decided was whether or not the carbides in the treated iron were in any way different to those in the untreated iron.

Author's Experiments.—The iron used for these experiments was one in which normally the whole of the carbon was in the combined state. To the molten metal varying quantities of 45 per cent. ferro-vanadium were added, and the analyses of the resulting materials are given in the following table:—

No.	Combined Carbon.	Graphite.	Silicon.	Mn.	S.	P.	Va.
V . . .	2·91	..	·66	·28	·03	·08	...
V1 . . .	2·92	...	·66	·28	·03	·08	·138
V2 . . .	2·9	...	·653	·28	·03	·08	·22
V3 . . .	2·9	...	·65	·28	·03	·082	·45
V4 . . .	2·9	...	·65	·28	·03	·084	·65

It will be seen that an interesting set of alloys were thus prepared similar in composition, except for the gradually increasing vanadium content.

The whole of these irons presented the normal fracture of white cast iron, and microscopically (figs. 70, 74, 78, 82, and 86) were found to possess the usual cementite-pearlite structure of white iron.

It was considered that the hardness test would be the most likely one to determine whether the vanadium had any influence over the physical properties, and the bars were therefore subjected to both the Brinell and scleroscope tests.

The results obtained are given in the following table:—

No.	Brinell.	Scleroscope.
V . . .	387	48
V1 . . .	418	48
V2 . . .	430	48
V3 . . .	418	47
V4 . . .	430	48

It will be seen that there is here no evidence in favour of any effect peculiar to the vanadium, and it was therefore considered that any influence which the element possibly had was simply indirect.

Conclusively to prove the manner in which the influence of the element was exerted, it was considered necessary to find out how it existed in the alloy.

If vanadium be added to pure iron it alloys in all proportions, and an interesting research[1] has resulted in the production of an equilibrium diagram. R. Vogel and G. Tammann made a series of alloys of iron and vanadium, and discuss the equilibrium of the system produced. The mechanical and physical properties, however, are not given.

If added to a steel of carbon content under saturation, it will be found that the vanadium, above the pearlite change point, exists in solid solution.

After the resolution of the hardenite into pearlite, although it is not as yet proved that the vanadium exists as a constituent of the pearlite carbide as distinct from the pearlite ferrite, it is believed to do so.

The alloys which we have under consideration belong to the supersaturated range, and it was therefore decided to determine what proportion of vanadium crystallised with the massive cementite, as distinct from the solid solution. In order that the massive cementite should alone be separated, the samples were quenched just above the recalescence, previous to the electrolytic separation. In this manner the solid solution was dissolved in dilute hydrochloric acid (SG 1·02), whilst the cementite carbide remained behind. The author appreciated the possibility of the vanadium compounds in the solid solution remaining undissolved; but experience showed that they did not apparently do so, as some vanadium was found in the HCl solutions.

The samples were treated for 48 hours in each case, and the following table gives the analyses of the cementite carbides thus produced :—

Bar.	Carbon per cent.	Vanadium per cent.	Silicon per cent.
V . . .	6·59	nil	·58
V1 . . .	6·54	0·414	...
V2 . . .	6·54	0·50	·32
V3 . . .	6·53	0·81	·31
V4 . . .	6·54	1·25	·31

It will be seen that the bulk of the vanadium crystallised with the cementite carbide, and it would be deduced that it was probably in chemical combination. The author has shown that, with a varying silicon content in an iron, the silicon content of the carbide of such an iron becomes modified, and further that this silicon content is responsible for the comparative stability of such carbide at high temperatures. It is thus interesting to find that not only does the vanadium crystallise with the carbide, but that it influences the percentage of silicon found in it. Here is possibly a further manner in which the influence may be asserted.

The carbon content of these alloys was approximately 2·90 per cent., and if the calculation be made it will be found that about 34·5 per cent. of the

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[1] *Zeitschr. für anorg. Chem.*, lviii., i. pp. 73–82, May 6, 1908.

alloy is really carbide. In connection with this fact, the following table is of interest as showing the yield of carbide obtained :—

No.	Grms. Carbide obtained.	Grms. of Alloy in solution.	Per cent. of Carbide obtained.
V . . .	2·319	5·339	30·2
V1 . . .	2·51	5·71	30·5
V2 . . .	2·54	5·608	31·17
V3 . . .	4·11	8·166	33·4
V4 . . .	3·12	6·18	33·54

The silicon not found in the carbide was invariably found in complete solution in the HCl, and as an instance of this the silicon in the solution of V3 worked out at 0·95 per cent. for the solid solution, thus clearly demonstrating that it had been probably partially prevented from crystallising with the carbide by the vanadium content.

Such experiments as these are somewhat crude, but they at any rate throw light upon the grouping of the elements in such materials.

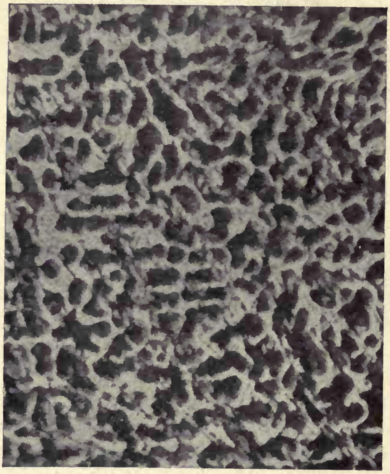
Heat-treatment Experiments.—It was next decided to determine by heat treatment exactly how far the stability of the carbide was influenced by the modified composition brought about by these additions. Bars of each number were heated in a Clinch-Jones muffle for about one hour at fixed temperatures and then quenched. In each instance the bars were introduced into the muffle already standing at the particular temperature, which was subsequently maintained within about 5° C. for the stated period.

Figs. 70, 74, 78, 82, and 86 clearly show that previous to each treatment the whole of the series were practically identical in structure: they consisted of cementite and pearlite.

The first experiment was the heating at 860° C. for 1 hour, followed by the rapid quenching. Microsections prepared and etched with dilute nitric acid revealed the structures shown in figs. 71, 75, 79, 83, and 87. Apart from a slight precipitation in the bar V, there is very little difference in the structures presented.

The second series were heated for 1 hour at 960° C. and rapidly quenched. The respective structures then presented are shown in figs. 72, 76, 80, 84, and 88. In bar V (fig. 72) the free carbide is nearly all broken down, only isolated areas being in evidence. In bar V1 (fig. 76) little change appears to have taken place apart from the gradual disappearance of the free carbide, owing to solvent action of the solid solution with increasing temperature; occasional nodules of annealing carbon are noticed. The same remarks apply to V2 (fig. 80). The structure of V3 (fig. 84) showed, however, no trace of the dissociation of the carbide: the whole of the carbide not in solution being presented as cementite V4 (fig. 88) naturally presented much the same appearance as V3.

The final heat treatment consisted of an hour's exposure at 1040° C., followed, as before, by a rapid quenching from that temperature. The microstructures presented after this treatment are portrayed in figs. 73, 77, 81, 85, and 89. It will be seen that in the case of V (fig. 73) containing no vanadium, the whole of the free carbide at this particular temperature has broken down, with the appearance of considerable quantities of annealing carbon, whilst the matrix presents the typical martensitic structure characteristic of the solid solution when quenched under these conditions. The sample



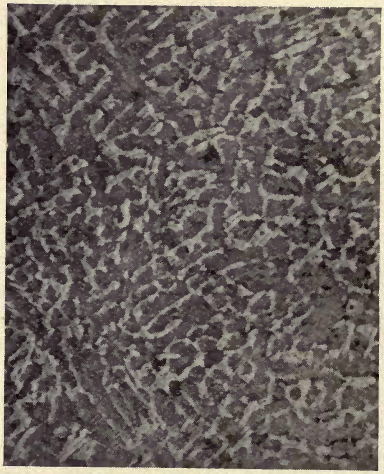


Fig. 70.—As cast.

Fig. 71.—Quenched 860° C.

V. White Cast Iron (no vanadium). Magnified 52 diameters and reduced. Etched HNO_3.

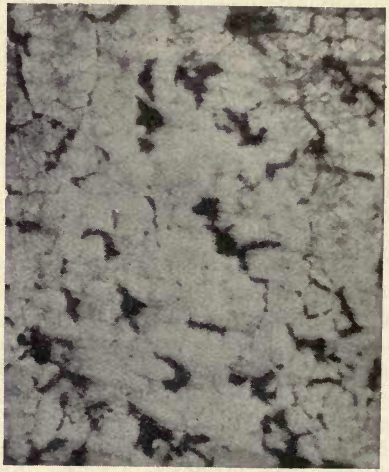


Fig. 72.—Quenched 960° C.

Fig. 73.—Quenched 1040° C.

V. White Cast Iron (no vanadium). Magnified 52 diameters and reduced. Etched HNO_3.

V1, containing only 0·13 per cent. of vanadium, still contains some free cementite carbide, along with a considerable proportion of free carbon. The sample V2 presents a similar structure, with still more free cementite carbide

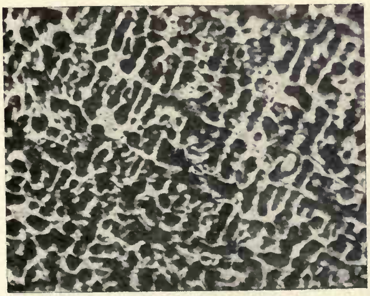


FIG. 74.—As cast.

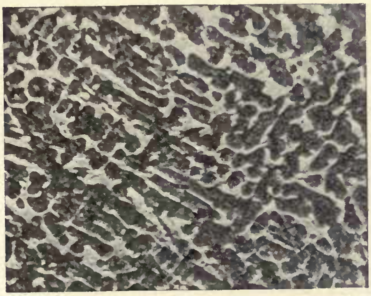


FIG. 75.—Quenched 860° C.

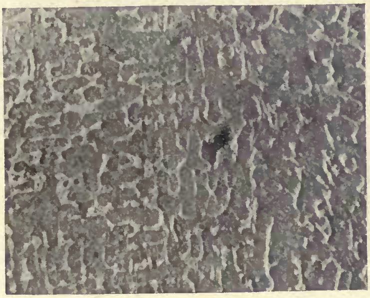


FIG. 76.—Quenched 960° C.

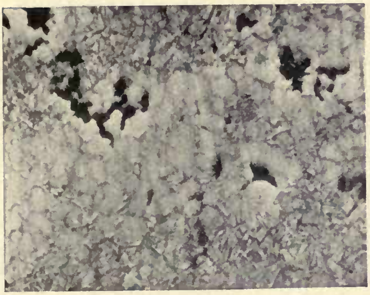


FIG. 77.—Quenched 1040° C.

V1. White Cast Iron (0·138 per cent. vanadium). Magnified 52 diameters and reduced. Etched HNO_3.

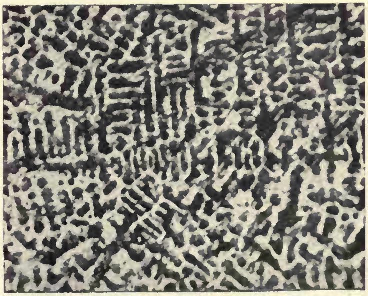


FIG. 78.—As cast.

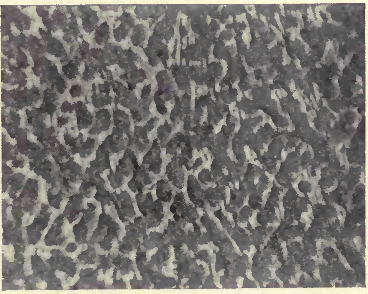


FIG. 79.—Quenched 860° C.

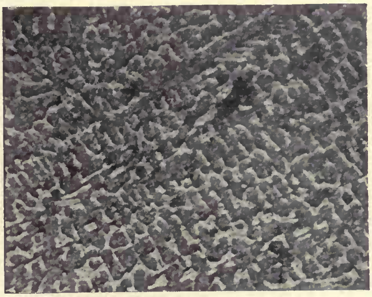


FIG. 80.—Quenched 960° C.

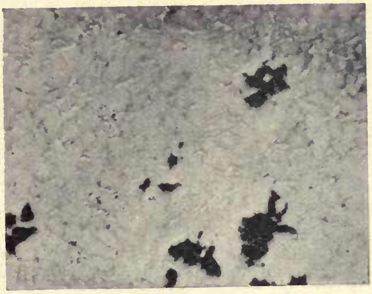


FIG. 81.—Quenched 1040° C.

V2. White Cast Iron (0·22 per cent. vanadium). Magnified 52 diameters and reduced. Etched HNO_3.

FIG. 82.—As cast.

FIG. 83.—Quenched 860° C.

FIG. 84.—Quenched 960° C.

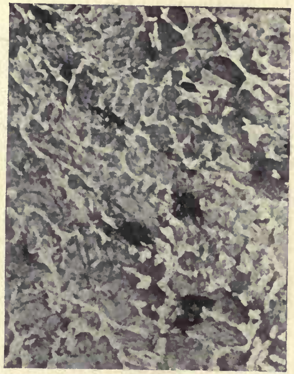


FIG. 85.—Quenched 1040° C.

V3. White Cast Iron (0·45 per cent. vanadium). Magnified 52 diameters and reduced. Etched HNO_3.

FIG. 86.—As cast.

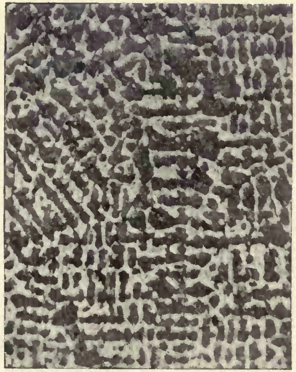


FIG. 87.—Quenched 860° C.

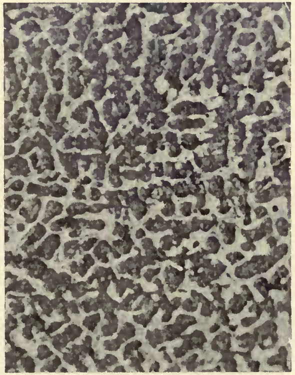


FIG. 88.—Quenched 960° C.

FIG. 89.—Quenched 1040° C.

V4. White Cast Iron (0·65 per cent. vanadium). Magnified 52 diameters and reduced. Etched HNO_3.

in evidence. The microstructure of V3 (fig. 85) is interesting: it will be remembered that this bar contains 0·45 per cent. of vanadium, and this no doubt explains the persistence of the bulk of cementite carbide, which is the most noticeable feature of the micrograph. There has, however, been a noticeable dissociation of the carbide, with the production of some annealing carbon. The most interesting micrograph is that obtained from the sample V4 (fig. 89). It will be seen that all the cementite carbide not redissolved of the solid solution has persisted intact, even after exposure to a temperature of 1040° C. for 1 hour.

Conclusions.—The deductions to be made from the results of the foregoing experiments are as follows:—

(1) Additions of vanadium have a definite influence upon the physical properties of cast iron.

(2) This influence is mainly that of assisting the carbon to persist in the combined state.

(3) The persisting carbides physically do not differ from the normal carbide found in the cast iron.

(4) Owing to the actual presence of much of the vanadium in the carbide, that carbide is rendered more stable.

Chromium in Cast Iron.—P. Goerens and A. Stadeler describe experiments made to determine the influence of chromium upon the solubility of carbon in iron. Their results are given in the following table:—

No.	Cr per cent.	C per cent.	Freezing point.	Pearlite change.
1	...	4·0	1130	711
2	0·7	4·1	1126	709
3	1·2	4·2	1126	709
4	1·5	4·2	1126	710
5	2·7	4·4	1128	710
11	3·5	4·5	1130	713
12	5·0	4·7	1128	713
13	10·4	5·4	1130	715
14	13·7	5·7	1145	715
15	15·9	5·9	1150	715
16	20·5	5·9	1161	710
17	21·0	6·1	1166	710
18	29·6	6·4	not observed	wanting
19	33·4	7·0	1270	,,
20	44·2	7·4	1370	,,
21	66·0	9·2	1535	,,

The melting point is not affected until 10 per cent. Cr is reached. The pearlite point disappears in alloys containing over 21·0 per cent. Cr.

The addition of chromium to iron-carbon alloys has a most pronounced effect, the action being of a chemical as well as physical nature.

The chromium added to iron-carbon alloys remains to a large extent as a constituent of the eutectic (carbide-austenite eutectic), and upon freezing is mainly carried in the cementite carbide, with the result that double carbides of iron and chromium are found in the alloy. Not only does this apply to the cementite carbide, but the carbide resulting from the resolution of the hardenite or solid solution at the pearlite change point is also found to contain much chromium. It should also be stated that the ultimate ferrite in alloys containing much of the element is also found to retain a considerable proportion in, presumably, solid solution. The action of the chromium is probably twofold:—

(1) By crystallising with the carbide it renders the combined carbon more stable, acting in this manner similarly to vanadium (see plates). The addition of chromium therefore tends to harden cast iron, and will be found to increase the chill. Graphite separates with increasing difficulty as the percentage of the element under discussion increases.

(2) It is most probable that the chromium remaining in the ferrite definitely modifies the characteristics of that constituent; and since, after all, ferrite frequently constitutes the matrix of cast irons, this phase is worth considering.

The author proposes in this connection to present some results obtained by Arnold and Read,[1] and to allow the reader to form his own inferences. Alloys of the following composition were prepared:—

No. of Steel.	Carbon per cent.	Chromium per cent.	Silicon per cent.	Phosphorus per cent.	Manganese per cent.	Sulphur per cent.	Aluminium per cent.
1147	0·64	0·65	0·04	0·02 or under	under 0·10	0·02 or under	under 0·01
1090	0·84	0·99	0·06				
1093	0·835	4·97	0·08				
1091	0·85	10·15	0·11				
1092	0·88	15·02	0·03				
1148	0·85	19·46	0·11				
1149	0·85	23·70	0·20				

These alloys were "drastically annealed by heating to a bright red heat for about one and a half days, and then allowed to cool during an additional three days." The mechanical tests were then performed with the following results:—

Bar No.	Yield Point, tons per sq. in.	Maximum Stress, tons per sq. in.	Elongation per cent.	Reduction of area per cent.	Carbon per cent.	Chromium per cent.
1147	20·52	43·2	24·5	40·56	0·64	0·65
1090	18·88	43·36	22·5	39·2	0·84	0·99
1093	16·12	37·80	31·5	41·48	0·84	4·97
1091	16·52	37·20	29·0	22·16	0·85	10·15
1092	20·80	43·92	20·0	36·00	0·88	15·02
1148	48·72	56·85	16·0	26·45	0·85	19·46
1149	34·80	49·52	12·0	23·08	0·85	23·70

Samples of each alloy were then electrolytically decomposed in 1·02 SG hydrochloric acid, and the most interesting figures, fully presented in the following table, were obtained.

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[1] *Jour. Iron and Steel Inst.*, vol. i., 1911.

No. of Steel.	Carbon per cent.	Chromium per cent.	Amperes.	Volts at terminals.	Time in acid.	Grms. dissolved.	Weight of dry residue.	Percentage of total Carbon obtained in the Carbide residue.	Analysis of Carbide.			Corresponding to the formula :—	Theory.		
									Carbon per cent.	Iron per cent.	Chromium per cent.		Carbon per cent.	Iron per cent.	Chromium per cent.
1147	0·64	0·65	0·55	0·9 to 1·6	12 hrs.	10·00	0·8742	94·28	6·95	88·93	4·12	$20Fe_3C, Cr_3C_2$	6·98	88·88	4·13
,,	,,	,,	,,	,,	,,	10·03	0·9037	99·37	7·08	88·35	4·56				
,,	,,	,,	,,	,,	,,	10·03	0·8912	98·84	7·12	88·47	4·41				
1090	0·84	0·99	,,	0·9 to 1·3	,,	8·74	0·9016	85·72	7·20	85·80	6·99	$12Fe_3C, Cr_3C_2$	7·18	86·15	6·66
,,	,,	,,	,,	,,	,,	8·74	0·8725	82·17	7·27	85·51	7·22				
1093	0·835	4·97	,,	0·9 to 1·2	,,	8·74	0·7113	85·54	9·04	45·29	45·67	$4Fe_3C, 3Cr_3C_2, Cr_4C$	8·92	45·40	45·67
,,	,,	,,	,,	,,	,,	8·71	0·6967	80·73	8·69	45·52	45·81				
1091	0·85	10·15	,,	0·9 to 1·2	,,	7·63	0·6918	87·05	8·16	28·38	63·51	Fe_3C, Cr_3C_2, Cr_4C	8·28	28·96	62·76
,,	,,	,,	,,	,,	,,	7·63	0·6579	84·77	8·23	28·93	62·83				
1092	0·88	15·02	,,	0·9 to 1·4	,,	9·83	1·3989	97·41	6·05	34·60	59·34	$2Fe_3C, 3Cr_4C$	5·88	32·94	61·18
,,	,,	,,	,,	,,	,,	9·79	1·4458	99·70	5·96	34·54	59·49				
1148	0·85	19·46	,,	0·9 to 1·4	,,	9·80	1·3746*	...	5·58	33·49	60·93				
,,	,,	,,	,,	,,	,,	9·97	1·6198	99·19	5·21	32·66	62·13				
1149	0·85	23·70	,,	0·9 to 1·4	,,	...†	...†	...†	5·05	32·12	62·83				

* Not the total weight of dry residue obtained. A small quantity was unavoidably lost

† Owing to the rough state of the bars, after solution in the acid, it was quite impossible to remove all the carbide (see fig. 1, bar on the left). Further, during the cleaning of the bars, thin bright strips of metal came away with the carbide. These strips of metal dissolved readily on treating the carbide residue with aqua regia in the cold.

A sufficient quantity of carbide, however, was obtained from the two bars for the analysis given, and the slightly lower percentage of carbon registered is probably due to the aqua regia treatment.

It will be seen that, with regard to the double carbides obtained, the presence of carbides of chromium discovered by Moissan would appear to be confirmed, and it will further be seen that much chromium remains in the ferrite. The authors state that in the highest percentage alloys the matrix consists of allotriomorphic crystals of chromiferous ferrite. The mechanical properties of these alloys suggest profound alteration in the mechanical properties of this matrix.

In conclusion, the author regrets that he is unable to present a set of cast irons showing the actual influence of chromium, but no doubt the before-described experiments indicate the action with sufficient clearness.

Aluminium.—Although interesting data had previously been published by Keep, Borsig, and Hogg, we are indebted to Melland and Waldron[1] for the systematic examination into the influence of aluminium upon cast iron.

Working with a white pig as the basis, they prepared alloys of varying aluminium content, and studied the variations in the constitution thus produced. From each melt two bars were cast, one in an open cast-iron chill mould, and the other in a compressed sand mould, previously heated. The latter sample was in each instance allowed to cool down slowly in sand under a layer of charcoal. The analysis of the original pig and the results obtained by simple melting and subjection to these conditions are given in the following table:—

	Original Pig.	Remelted.	
		Slowly cooled.	Rapidly cooled.
Total Carbon	3·9	3·98	3·98
Graphite	0·38	0·76	0·48
Combined Carbon (by diff.) . .	3·52	3·22	3·50
Silicon	0·24	0·28	0·28
Manganese	0·09	0·087	0·089
Sulphur	0·032	0·032	0·033
Phosphorus	0·066	0·065	0·065

The data obtained from the laboratory examination of the whole series is given in the following table:—

No.	Aluminium.	Silicon.	Total Carbon.	Graphite.		Relative density at 20°C.
				Rapidly cooled.	Slowly cooled.	Slowly cooled.
1	Original Pig (none)	0·24	3·90	0·38	0·38	...
2	Pig remelted (none)	0·28	3·98	0·48	0·76	7·64
3	trace	0·27	3·96	0·52	0·78	...
4	trace (0·002)	0·25	3·94	0·43	1·06	...
5	0·003	0·22	3·98	0·36	1·2	...
6	0·023	0·23	...	0·55	2·32	...
7	0·024	0·23	3·93	0·30	1·20	7·58
8	0·026	0·27	4·07	0·50	1·87	...

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[1] *Jour. Iron and Steel Inst.*, vol. ii., 1900.

No.	Aluminium.	Silicon.	Total Carbon.	Graphite.		Relative density at 20° C.
				Rapidly cooled.	Slowly cooled.	Slowly cooled.
9	0·058	0·28	...	0·50	1·73	...
10	0·114	0·22	...	0·54	2·64	...
11	0·160	0·21	4·00	0·32	3·01	...
12	0·179	0·22	...	0·41	2·50	...
13	0·180	0·20	3·90	0·57	1·55	...
14	0·185	0·20	...	0·55	2·8	...
15	0·232	0·22	3·91	0·59	3·15	...
16	0·250	0·19	3·96	0·91	3·49	...
17	0·325	0·19	...	0·92	2·91	...
18	0·389	0·20	...	1·51	2·96	...
19	0·438	0·25	3·95	1·36	3·35	...
20	0·527	0·21	3·83	3·06	2·93	7·12
21	0·566	0·21	...	2·91	3·37	7·11
22	0·722	0·21	3·96	2·64	2·92	...
23	1·239	0·21	4·08	2·95	2·97	...
24	1·246	0·23	...	2·81	2·87	...
25	1·25	0·29	...	2·91	3·01	...
26	1·78	0·28	4·07	2·96	2·93	7·11
27	2·375	0·19	3·76	2·73	2·60	...
28	3·82	0·22	3·59	2·53	2·54	...
29	4·24	...	3·57	2·28	2·49	6·88
30	8·31	...	3·32	0·66	0·99	6·53
31	11·80	0·26	3·12	0·20	0·20	6·69

Influence upon Total Carbon Content.—It should be recorded that the melts were made under conditions which favoured the absorption of further carbon, and it is therefore of interest to note that up to 2·0 per cent. of aluminium the total carbon content remained practically stationary. Further additions, however, were responsible for a decrease in the carbon content. As the authors state, some decrease would naturally follow from the addition of any bulk of aluminium, but after allowing for this it was still found that the decrease took place. This is illustrated by the following table:—

No.	Aluminium per cent.	Other elements per cent.	Actual total Carbon.	Calculated total Carbon.	Loss of total Carbon.
27	2·375	97·625	3·76	3·89	0·13
28	3·82	96·18	3·59	3·83	0·24
29	4·24	95·76	3·57	3·81	0·24
30	8·31	91·69	3·32	3·65	0·33
31	11·80	88·2	3·12	3·51	0·39

Aluminium therefore acts in this way, although in much less degree, very similarly to silicon.

Effect of Aluminium upon the Production of Graphite.—If the results obtained from the rapidly cooled specimens are considered, it will be found that it was necessary to have 0·25 per cent. present before any decided action was noticeable. With, however, 0·50 per cent., it will be seen that the bulk of the carbon was obtained in the graphite state. It is then most curious to observe that the larger additions of aluminium seem to be responsible for a reversion to the combined state. The investigations of the authors failed to produce any satisfactory explanation of this effect, but they suggest the possibility of the formation of a double carbide of low carbon content. Further investigation will possibly be found necessary before the correct solution of this reappearance of the combined carbon is obtained.

In the slowly cooled samples the effect of the aluminium is more pronounced, and, incidentally, is very variable. The influence of the element would seem to be as susceptible to varying conditions (such as casting temperature, etc.) as the influence of silicon, and appears to be of a similar nature. It will, however, be noticed that in the slowly cooled bars the combined carbon reappears with the larger additions.

It is to be observed that in the alloys containing from 0·527 to 4·24 the rate of cooling has very little effect upon the percentage of graphite to be found in the iron. Another point deserving attention is the retention in the combined state of about 0·90 per cent. of carbon, whether slowly or rapidly cooled, through the whole of the series.

It will be thus seen that the action of aluminium is twofold—

(1) It decreases the solubility of carbon in iron.

(2) Like silicon, it has a softening effect (within the limits shown).

Added to cast irons in reasonable quantities, it therefore, whilst no doubt weakening them, renders them softer for the purposes of the machine shop.

The following tests carried out upon samples (the particulars of which are given in Table, pp. 98 and 99), will give some idea of the mechanical properties of the cast irons which have been under discussion.

No.	Aluminium per cent.	Crushing Load, tons per sq. in.
2 . . .	none	101·2
16 . . .	0·25	42·5
18 . . .	0·389	50·63
22—A . .	0·722	77·00
22—B . .	0·722	42·31
23 . . .	1·239	43·15
24 . . .	1·246	48·76
25 . . .	1·25	45·18
27 . . .	2·375	51·00
31 . . .	3·82	50·10

Nickel in Cast Iron.—Guillet added nickel in varying proportions to cast iron, and found that it favoured the precipitation of graphite, acting in a similar manner to Al and Si.

He also records that the constitution of the pearlite becomes more emulsified, attaining eventually the condition known by one school of metallurgists as "Troosto-Sorbite."

The author also has found that the addition of nickel to cast iron greatly assists the precipitation of free carbon, having in this manner a marked softening action. In no other direction does the addition appear to have a useful effect.

The energetic action of assisting the carbide to dissociate in iron-carbon alloys was particularly emphasised by McWilliam and Barnes[1] in a recent paper upon nickel steels. They found that even in steels under saturation (carbon), free carbon was precipitated by drastic annealing. Now, as shown by the author,[2] the precipitation could not in such instances have taken place previous to the resolution of the solid solution at the pearlite change, and it is therefore demonstrated that 3·0 per cent. of nickel renders even the pearlite carbide unstable at comparatively low temperatures. The results are here given :—

Nickel per cent.	Total Carbon per cent.	CC per cent.	Free Carbon, per cent.
3·15	0·30	0·27	0·03
2·92	0·47	0·41	0·07
2·96	0·67	0·37	0·30
2·98	0·74	0·04	0·70

Titanium.—The addition of titanium was for a long time firmly believed by some metallurgists to render iron exceptionally tough. Much of the well-known pig iron produced in Upper Styria has a small content of this element. Owing, however, to the great affinity which this element has for oxygen, it was seldom found in the final steel or castings. There is not much published data to hand, and what exists is hardly convincing as to the utility of the element in iron foundry practice. It would not, however, be advisable to make up our minds upon the subject without more data.

R. Moldenke, in his paper of 1908 before the American Foundrymen's Association, gave the results of his experiments made to determine the influence of this element upon cast iron.

Two series were cast, one of grey iron and one of white iron, and in each case the titanium was added in the form of 10 per cent. ferro-titanium. The bars were cast 1¼ in. dia., as in the vanadium experiments performed by the same worker, and the results are given in the following table :—

Iron used.	Per cent. added Titanium.	If Carbon added.	Broke at lbs.	Deflection.
Grey machinery	none	no	2·020	0·09
,,	·05	no	3·100	0·09
,,	·05	yes	3·070	0·10
,,	·10	no	3·030	0·09
,,	·10	yes	2·990	0·095
,,	·15	yes	3·190	0·100
White Iron	none	no	2·050	0·05
,,	·05	no	2·400	0·05
,,	·05	yes	2·420	0·05
,,	·10	yes	2·400	0·05
,,	·15	yes	2·520	0·06

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[1] *Jour. Iron and Steel Inst.*, vol. i., 1911.

[2] *Royal Society*, vol. lxxxv., 1911.

If we examine these results, we shall find that a distinct advantage was obtained by adding a small percentage to the grey iron, but that further larger additions produced no further advantage. In the case of the white irons, a slight advantage would appear to have been obtained. Moldenke attributes the action to deoxidation, and considered that there is no advantage to be gained by more Ti than is necessary for this purpose.

He further proceeds to discuss the effect upon the chilling action, and records experiments made at the Keystone Car Wheel Works, Homestead, Pa. Iron which gave 1½ in. depth of chill untreated, upon being treated with titanium in the ladle gave only 1 in. of chill. Cubes cut from the respective chilled portions were tested for compression and hardness with the following results:—

Iron.	Lbs. per sq. in.	Hardness.
Treated . . .	298,000	557
Untreated . .	173,000	445

C. V. Slocum discusses the influence of this element upon steel and iron castings. He describes how in steel practice the alloy is added to the ladle as the metal is flowing from the furnace, and from his observations it would appear that the resulting action is one of deoxidation. This should be, and is, entirely unnecessary if the charge is properly worked, and if sufficient manganese and silicon are present at the time of casting, as then deoxidation is not necessary. It is, however, stated by this writer that blowholes are prevented, and the elastic limit and reduction of area increased; that the material is more easily machined, and that the tool is less heated. With regard to cast iron, it is stated that the crushing test is increased 100 per cent. with the addition of 1·0 per cent of a 10/15 per cent. Ti alloy, and grey irons 20 to 40 per cent.; it is supposed to increase resistance to shock, and to increase the life of such articles as dies and die blocks. It is stated that 0·10 per cent. of Ti is a good proportion to use, and that it is found to practically all pass into the slag.

L. Treuheit,[1] after experiments upon the addition of 10 per cent. to 15 per cent. Ferro-Ti and 25 per cent. Ferro-Ti respectively, comes to the conclusion that the improvements in the iron are unimportant.

The claims put forward generally are—

(1) Improvement in machining qualities.
(2) Increase in hardness of chill.
(3) Increase in general mechanical tests.
(4) Increase in soundness and clearness of castings.
(5) Only very small percentages are required to produce the above result, ·05 per cent. being recorded as very effective.

Nos. 1 and 2 can hardly take effect together.

No. 3. The variations in the tests given by cast iron under normal conditions are such that it does not follow that the improvements recorded can safely be attributed to the titanium.

No. 4. It probably does tend to improve the soundness, but under normal conditions the percentages of silicon present are quite enough for this purpose.

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[1] *Stahl und Eisen*, vol. xxx. pp. 1192–1201.

No. 5. Only small percentages are required. Here we come to a discussion as to the manner in which any influence is likely to be exerted. It must not be overlooked that the element rapidly enters the slag, and that only traces are left in the metal, so that if it is of value it must be considered as a "scavenger." Le Chatelier is recorded as having not only admitted the value, but also to have given the reason for the action of this element, *i.e.* its combination with the nitrogen. It is by no means certain as to how much nitrogen is actually present in cast irons (see below); but if it had been determined, it is still a very open question as to whether the presence of nitrogen is beneficial or otherwise. With due deference, then, to the recorded opinion of the distinguished French savant, we must insist upon other solutions of this supposed beneficial influence of Ti.

Influence of Copper upon Cast Iron.—W. Lupin, after reviewing[1] other work, proceeds to describe experiments performed to determine the influence of this element upon cast iron. He concludes that whilst the addition of the element is not beneficial, its presence in pig iron has no detrimental effect upon the finished castings. It would appear to have practically no effect upon the condition of the carbon. An addition of 4·9 per cent. of the element left the iron quite grey, although it is recorded that the gradual addition had a tendency to increase the tensile strength. It is, however, claimed that the iron is rendered more fluid.

These observations have the support of other workers, and it would thus seem that copper is not likely to play an important part in the metallurgy of cast iron.

Antimony and Tin in Cast Iron.—P. Goerens and K. Elligen[2] in their experiments made bars containing varying percentages of both tin and antimony by adding the metal to molten Swedish pig iron. It was found in the case of antimony that the temperature of the primary separation of the austenite and also the solidification of the eutectic were lowered; the temperature of the pearlite change is unaffected, but the magnitude of the recalescence decreases with the increase of the antimony content. Tin was found to have a very similar influence. The effect of these elements upon the mechanical properties was not discussed.

Nitrogen.—A. Grabe[3] states as a result of very careful research, that 12 Swedish wrought irons give a percentage of N varying from ·002 to ·0045 per cent., 38 various steels ·0025 per cent. to ·0125 per cent., and 20 cast irons ·001 to ·0065 per cent. These determinations were made after the worker had critically examined the methods employed by other investigators, and would seem to be reliable. N. Tschischewski[4] gives the amount of N found in samples of iron and steel. In cast irons he found that the percentage ranged from ·0011 to ·0053, in open hearth steel from ·003 to ·0053, in Tropenas steel from ·0068 to ·0075, and in Bessemer steel from ·012 to ·015.

It will thus be seen that the nitrogen content of cast iron varies from ·001 to ·0065, and it will really be necessary for the deleterious or beneficial influence of such percentages to be determined before nitrogen as a constituent of cast iron can be considered seriously.

There is, however, still much work to be done upon the influence of gases known to exist in the iron-carbon alloys.

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[1] *Stahl und Eisen*, vol. xx. pp. 536–541, 583 and 590.

[2] *Revue de Metallurgie*, 5.

[3] *Metallurgie*, vii. pp. 72–79, Feb. 8, 1910.

[4] *Stahl und Eisen*, March 18, 1908.

CHAPTER VII.

INFLUENCE OF CASTING TEMPERATURE.

WHAT is the actual influence of varying casting temperature upon the properties of the castings produced? This is a very important question when one considers the actual works practice in many of our large foundries. Frequently the molten cast iron issues from the furnace or cupola "steaming hot," to use a colloquial phrase; yet by the time the last casting is made the metal may be hardly hot enough successfully to teem. The question naturally subdivides itself, since, in making a casting, we must consider not only the physical properties of the metal in the finished state, but also the degree of perfection with which the duplicates of the pattern are reproduced.

Influence of Casting Temperature from the Practical Standpoint.—Looking from the moulder's standpoint, it is obvious that unless the temperature is correct his work will not be good. If the iron has not sufficient superheat, his mould will be misrun, a correct impression of the mould being impossible, owing to the sluggishness of the iron. This sluggishness will also prevent the feeders from accurately performing their work, since the gates would be solid before the feeding could be accomplished. Incidentally, one would possibly discover draws, due to this absence of proper feeding; and such metal, owing to increased viscosity, is frequently found to entrap the gases of the mould, thus causing blowholes. If the metal be too hot when the casting is poured, a superabundance of "fash" results, owing to the penetration of the joints of the mould, and sometimes this trouble may even result in the metal forcing its way out. The chief trouble, however, resulting from teeming too hot is that of "scabbing"; *i.e.* pieces of the mould's face are washed off. This causes not only the direct defect of the local scab, but the sand thus released most likely occasions a further defect in some other portion of the casting. Large cores in particular are liable to scab from this cause. It will be obvious that the correct temperature for one size of casting will not be suitable for a larger or smaller one, and hence great discretion must be used by the practical man. McWilliam has stated[1] that in his opinion the correct casting temperature is that which will allow the last drop of metal just to leave the ladle, and this is a good guide in practice.

The moulder should cast his light and intricate work as early as possible, whilst his heavy lumps he should leave till the last. It is no uncommon sight in a foundry to see a moulder putting cold scrap into his iron if he thinks it too hot for his mould, but his ingenuity is, as yet, hardly equal to finding a similarly simple remedy if the metal be too cold.

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[1] *Jour. Iron and Steel Inst.*, 1904.

So much, then, for the practical foundrymen's aspect of the question.

Influence of Casting Temperature upon the Physical Properties.—It is a much debated point as to how and whether the casting temperature materially influences the physical properties of the casting. Here, again, the question is subdivided: for instance, the author considers that if the condition of the carbon or its carbide be modified by the casting temperature, as he has shown may occur under certain conditions,[1] naturally the properties are much modified; but if the microstructure does not indicate any apparent modification, he is not inclined to accept the influence as being in such cases of importance. As Professor Turner has so truly stated, "cast iron is not so sensitive to the effect of variations due to pouring temperatures as some other metals, and herein lies one of its great advantages, in that castings are not so readily spoiled by a little want of care and attention." This question has been made the subject of several researches of late years, and the author proposes now to discuss the data thus produced.

Sir Robert Hadfield, F.R.S., in discussing the influence of casting temperature on steel, recorded the deteriorating influence of either abnormally low or high temperatures, the latter giving rise to the "scalded condition of steel well known to metallurgists"; and he further indicated that this primary influence was not altogether removed even with a subsequent judicious heat treatment.

Dr Arnold, in his paper on Steel Castings, gave the mechanical properties of two exceptionally low carbon castings made from wrought iron. One of these gave phenomenal tensile results, at any rate for the time at which the paper was published, whilst the other was very inferior in its performance upon the testing machine. Arnold, at the time, stated that the analyses and conditions under which the castings were produced were identical, with the one exception, that he had no control of the casting temperature; and here, he thought, was the only explanation of the diverse tests obtained.

Howe, Sauveur, Heyn, Turner, and Stead have all expressed their opinions upon this interesting subject, but it was left for the author's friend, Percy Longmuir, whose most interesting results are given in his Carnegie Research Memoirs of 1903 and 1904,[2] to take up the systematic investigation of the subject.

One of Longmuir's early observations was of the transverse results obtained from a series of standard bars cast progressively during the teeming of a 5-ton ladle of cast iron. The period between the first and last bar was 15 minutes, and he records that he actually obtained a range of tests varying from 22 to 35 cwt.

In the same paper he records an instance of a special alloy from which he cast over 30 test bars under conditions which were identical, with the exception of a variable casting temperature. He obtained results varying from 12·5 tons MS accompanied with 5 per cent. elongation in 6 in. to 26·2 tons MS accompanied by 51·6 per cent. elongation. Now, to the author's mind, such susceptibility to the influence of casting temperature much reduces the commercial utility of an alloy. Longmuir does not state the range of casting temperatures in this particular instance, but it is easily conceivable that some low melting point alloys may be cast at several times the temperature of their melting point, whereas, in the case of the cast iron, which is the subject of our immediate study, with a melting point of

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[1] *Jour. Iron and Steel Inst.*, 1906.

[2] *Jour. Iron and Steel Inst.*, vol. i., 1903, vol. i., 1904.

1100° to 1200° C., practical limitations almost prevent the casting temperature exceeding by half the melting temperature. In the iron-carbon alloys which we have to consider, the influence, to be of importance, must be felt from the variation of, say, 100° or so either way. The results from Longmuir's earlier research are given in the following Tables.

Alloy on metal.		Analysis.			Casting of Temperature.	E.L. tons. sq.	MS tons sq.	Elong. per cent. in 2 in.	Red. of area per cent	Bending Angle.
		C.	Zn.	Sn.						
Gun-metal.	1	87·5	1·8	10·2	1173	6·468	8·376	5·5	4·23	30°
	2	87·5	1·8	10·2	1069	8·482	14·838	14·5	16·71	40°
	3	87·5	1·8	10·2	965	8·984	11·018	5·0	6·36	40°
Yellow brass.	4	73·0	26·0	...	1182	4·432	11·484	37·75	31·40	parallel
	5	73·0	26·0	...	1020	3·974	12·713	43·00	35·66	,,
	6	73·0	26·0	...	850	4·150	7·447	15·00	15·25	,,
Red brass.	7	89·6	10·2	...	1308	4·284	6·855	13·25	12·65	,,
	8	89·6	10·2	...	1073	4·263	12·649	16·00	30·28	,,
	9	89·6	10·2	...	1058	4·376	5·670	5·5	6·64	cracked 105
Muntz metal.	10	58·6	40·5	...	1038	8·753	12·454	6·0	10·60	80°
	11	58·6	40·5	...	973	9·637	18·888	15·0	16·10	180°
	12	58·6	40·5	...	943	9·526	16·287	9·5	14·81	180°

		CC.	Gr.	Si.	Mn.	S.	P.	Casting Temp.	E.L.	MS.	El. % 2 in.	Red. of area.	Bending angle.
Cast Iron.	13	·55	3·03	1·7	·66	·042	1·365	hot	...	12·271	...	...	...
	14	·54	3·11	1·77	·63	·048	1·340	fair	...	13·104	...	...	...
	15	·50	3·16	1·76	·58	·044	1·300	cold	...	11·094	...	...	...
Malleable Cast Iron.		...	...	·65	·15	·304	0·049	hot	17·41	24·335	1·57	...	...
		...	...	·71	·13	·392	0·052	fair	16·16	26·937	5·75	10·16	...
		...	...	·71	·14	·400	0·053	cold	12·24	24·02	3·50	6·24	...

The specific gravities, as a rule, increased with each lowering of the temperature.

Longmuir states that, generally speaking, the "high" casting temperature bars were dry and open, the "fair" were "close" and uniform, and the "low" temperature test bars were "open" in fracture. The "high" and "low" were not comparable in soundness with those cast at the "fair" temperatures.

We have now to consider the influence upon the mechanical properties as indicated by the figures in the tables.

The evidence would certainly point to a remarkable influence of casting temperatnre. Without exception, the "fair" test bars give the best results.

If, however, we consult the actual casting temperatures we shall be astonished at the narrow range in some of the alloys. Consider the remarkable Red brass results; here we have a drop of 15° C., producing a variation of 7 tons in the maximum stress and 15 per cent. variation in the elongation. Again, if we refer to the malleable cast-iron results, we shall observe that the indications are that the initial variation has persisted after drastic heat treatment and rearrangement of structure. Longmuir, in an interesting chapter, endeavours to explain, by the microstructure, these important inequalities in the properties of the material. He reminds us that Guillemin has stated that it is possible thus to determine whether a bronze has been cast "hot" or "cold." Charpy states that "the size of the crystals varies with the speed of solidification, and the slower the solidification the more the crystals are developed, etc." Longmuir in discussing his own results states that his microscopical examinations convince him that low temperatures favour a sharper crystallisation than higher temperatures and that, "apart from a distinct crystallisation, the crystal junctions are very sharply defined, and apparently form routes along which fracture readily travels. With fair temperatures the crystalline junctions are not at all distinct when compared with others of the series, whilst the high temperatures are considered to produce "loose" structures.

Arnold made some interesting observations upon this question, which Longmuir thoughtfully includes in his review of the matter. He suggests that the mechanical properties of a pure metal are chiefly determined by the cohesive force acting between the crystals; and he is also of the opinion, based upon his own experiments, that the actual crystals, in an alloy containing impurities, may be ductile, whilst in mass the alloy is brittle. This theory of intercrystalline cohesion would, in the author's opinion, seem to be introduced owing to the failure of the microscope to give any definite and conclusive evidence in explanation of the variations observed.

TABLE SHOWING THE INFLUENCE OF VARYING CASTING TEMPERATURE ON THE PROPERTIES OF CAST IRON.

No.	Analysis.						Casting Temperature.	Condition.	Mechanical Properties.		
	CC.	Gr.	Si.	Mn.	S.	P.			Elastic Limit, tons per sq. in.	Maximum Stress tonsp. sq. in.	Elongation per cent. on 2 in.
34	3·4	..	0·39	0·05	0·02	0·02	1320° C.	As cast	..	10·7	..
35	,,	..	,,	,,	,,	,,	1230° C.	,,	..	15·9	..
36	,,	..	,,	,,	,,	,,	1120° C.	,,	..	12·1	..
34 HT	0·77	2·57†	,,	,,	,,	,,	1320° C.	Heated to 1000° C. and slowly cooled	..	18·6	..
35 HT	,,	,,	,,	,,	,,	,,	1230° C.		..	24·0	..
36 HT	,,	,,	,,	,,	,,	,,	1120° C.		..	21·6	..
34 A	0·2 to 0·5*	3·2	,,	,,	,,	,,	1320° C.	Annealed 100 hours in ore	20·0	20·6	1·0
35 A	,,	,,	,,	,,	,,	,,	1230° C.	,, ,, ,,	24·8	29·2	8·5
36 A	,,	,,	,,	,,	,,	,,	1120° C.	,, ,, ,,	22·5	26·5	2·0
37	0·52	3·4	1·78	0·28	0·04	0·27	1400° C.	As cast	..	9·7	..
38	,,	,,	,,	,,	,,	,,	1350° C.	,,	..	14·1	..
39	,,	,,	,,	,,	,,	,,	1245° C.	,,	..	10·6	..

* Varies, according to proximity of drillings to outside or centre of bars, from 0 to 0·2 and 0·5.

† Results obtained from average drilling.

INFLUENCE OF VARYING CASTING TEMPERATURE—*contd.*

No.	Analysis.						Casting Temperature.	Condition.	Mechanical Properties.		
	CC.	Gr.	Si.	Mn.	S.	P.			Elastic Limit, tons per sq. in.	Maximum stress tons p. sq. in.	Elongation per cent. on 2 in.
37 HT	not estimated		1·78	0·28	0·04	0·27	1400° C.	Heated to 940° C. and cooled in air	..	7·1	..
38 HT	"	"	"	"	"	"	1350° C.		..	9·9	..
39 HT	"	"	"	"	"	"	1245° C.		..	8·5	..
37 A	not estimated		"	"	"	"	1400° C.	Annealed for 48 hours in a Clench-Jones muffle.	..	6·5	..
38 A	"	"	"	"	"	"	1350° C.		..	7·2	..
39 A	"	"	"	"	"	"	1245° C.		..	2·6*	..
37 Q	not estimated		"	"	"	"	1400° C.	Heated to 940° C. and quenched in water	..	2·5	..
38 Q	"	"	"	"	"	"	1350° C.		..	3·0	..
39 Q	"	"	"	"	"	"	1245° C.		..	2·7	..
43	3·35	"	0·03	0·03	0·02	0·02	1440° C.	As cast	..	9·4	..
44	"	"	"	"	"	"	1299° C.	"	..	12·1	..
43 HT	not estimated		"	"	"	"	1440° C.	Heated to 1000° C. and cooled in air	..	13·3	..
44 HT	"	"	"	"	"	"	1299° C.		..	17·2	..
43 A	not estimated		"	"	"	"	1440° C.	Heated to 1000° C. and cooled in muffle	..	18·8	..
44 A	"	"	"	"	"	"	1299° C.		..	20·5	..

* Flaw.

In a second paper given before the Iron and Steel Institute, Longmuir included some further interesting experiments upon cast iron, from which the preceding Table is extracted. It will be seen that here again the same variation is to be observed, and that subsequent heat treatments failed to eliminate the initial variations.

Although somewhat irrelevant, it will be of interest to record that Longmuir obtained precisely the same results with steel castings. Those cast "hot" and "cold" gave inferior results to those cast at the mean temperature. In the experiments with steel castings, the tests included the Arnold Alternating Stress test; and whatever the ultimate explanation of the meaning of this test, the figures obtained were remarkable.

The results will be found detailed below :—

No.	Casting Temperature.	Condition.	Reversals to complete fracture.	Maximum stress.	E.L. per cent.
97	1550° to 1600°	as cast	68	3·58	12·5
98	1470° to 1500°	as cast	48	34·2	11·5
97 A	1550° to 1600°	annealed	122	27·0	17·5
98 A	1470° to 1500°	annealed	62	28·2	18·5
99	1550° to 1600°	forged	546	40·9	27·5
100	1470° to 1600°	forged	172	40·1	28 0

It is now proposed to lay before the reader the results of some experiments made by the author in conducting his own research[1] upon the "influence of the varying condition of the carbon, etc," which were designed

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[1] *Jour. Iron and Steel Inst.*, 1906.

to weigh the influence of casting temperature in that connection. The following Table contains the results first obtained, and it will be seen that the results hardly confirm the figures obtained by Longmuir.

Test No.	Analysis.						Casting Temperature, °C.	Maximum Stress, tons per sq. in.	Fracture.
	Combined Carbon.	Graphite.	Si.	Mn.	S.	P.			
	per cent.	per cent.	per cent.		per cent.	per cent.			
A1	3·25	trace	1·29	Not exceeding 0·20 per cent.	0·036	0·023	1403, hot	13·4	White.
A2	3·25	,,	1·29		0·036	0·023	1250, fair	12·3	,,
A3	3·25	,,	1·29		0·037	0·023	1200, too cold	not run	,,
B1	3·16	0·1	1·52		0·039	0·024	1403, hot	11·75	White; little mottled.
B2	3·10	0·16	1·52		0·039	0·023	1300, fair	10·78	White; more mottled.
B3	3·00	0·26	1·52		0·039	0·024	1201, cold	7·5	White; still more mottled.
C1	1·5	1·8	1·70		0·033	0·027	1403, hot	10·7	Grey; close grained.
C2	1·1	2·19	1·70		0·033	0·027	1250, fair	10·74	Grey; fine grained.
C3	1·0	2·23	1·70		0·033	0·026	1180, cold	11·3	Grey; coarse grained.
D1	0·8	2·50	3·00		0·033	0·027	1366, hot	9·14	Grey; finely crystallised.
D2	0·71	2·61	2·00		0·034	0·026	1215, fair	9·17	,, ,,
D3	0·80	2·51	2·00		0·033	0·026	1154, cold	8·42	,, ,,
E1	0·70	2·6	2·30		0·032	0·027	1300, hot	9·85	Grey; finely crystallised.
E2	0·74	2·55	2·30		0·032	0·026	1215, fair	10·32	,, ,,
E3	0·73	2·57	2·30		0·032	0·027	1135, cold	7·56	Fibrous.
F1	0·80	2·4	2·50		0·031	0·027	1290, hot	9·37	Grey; coarser grain.
F2	0·82	2·45	2·50		0·031	0·027	1243, fair	7·53	,, ,,
F3	0·80	2·4	2·50		0·032	0·029	1210, fairly cold	8·50	,, ,,

The silicon content of the six sets varied from 1·29 per cent. to 2·50 per cent., and the bars measured 1 in. by $\frac{3}{8}$ in. in section. B1–2 and 3 are typical of the bars containing the carbon in combination, and it will be seen that the maximum stress per sq. in. gradually decreases over a range of casting temperature of 200° C., and it may here be stated that heat treatments did not alter the ratio of the figures given by these bars. E. 1–2 and 3, which fairly represent the grey irons, are the only instances in which a slight advantage is obtained from the "fair" bar; and it is interesting to record that the superiority of this bar did actually persist after heat treatment.

The variation of the results in these experiments was generally explained by the condition of the carbon; and it is important here to emphasise that the casting temperature, under certain conditions, actually influences the amount of combined carbon present in the casting. The higher the casting temperature, the higher the percentage of combined carbon is likely to be. This fact, of course, would preclude the "fair" temperature from giving the highest result; and indeed, neither in the experiments just described nor in the later ones did the advantage of the fair casting temperature appear to be such as would be deduced from Longmuir's results.

A later set of confirmatory tests[1] were made with a view to deciding the doubts thus raised, and the results are given in the Table on p. 110. They consist of a white iron and a grey iron as cast at the three temperatures, and also as subsequently heat-treated. These results would seem to point only to one conclusion, and that is, that with bars of such dimensions the strength of

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[1] *Jour. Iron and Steel Inst.*, 1907.

cast iron is likely to be variable. These tests were performed by the author with considerable care, and the mechanical tests made upon the Sheffield University testing machine by Professor McWilliam and the author may be taken as correct. The curious fact is the uniformity of the results obtained after heat treatment. It will be seen that B2 and C3, with maximum stress per sq. in. of 7·95 tons and 17·20 tons respectively as cast, give, after identical heat treatment, 34·4 and 34·70 tons per sq. in. In the grey bars, a variation in the "as cast" bars of 4 tons in the maximum stress per sq. in. was reduced to a variation of only 1·17 tons.

Test No.	Analysis.						Casting Temperature.	Condition.	Maximum Stress.	Elongation.	Reduction of Area.	Fracture.
	CC.	Gr.	Si.	Mn.	S.	P.						
	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.			sq. in.	per cent.	per cent.	
A1	3·43	..	0·93	0·10	0·056	0·03	hot	as cast	11·14	..	..	White; fairly sharp crystallisation.
B2	3·40	..	0·93	0·10	0·056	0·03	fair	,,	7·95	..	..	White; sharp crystallisation.
C3	3·41	..	0·93	0·10	0·056	0·03	cold	,,	17·20	..	..	White; well mixed crystals.
D1*a*	0 56	2·61	0·93	0·10	0·057	0·03	hot	heat-treated	24·40*	1·0	1·5	Steely; finely crystallised.
E2*a*	0·55	2·58	0·93	0·10	0·056	0·03	fair	,,	34·40	1·16	1·47	Steely; finely crystallised.
F3*a*	0·56	2·59	0·93	0·10	0·057	0·03	cold	,,	34·70	2·0	2·7	Steely; finely crystallised.
G1	0·52	2·93	2·14	0·11	0·051	0·04	hot	as cast	7·01	..	..	Grey; crystalline.
H2	0·54	2·94	2·14	0·11	0·053	0·04	fair	,,	8·40	..	..	Grey; crystalline.
I3	0·54	2·96	2·14	0·11	0·051	0·04	cold	,,	12·98	..	..	Grey; crystallised, but much finer.
J1*a*	0·20	3·21	2·14	0·11	0·053	0·04	hot	heat-treated	2·82	..	..	Dry and grey crystallisation.
K2*a*	0·21	3·22	2·14	0·11	0·053	0·04	fair	,,	3·20	..	..	Dry and grey crystallisation.
L2*a*	0·18	3·17	2·14	0·11	0·052	0·04	cold	,,	3·99	..	..	Dry and grey crystallisation.

* Unsound.

To sum up the results of the various experiments, it is the author's opinion that it is somewhat futile to work upon the hypothesis that there is a temperature at which a superior result can be obtained from cast iron. As shown in Longmuir's results, the range of what, from his experiments, appears to be the correct temperature is very small, and the author thinks that the secondary structure of the carbides and of the free carbon in cast iron tend to obscure the results which might possibly have been obtained from pure iron.

The publication of further results by independent observers will be awaited with considerable interest, and no doubt much further light will be thrown upon this interesting subject. Students cannot do better than test the matter for themselves.

CHAPTER VIII.

SHRINKAGE AND CONTRACTION IN CAST IRON.

It is found in works practice that if a certain sized casting is required, a pattern must be prepared slightly larger than the required dimensions of the finished casting. This is well known to be "allowance made for contraction," or "allowance for the final difference in size between the casting and pattern."

Irons of varying compositions behave very differently; and, in the light of recent researches by Keep, Turner, and others, we have now a very fair knowledge of what actually takes place during the solidification and subsequent cooling down of the iron, although it can be truthfully asserted that as yet we have not obtained a complete explanation of the cause of all the phenomena observed.

During the cooling down of cast irons, both contraction and expansion take place between varying temperatures according to the composition, and hence the "allowance for contraction" really refers in practice to the "net" result.

The influences governing the contraction are—

(1) The change in volume due to the change from the liquid to the solid state.
(2) The natural contraction of a hot metal during cooling.
(3) The changes in volume due to the chemical and physical changes actually taking place in the iron between the moment of solidification and the reaching of normal temperatures.

The molten metal is poured into the mould and solidifies. Metal, such as type metal, which expands slightly at this point, is an exception, and cast irons simply follow the general rule and occupy less space during than before solidification. The first to set is the metal in contact with the mould, and this outer surface takes to itself both the shape and to a great extent the size of the mould. The casting then freezes from the outside gradually to the inside, the metal nearest the centre of the thickest portion being the last to set, and over this portion, naturally, if no means of "feeding" the casting is used, more or less of a cavity or "sponginess" is found. This is due to shrinkage.

Influence of Casting Temperature upon Shrinkage.—Shrinkage varies with the composition and heat of the metal; the hotter the casting temperature of the metal, the greater the shrinkage. The casting of steel ingots is the most simple instance in which this shrinkage is observed; and to anyone familiar with the casting of steel, it is well known how much the shrinkage is accentuated by raising the initial casting temperature of the metal.

Influence of Composition upon Shrinkage.—With regard to composition, in cast iron the shrinkage is always higher with an increase in combined carbon, and may therefore be influenced by any element or circumstance which increases the percentage of this state of the carbon. The art of eliminating the defect due to shrinkage in castings belongs to the moulders' craft; and since it is fully treated by other writers,[1] it is considered unnecessary here to deal with it. Once the metal has begun to set, and during the subsequent cooling, various changes in volume take place.

As pointed out earlier in this work, immediately upon solidification, the iron carbon eutectic splits up into carbide and austenite, which action in itself most likely causes an expansion. In irons high in silicon, however, this carbide immediately dissociates, with the production of graphite, and hence a marked expansion takes place, presumably in proportion to the percentage of free carbon liberated. This is within 30° to 40° C. of the point of solidification. Further precipitation of carbon depends upon the size and composition of the mass, and there is really nothing further to note in the phenomena of expansion in an iron-carbon-silicon alloy except a gradual contraction until the recalescence point in the neighbourhood of 700° C. is reached. At this point the solid solution resolves into pearlite and the expansion due to this physical change is also under certain conditions increased by the dissociation of the pearlite carbide thus produced.

Mallet, Roberts-Austen and Wrightson, Keep, West, and Turner, are the workers to whom we are most indebted for our knowledge of this subject.

Mallet[2] conducted a series of interesting experiments to determine the accuracy of earlier workers. He became convinced that cast iron did not expand during solidification. His work was performed in a most careful manner, and was discussed by Turner[3] in an excellent paper given before the Iron and Steel Institute in 1906.

A hollow cast-iron shell "was filled with fluid cast iron of projectile quality, and the volume was measured by means of finely graduated steel-beam calipers." The results of this experiment are found in the following curve (fig. 90).

Perhaps one of the most noticeable features is the point A in the curve which Mallet endeavours in his paper to explain away as an experimental error. This point is interesting, as it has been shown by Turner to be a truthful rendering of the change in volume that takes place owing to the presence of a fair percentage of phosphorus in the iron.

Roberts-Austen and Wrightson,[4] using Wrightson's "tektometer," endeavoured to determine the densities of the various metals at the moment of solidification; but although their research points to an increase in density of cast iron, their work cannot be considered quite conclusive.

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[1] McWilliam and Longmuir, *Foundry Practice*, second edition, 1912.
[2] *Royal Society*, vol. xxiii. p. 222, 1874.
[3] *Jour. Iron and Steel Inst.*, vol. i. p. 48, 1906.
[4] *Phil. Mag.*, vol. xi., 1881, and vol. xiii., 1882.

West has done much work of value upon this question, but for the next great advance we are indebted to Keep.

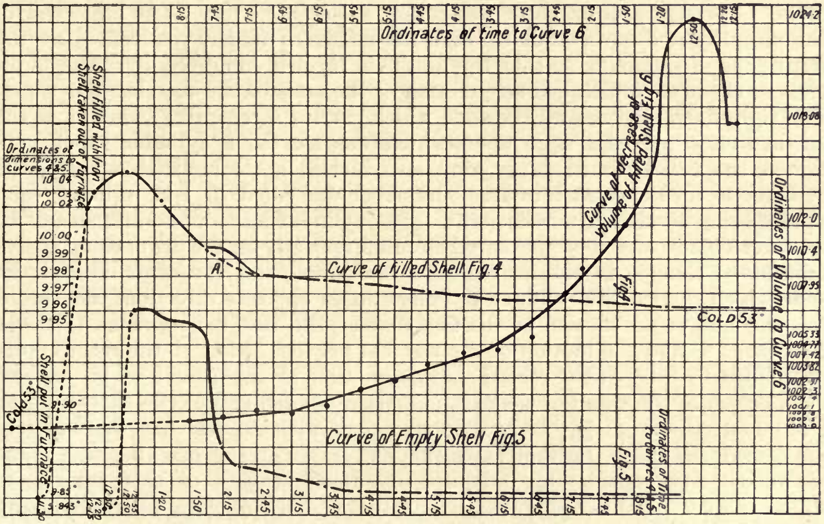


FIG. 90.

Keep's Experiments.—In the illustration (fig. 91) is to be seen Keep's apparatus for determining the changes in volume taking place during the cooling of cast iron. This illustration is taken from his book, and it will be seen to be an ingenious method of taking an autographic record of the contractions and expansions after the casting of the test bar inside the moulding box shown. A description is best in Keep's own words: "A mold

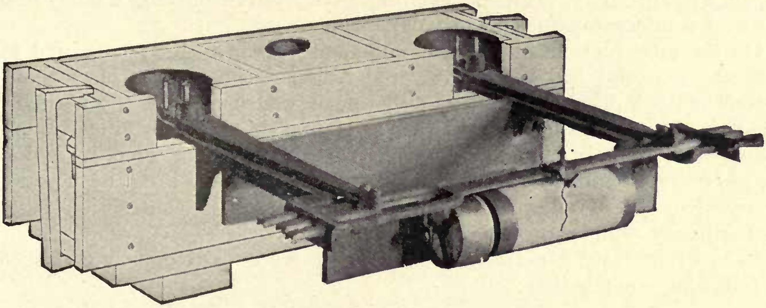


FIG. 91.

was made of a test bar 1 in. sq. by 26 in. long. In the front of the flask, near the ends of this mold, recesses were cut to allow the ends of the mold to be reached. The top of each end of the mold was covered with a piece of tin, having a $\frac{1}{4}$-in. round hole through it, the two holes being $24\frac{1}{2}$ in. apart. The autographic machine was attached to the mold in each recess by a $\frac{1}{2}$-in. round pin, which projected upwards to form a bearing for the arms which were to transmit the motion of the test bar. The inner end of each arm was 2 in. long and the outer end was 20 in. long. Through the inner end of the arm was a $\frac{1}{4}$-in. hole, corresponding with the hole in the tin cover of the mold. Through each of these was passed a $\frac{1}{4}$-in. steel pin. The inner end of the pin projected downwards through the mold. This pin was located at the front edge of the mold, so that the first skin formed embraced it. The outer ends of the arms multiplied any motion of the ends of the test bar ten times. The right-hand arm moved the slide which carried a recording pencil, and the left-hand arm moved a slide upon which was located a cylinder which contained the ruled record paper, and also carried a clock which allowed the cylinder to turn once each hour. The paper was ruled in 1-in. squares, each square being divided into twentieths. The cylinder had a circumference of 12 in., which made each inch measured circumferentially on the drum equal to five minutes of time. As one arm moved the pencil, and the other moved the slide which carried the cylinder and clock in an opposite direction, the record was the sum of the motion of the two ends of the test bar; and as this was 2 ft. long, to find the motion of the test bar per foot of length the record must be divided by 20. If the record shows a motion of the pencil to be half an inch, or ten of the small divisions, the motion of each end of the bar would be $\frac{1}{2}$ of one division, or $\frac{25}{1000}$ in." The apparatus with the test bar was entirely self-contained, and to prevent expansion the frame of the machine was made of wood. The considerable advance in our knowledge of this subject to which the use of this apparatus led is the author's apology for reproducing Keep's description at such length.

There is one important disadvantage to be found with the method under which these experiments were conducted, and that is that, in the absence of pyrometric readings, the changes in volume could not be correlated with the temperatures at which they took place. Valuable facts were, however, ascertained, and may be epitomised as follows:—

Readings were taken of the behaviour of different well-known metals after casting and during cooling down. It was found that, melted by themselves, copper, tin, antimony, lead, and bar iron gave a curve showing a fairly normal contraction unaccompanied by any expansions.

On the introduction, however, of sufficient carbon to produce a tool steel, when the material had reached a "red heat" a considerable arrest in the contraction took place, followed by a distinct expansion before the normal rate of contraction was resumed. On testing a cast iron low in silicon, a slight expansion took place immediately after solidification, succeeded by a normal rate of contraction, until at what might roughly be called a red heat a further expansion was observed, after which the normal rate of contraction followed until ordinary temperatures were reached.

In one important experiment, observations were made upon a cast iron of the following composition:—

Carbon	3·10	per cent.
Silicon	3·85	„
Manganese	0·50	„
Sulphur	0·10	„
Phosphorus	1·00	„

Apart from the rather high percentage of silicon, this may be considered an average foundry iron.

Eighteen test bars 1 in. sq. by 1 ft. long were cast, together with one bar 24 in. long. On the latter bar the changes in volume during cooling were taken by means of the autographic method recently described. This is one of Keep's most interesting experiments, since to obtain information as to the changes taking place in the iron he quenched one of the 18 1-ft. bars at each stage of the cooling down, thus hoping roughly to obtain by this method some idea of the condition of the iron at the temperature from which the bar was quenched. The cooling diagram of the 24-in. bar is given in fig. 92.

This curve is of considerable interest, and clearly shows that during the cooling down of this test bar there were three actual expansions, followed in each case by a resumption of the normal rate of contraction. The expansion began 1½ minutes after the test bar was cast, "increased until 3½ minutes, then decreased until 7 minutes." This was the first expansion. The expansion "then increased until 8 minutes, and decreased again until 10 minutes." This is the second expansion. "A very great expansion then takes place, reaching its maximum between 12½ and 14 minutes, and decreasing until 16 minutes." This is the third expansion. After the third expansion, contraction proceeds at a normal rate. The examination of the 1-ft. bars did not lead to any solution of the first and second expansions, but the interesting fact was disclosed that the combined carbon decreased during the third expansion from 0·40 per cent. to 0·06 per cent., according to the analysis given; and further, that whilst the bars quenched above the third expansion were hard, those quenched below were soft. Since the combined carbon at this point was reduced to 0·06 per cent., it is apparent that at this temperature the dissociation of the carbide of the pearlite had taken place.

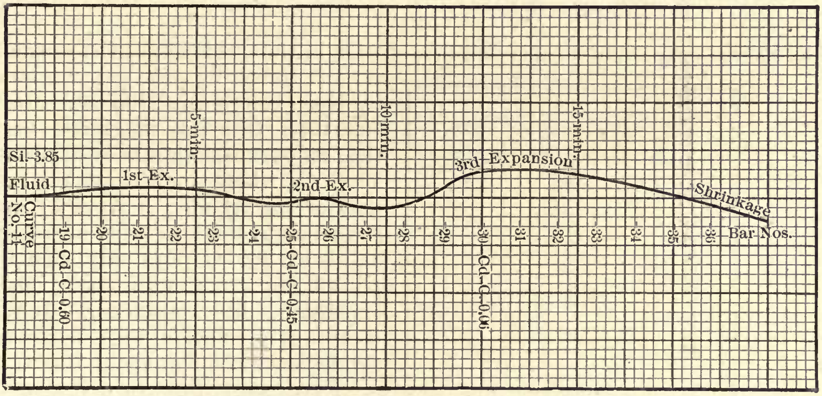


FIG. 92.

After trials with irons of varying composition, it was found that the first expansion was mainly dependent upon the percentage of silicon present: the higher this percentage, the higher the expansion. Further investigation showed, however, that if through other influences the action of the silicon upon the carbon was neutralised, then in such cases the effect of the silicon upon the shrinkage was modified. Thus Keep deduces from his experiments that the first expansion is also due to a change in the condition of the carbon.

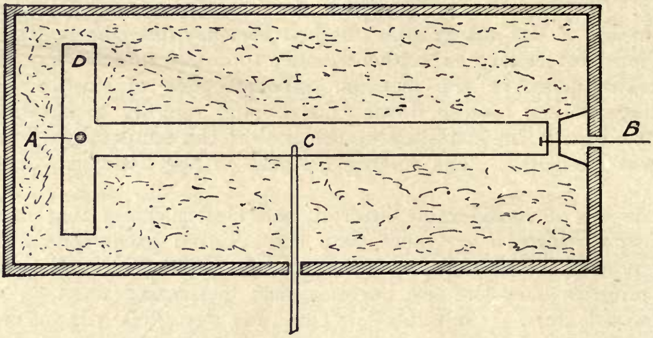


FIG. 93.—Plan of lower half of mould.

A. Fixed vertical pin. B. Movable horizontal pin.
C. Thermo-couple. D. Position of gate.

In discussing the paper given by Keep before the Iron and Steel Institute, Osmond suggested that the first expansion might be at about 1100° C., where, in his opinion, the bulk of the graphite separated; the second point would most likely occur at about 900° C., and only then in phosphoric iron; whilst the third expansion, he considered, would most likely coincide with Barrett's recalescence point at about 700° C.

Professor Turner's Experiments.—In 1906 Professor T. Turner gave a most interesting paper on this question. He had endeavoured, by careful experiment, actually to correlate the temperatures with the expansions, and undoubtedly met with considerable success.

His apparatus is shown in figs. 93 and 94, and will be seen to be quite simple: the test bar is in the form of a T, and being secured at A, the whole of the expansion is transmitted through the thin rod to the pointer at B. In this way the pointer indicates, with fair precision, the changes in volume which take place in the test bar. A naked pyrometer couple was used for determining the temperatures in the position indicated in fig. 93.

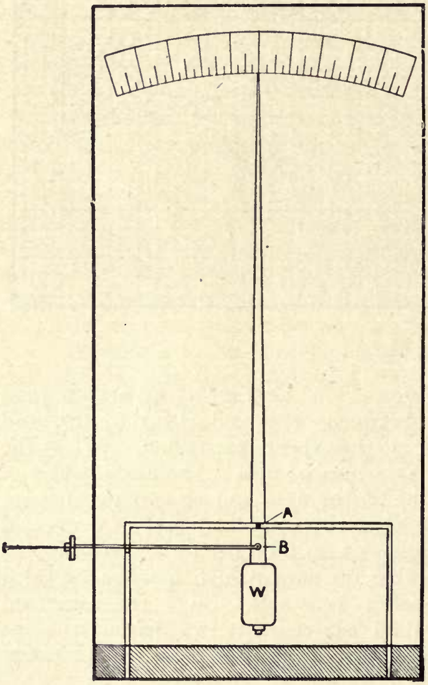
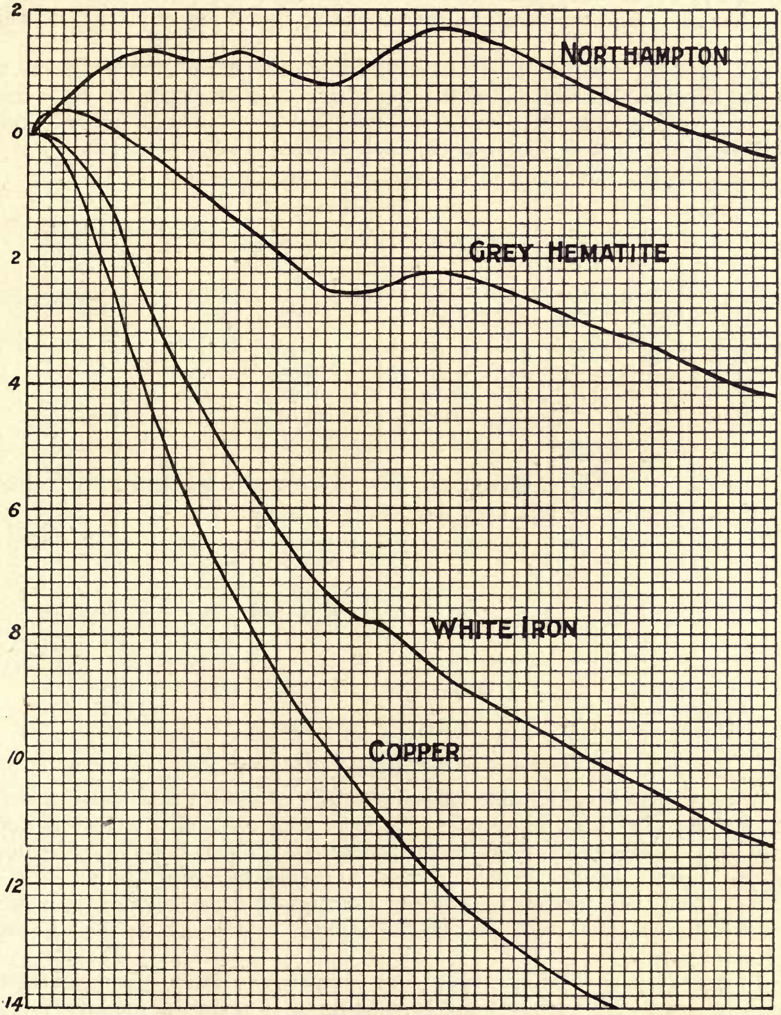


FIG. 94.—Extensiometer.

The curves given in fig. 95 summarise Turner's results with regard to expansion, and it will be seen that they completely confirm the facts as given by Keep.



Time : each division equals five seconds.

FIG. 95.

Turner found—

(1) That pure electrolytic copper, aluminium, antimony, lead, tin, and zinc yield a uniform curve, as typified by copper, without any arrest in the decrease in volume.

(2) The curves produced by white irons and carbon steels, present one marked change taking place at comparatively low temperatures.

(Turner also records the fact that he has discovered that some of the zinc-copper alloys expand similarly.)

(3) In grey non-phosphoric irons, as typified by the grey hematite, he obtained two notable expansions, one immediately following solidification, and the other at a lower temperature, corresponding to the one occurring in white irons.

(4) As a type of what is obtained from phosphoric foundry irons, the curve of Northamptonshire iron is given. Here a third expansion is evident, occurring intermediately between the two noticed in non-phosphoric irons. All the expansions were found to be much greater in such materials.

The analysis of the materials producing these typical curves were:—

	White Iron.	Grey Hematite.	Northamptonshire Iron.
CC per cent.	2·73	0·86	0·15
Gr ,, ...	...	2·53	2·60
Si ,, ...	0·01	3·47	3·98
P ,, ...	0·01	0·04	1·25
S ,, ...	trace	0·03	0·03
Mn ,, ...	trace	0·50	0·50

The cooling curves of these materials, which really constitute the value of this research, gave the following important figures:—

	Iron containing		
	Carbon only.	Carbon and Silicon.	Carbon, Phosphorus, and Silicon.
First arrest . .	almost absent	at 1135°	at 1060°
Second arrest . .	absent	absent	at 900°
Third arrest . .	at 665°	at 695°	at 730°

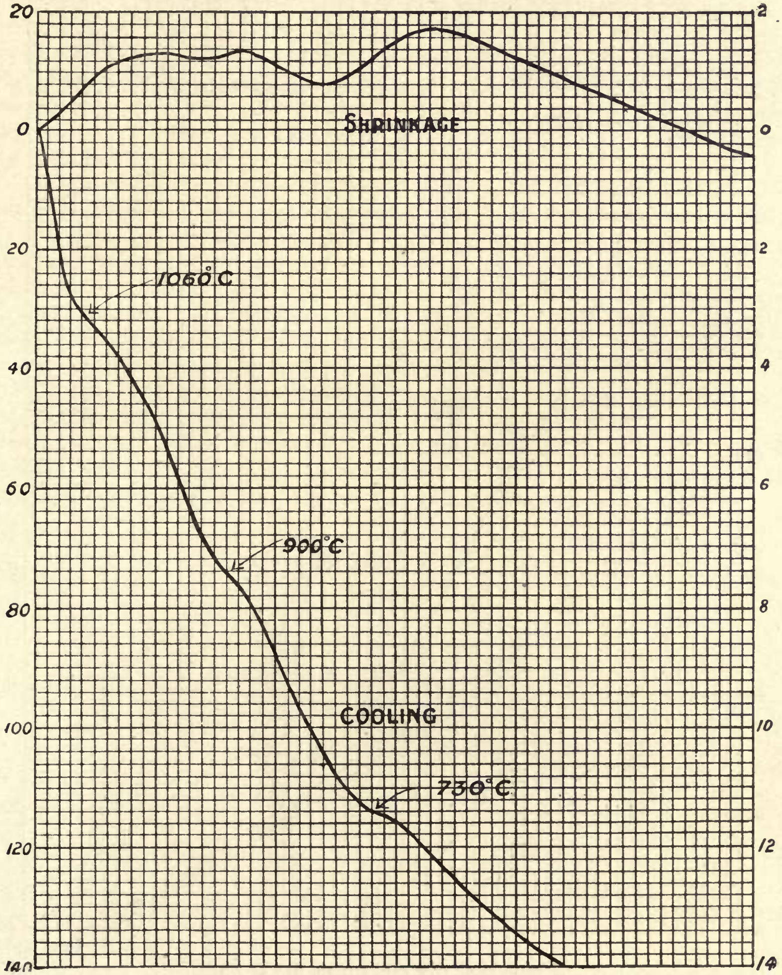
According to these figures, the temperature of the third arrest is raised by the presence of greater percentage of silicon, whilst the first arrest is apparently abnormally lowered by the presence of 1·25 per cent. of phosphorus. By the careful manner in which these experiments were conducted, it was proved that these arrests correspond exactly with the changes in volume, and therefore confirm the explanation suggested by Osmond in the discussion of Keep's paper.

In figs. 96 and 97 will be found the comparative cooling and contraction curves obtained by Turner from Northampton iron and a foundry mixture respectively. The foundry mixture analysed:—

Combined Carbon	0·79 per cent.
Graphite	2·73 ,,
Silicon	1·41 ,,
Sulphur	0·07 ,,
Phosphorus	0·96 ,,
Manganese	0·43 ,,

Now that the phenomena have been fully described, a discussion of the cause will be of interest.

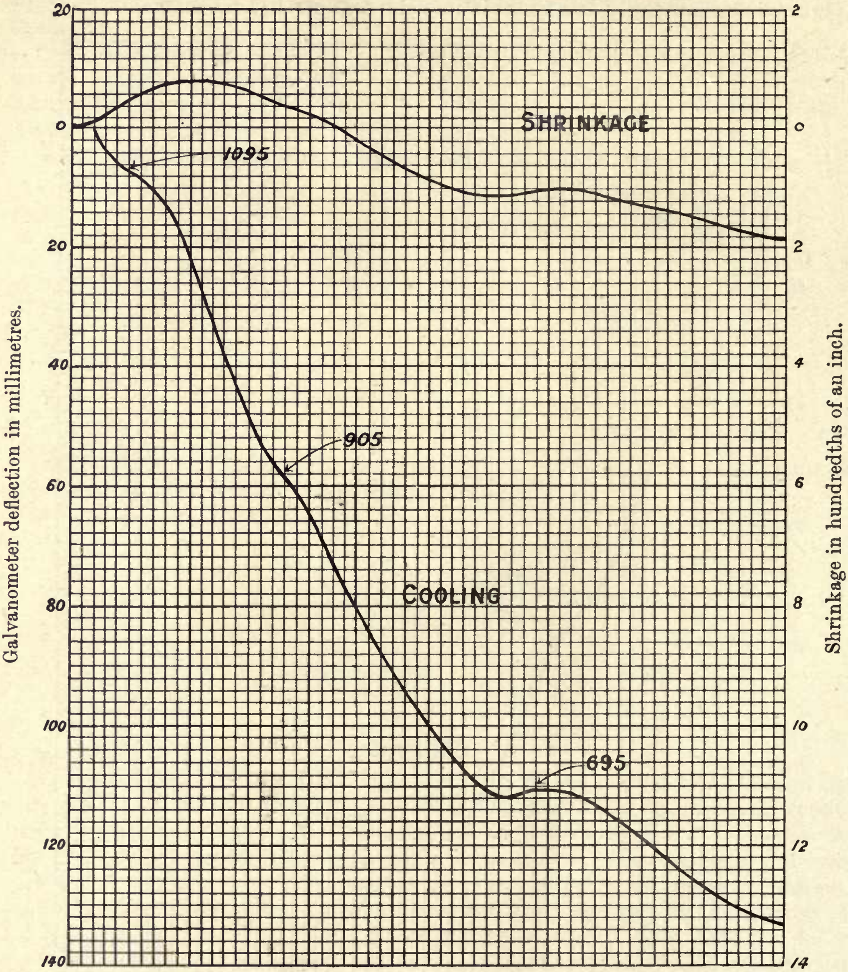
It is evident that the precipitation of free carbon is the cause of two of the expansions, whilst the intermediate expansion noticed in the presence of phosphorus is undoubtedly attributable in some manner to that element.



Time: each division equals five seconds.

FIG. 96.—Grey Northampton Iron.

With regard to the first expansion, it will be noticed that unless free carbon is present in the final casting, the expansion is of little importance, and in such instances may be explained by the production of the eutectic mixture. The splitting up of the eutectic into cementite and austenite might reasonably be expected to cause some expansion. When, however, graphite is present, the bulk of it has been shown (by Heyn and Bauer, and also by the author) to be due to the dissociation of the cementite immediately after separation, and hence the greatly increased expansion noticed in such irons.



Time : each division equals five seconds.

Fig. 97.—Foundry casting.

The second expansion seems undoubtedly to be due to phosphorus; and if reference is made to the chapter dealing with the influence of phosphorus it will be found that the solidification and breaking down of the ternary eutectic of iron, phosphorus and carbon takes place at this temperature. Here, then, is the explanation.

The third expansion takes place at the change point of hardenite into pearlite; and since it is strongly marked in the absence of free carbon, it would be reasonable to charge it to this hardenite to pearlite reaction.

The breaking up of the hardenite or "pearlite" eutectic into the ferrite and the pearlite cementite might reasonably be expected to be accompanied by a change in volume. It may not be irrelevant here to refer to the interesting experiments described in Rosenhain and Humphrey's paper before the Royal Society. As a result of a micrographic examination of almost carbonless iron which had been heated in vacuum, they come to the conclusion that the change from "Alpha" to "Beta" iron, which is the allotropists' description of the change taking place near this temperature, is accompanied by a change in volume.

It was found by Keep that a precipitation of free carbon took place whilst passing through this zone, and this, of course, would accentuate the expansion. The author has conclusively proved elsewhere that carbon must be precipitated to the extent of the percentage required to produce "hardenite" during or immediately after this recalescence; and in cast iron containing no combined carbon such precipitation must logically have taken place at or about this temperature. Such are the explanations of these changes in volume, in the light of recent research.

The change of volume produced upon reheating cast iron recorded by Percy, Outerbridge, and Carpenter and Rugan is quite another question, and is therefore treated separately in the next chapter.

With regard to the "net contractions" of cast irons of varying silicon content, Keep's table is most useful, and is here presented.

Kind of Iron.	Average per cent. Silicon.	No. of Series.	Test Bars ½″ □.	1″ □.	2″ × 1″.	2″ □.	3″ □.	4″ □.
"Iroquois" with silicon added by Pencost ferro-silicon	0·80	1	·183	·160	·148	·131	·116	·102
	1·21	2	·172	·150	·138	·125	·110	·106
	1·88	3	·166	·145	·130	·109	·069	·039
	2·01	4	·162	·143	·123	·099	·066	·128
	3·19	5	·157	·105	·094	·075	·067	·057
	3·04	6	·169	·130	·086	·077	·085	·033
"Hinkle" and Pencost	0·93	7	·176	·149	·144	·139	·115	·072
	1·17	8	·160	·145	·126	·122	·093	·092
	1·67	9	·156	·141	·134	·128	·083	·036
	2·23	10	·154	·124	·092	·094	·075	·067
	2·71	11	·157	·102	·090	·062	·053	·023
	3·50	12	·144	·098	·092	·068	·043	·023
Ulich Stove Co. . .	2·82	14	·148	·098	·083	·072	·063	·035
,, . .	3·18	13	·130	·095	·091	·079	·072	·052
,, . .	3·50	15	·123	·094	·096	·091	·078	·032
Car-wheel Iron . .	0·77	19	·238	·153	·142	·144	·126	·115
Light machinery . .	1·76	16	·171	·151	·143	·129	·100	·069
Heavy machinery . .	2·06	18	·161	·139	·120	·091	·067	·042
Air furnace for malleable	0·89	17	·248	·247	·221	·201	·157	·144

N.B.—All the bars were 12 in. long.

It will be seen that for the same silicon the heavier bars give less contraction, and this is probably to some extent explained by the precipitation of free carbon being more complete in such bars. This is not a sufficient explanation of this variation, as any one, such as the author, who is actively engaged in manufacture, well knows; but it may be understood by a complete consideration of the whole question of solidification and cooling of the material. Owing to the outside setting first, as previously explained, the bar to some extent takes the size of the mould, and the subsequent shrinkage, as distinct from contraction, is therefore internal. The usual works allowance for contraction in grey cast iron is $\frac{1}{8}$ of an inch to the foot, whilst in white iron the allowance is made from $\frac{3}{16}$ to $\frac{1}{4}$ in. If white iron is to be annealed, some of this contraction is lost, and the finished casting, owing to the precipitation of free carbon, will approximate in contraction to the $\frac{1}{8}$th of an inch to the foot allowed for grey cast iron.

CHAPTER IX.

THE GROWTH OF CAST IRONS AFTER REPEATED HEATINGS.

This peculiar property of cast iron has been known for many years, but it is only very recently that the explanation has been forthcoming.

T. Beddoes, in a paper communicated to the Royal Society in 1791, stated that "in annealing crude iron with or without charcoal it is known to increase in all its dimensions. I have seen bars originally straight bent like an S when long exposed to heat in circumstances where they could not extend themselves."

Percy, in his classical book upon the metallurgy of iron and steel, recapitulates the occurrences of this kind with which he had come in contact, and ends his article upon the subject as follows:—

"Advantage has been taken of this permanent increase in volume which cast iron acquires by long exposure to a high temperature, in rendering cannon-shot serviceable which had been cast too small. The shot was heated in a charcoal fire, well imbedded in the charcoal, and allowed to cool under charcoal dust. Their surface was bluish-grey, and did not require any cleaning to fit the shot for use; whereas in previously attempting to employ a hot-blast oven for the same purposes, the surface became coated with firmly adherent red oxide, so difficult to detach that it was found preferable to recast the shot than incur the labour and expense of cleaning them."

The author has himself come across many instances of this growth of cast iron on exposure to high temperatures, in grate bars, oven plates, furnace castings generally, and in chills used in the iron foundry.

It has been suggested that the discovery of this property of cast iron, which has since been proved to be peculiar only to certain varieties of iron, would be of considerable use in the industrial world, and that castings made too small have been rendered the correct size by these means. Unfortunately it is a fact that this very process of expansion ruins the material itself at the same time, and it is one which the author does not, therefore, recommend. It is, however, of great importance that we should understand the cause, so that we may prevent the occurrence of this phenomenon, since in many instances great trouble has already arisen and will continue to ensue from it.

During the Baltimore fire, structures which had been considered fireproof were proved unsatisfactory owing to the damage done to the masonry by the "growth" of the cast-iron members of the ironwork construction. Floor levels and walls were found to be unsuited for further use owing to this very cause.

A. E. Outerbridge[1] (Jr.), of Philadelphia, was the first to bring the question seriously to the front in recent years, and we are indebted to him for some very interesting experiments.

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[1] Franklin Institute, 7th January 1904.

He intentionally reproduced this phenomenon in grey cast-iron test bars, and was actually enabled by repeated heatings and coolings to make a bar 14–13/16 in. by 1 in. by 1 in. "grow" until it measured 16½ in. by 1⅛ in. by 1⅛ in. To do this it was found necessary to heat the bar twenty-seven times to about 800° C. Outerbridge, curiously enough, says that this increase of 40 per cent. in volume is unaccompanied by any change in weight, and hence deduces the fact that the change is due to some intermolecular rearrangement. This has since been proved a fallacy, as will be seen upon an examination of the researches of Rugan and Carpenter. However, every honour is due to Outerbridge for the systematic way in which he attacked this problem, and for the valuable data he obtained. He found—

1. That grey cast iron expands more rapidly than white cast iron.
2. That the deposition of free carbon by the dissociation of the carbide did not account for the great change in volume.
3. That wrought iron and steel contracted slightly under the same treatment.

Whilst the application of this phenomenon made by Outerbridge is very interesting, the inevitable deterioration of the quality of the iron owing to its treatment must prevent its use in practice.

We will now turn to the paper on this subject given by H. F. Rugan and H. C. Carpenter before the Iron and Steel Institute in May 1909. This research is particularly to be admired for its exhaustive examination of the subject. The question is taken up practically where Outerbridge left it, and, in the author's opinion, is worked to a satisfactory conclusion.

Rugan and Carpenter began their investigation by determining the temperature at which the "growth" proceeded with the greatest rapidity, using a grey cast iron for the purpose. Although in the case of iron valves subjected to a superheated steam at 366° C. permanent increase in size was considered to take place, they considered this to be a different phenomenon, since at 600° C. they obtained no expansion. Growth was determined to commence at about 650° C., but at 675° C. the expansion increased eightfold, and the rate of growth at 730° C. was such that it almost appeared to have reached its maximum, since at 900° C. the further increase was only just perceptible. Possibly the most interesting feature was the fact disclosed that the maximum result was obtained by three hours' heating at a given temperature, and that the increase in time to seventeen hours did not appear to make any appreciable difference.

The results are given in the following table :—

Heat No.	Temperature.	Bar No. 1.		Bar No. 2.		Bar No. 3.	
		Time.	Growth in ins.	Time.	Growth in ins.	Time.	Growth in ins.
1	600° C.	1 hour	nil	2 hours	nil	3 hours	nil
2	650° C.	,,	nil	,,	0·0020	,,	0·0050
3	675° C.	,,	0·0156	,,	0·0250	,,	0·0300
4	700° C.	,,	0·0234	,,	0·0342	,,	0·0312
5	730° C.	,,	0·0312	,,	0·0346	,,	0·0352
6	760° C.	,,	0·0313	,,	0·0350	17 hours	0·0352
7	800° C.	,,	0·0313	,,	0·0350	,,	0·0352
8	860° C.	,,	0·0313	,,	0·0350	,,	0·0352
9	900° C.	,,	0·0315	,,	0·0352	,,	0·0355

They next subjected several commercial irons to the treatment likely to produce this phenomenon. Amongst the bars was one cut from a new annealing oven casting, the composition of which was—

Carbon	3·14 per cent.
Silicon	·96 ,,

The bars were heated ninety-nine times for four hours at temperatures varying from 850° C. to 950° C., and the following table gives the data obtained from the before-mentioned bar:—

SAND CASTING.

	per cent.
Carbon	3·14
Silicon	0·965

Length. Inches.	Diameter. Inch.	Volume. Cubic Inches.	Increase per cent.	Weight. Grms.	Increase per cent.	Heat No.
*5·9968	0·7500	2·648	...	305·70	...	...
6 0540	0·7570	2·725	2·91	...	...	1
6·0862	0·7620	2·775	4·80	...	...	2
6·1150	0·7660	2·820	6·50	...	...	3
6·1495	0·7722	2·870	8·39	...	...	4
6·1720	0·7789	2·940	11·01	...	...	5
6·2620	0·7743	3·010	13·70	...	...	6
6·2785	0·7862	3·040	14·80	311·51	1·91	7
6·3075	0·7894	3·110	17·40	312·01	2·07	8
6·3277	0·7915	3·120	17·80	312·56	2·25	9
6·3635	0·7957	3·160	19·30	312·75	2·31	10
6·3822	0·7976	3·180	20·10	313·24	2·47	11
6·4030	0·7993	3·210	21·20	313·53	2·56	12
6·4260	0·8010	3·230	22·00	313·90	2·69	13
6·4420	0·8022	3·250	22·70	312·69	2·29	15
6·4490	0·8023	3·255	22·90	312·79	2·32	17
6·4570	0·8039	3·260	23·15	313·40	2·52	21
6·4580	0·8040	3·275	23·65	312·81	2·33	22
6·4590	0·8046	3·280	23·90	313·18	2·45	23
6·4620	0·8048	3·285	24·10	313·40	2·52	24
6·4620	0·8050	3·285	24·10	313·01	2·39	25
6·4625	0·8050	3·285	24·10	313·41	2·53	26
6·4520	0·8044	3·270	23·45	...	...	27
6·4625	0·8050	3·285	24·10	313·02	2·40	28
6·4670	0·8058	3·290	24·30	313·68	2·62	30
6·4772	0·8064	3·300	24·65	313·82	2 66	32
6·4810	0·8065	3·305	24·80	314·64	2·93	34
6·4890	0·8056	3·300	24·65	313·73	2·64	38
6·5130	0·8097	3·350	26·50	316·91	3·68	42
6·5135	0·8108	3·360	26·75	316·16	3·44	47
6·5310	0·8125	3·380	27·70	316·93	3·70	52
6·5450	0·8136	3·390	28·01	317·22	3·77	57
6·5670	0·8173	3·435	29·70	319·18	4·42	61
6·5970	0·8230	3·500	32·25	321·46	5·16	71
6·6250	0·8275	3·550	35·40	324·89	6·29	81
6·6240	0·8273	3·540	34·90	323·35	5·80	84
6·6450	0·8314	3·610	36·20	328·50	7·46	94
6·6540	0·8340	3·625	36·80	329·79	7·90	99

* Original.

The above typifies the results obtained in this experiment, as all the bars were comparatively alike in composition. It will be found on examining this table that the bar has finally grown in length from 5·9968 to 6·654 in., and in diameter from ·75 to ·834 in. This is equal to an increase in volume of 36·8 per cent. and thus confirms Outerbridge's experiments. One discrepancy between the results, however, is observable, and that is, that whereas Outerbridge obtained no increase in weight along with the growth in volume, Rugan and Carpenter, as will be seen, obtain a gradually increasing weight with the increasing volume.

During this early work the authors became convinced that it would be necessary, before they could arrive at the cause or causes of this phenomenon, to correlate "growth" with the composition of the material. With this end in view several series of test bars were prepared with a view to finding the influence which the various elements in different proportions had in the matter.

The first series prepared was to determine the influence of varying percentages of carbon; and if the following table is examined, it will be seen that the percentage of this element varied from 4·03 to 0·15, that is, from a normal 4·0 per cent. carbon pig iron to ingot iron.

Alloy.	Percentage.				
	Carbon.	Silicon.	Manganese.	Sulphur.	Phosphorus.
A	4·03	0·243	0·15	0·018	0·010
B	3·70	0·233	0·16	0·018	0·011
C	3·08	0·172	0·13	0·019	0·010
D	2·59	0·146	0·12	0·016	0·012
E	1·96	0·215	0·20	0·013	0·015
F	1·58	0·168	0·17	0·015	0·014
G	0·99	0·233	0·19	0·015	0·012
H	0·55	0·182	0·20	0·013	0·014
I	0·15	0·186	0·15	0·040	0·017

These bars are all described as being white and free from graphite, and being too hard to true up by turning, were ground to size. It may here be said that the series was cast in both sand and chill moulds; but since the chilled ones behaved very much the same as the others, only those cast in sand will be here dealt with.

The whole retained their shape to the end of the treatment, and, it may be said, scaled very little. A produce scale to the extent of 0·0015 in., and the others more as the carbon decreased. This is of interest as showing that, owing to greater affinity of oxygen for carbon than iron, the latter was preserved at the expense of the former.

It is deserving of attention that the alloys E.F.G.H contained blowholes, whilst A.B.C.D.E did not. Since the silicon and manganese were fairly constant through the series, it would appear that the "Density Quotient" was modified in the richer carbon alloys by the presence of a greater percentage of carbon. Now, as a matter of fact, according to Wahlberg's excellent exposition of Brinnell's interesting researches, it would seem that even the sound bars contained barely enough silicon and manganese to render them so. It would be interesting to determine this influence of the presence of varying percentages of carbon upon the solvent power of iron for "occluded gases." In the steel foundry it is generally accepted that the milder the material the greater the care required to render it sound.

To return to the subject, it is stated that these bars were again heated between 860° and 960° for the considerable number of times specified in the paper. The following table summarises the results:—

Alloy.	No. of Heats.	Percentage change of Volume.	Percentage change of Weight.
B	78	-0·350	-1·72
C	78	-1·675	-1·19
D	78	-0·915	-1·19
E	78	-0·026	-1·47
F	39	-0·405	-0·64
G	39	-0·470	-0·52
H	34	-0·507	-0·17
I	39	-0·060	+0·02

It will be seen that A is not included: the reason is that, in that instance, the chilled bar was used. Presumably that was because it was necessary to "chill" it to retain the carbon in combination. As a matter of fact, this bar on being heated ninety times increased in volume 6·88 per cent., but in weight showed a slight loss. The complete figures obtained from this particular bar are now given:—

ALLOY A.—CAST IN CHILL.

	Per cent.
Carbon	4·03
Silicon	0·243
Manganese	0·15
Sulphur	0·018
Phosphorus	0·010

Length. Inches.	Diameter. Inch.	Volume. Cubic Inches.	Change. Per cent.	Weight. Grams.	Change. Per cent.	Heat. No.
*5·9587	0·9486	4·2104	...	618·06	...	...
5·9440	0·9483	4·1976	-0·305	618·00	- 0·01	1
5·9405	0·9490	4·2013	-0·216	617·82	- 0·04	2
5·9427	0·9490	4·2027	-0·183	617·72	- 0·05	3
5·9425	0·9487	4·1992	-0·266	617·57	- 0·07	4
5·9400	0·9487	4·1977	-0·303	617·18	- 0·12	7
5·9375	0·9477	4·1867	-0·562	617·00	- 0·17	11
5·9420	0·9477	4·1902	-0·480	616·71	- 0·22	13
5·9380	0·9480	4·1910	-0·460	616·55	- 0·24	17
5·9360	0·9473	4·1831	-0·650	616·35	- 0·27	18
5·9340	0·9472	4·1805	-0·710	616·34	- 0·28	19
5·9360	0·9472	4·1825	-0·663	616·15	- 0·31	20
5·9340	0·9474	4·1822	-0·670	616·00	- 0·33	21
5·9340	0·9472	4·1810	-0·700	615·96	- 0·34	22
5·9360	0·9475	4·1848	-0·609	...	...	23
5·9365	0·9470	4·1807	-0·710	615·59	- 0·39	24
5·9355	0·9460	4·1711	-0·935	615·55	- 0·40	26
5·9345	0·9467	4·1757	-0·826	615·22	- 0·46	28
5·9400	0·9470	4·1835	-0·639	615·08	- 0·48	30
5·9550	0·9470	4·1941	-0·388	614·44	- 0·58	34
5·9660	0·9480	4·2108	+0·009	614·15	- 0·63	38

* Original.

ALLOY A.—*contd.*

Length. Inches.	Diameter. Inch.	Volume. Cubic Inches.	Change. Per cent.	Weight. Grams.	Change. Per cent.	Heat. No.
5·9700	0·9482	4·2148	+0·015	614·24	- 0·62	43
5·9780	0·9496	4·2330	+0·535	613·63	- 0·71	48
5·9535	0·9509	4·2269	+0·392	612·62	- 0·88	53
5·9645	0·9527	4·2500	+0·940	612·19	- 0·95	57
6·0190	0·9594	4·3600	+3·550	611·17	- 1·11	67
6·0770	0·9665	4·4500	+5·700	611·10	- 1·12	77
6·0840	0·9665	4·4600	+5·940	610·29	- 1·26	80
6·0870	0·9680	4·5000	+6·880	610·56	-01·21	90

It will be noticed from the above results that until the thirty-eighth heating no real expansion was recorded, and not until towards the last heatings did it become of importance. "Broadly speaking, then, pure iron carbon alloys do not expand permanently, but, on the contrary, shrink."

Our authors consider that the question as to what material is suitable for purposes where expansion under repeated heating and cooling is to be guarded against is here answered. They suggest that an iron containing about 3 per cent. of carbon with only very small percentages of other elements present will meet the case, and the author considers their deduction correct. Before proceeding to the next part of the work, it is worth while recording that the losses in weight are accounted for by the furnace gases penetrating into the muffle in which the heating was done, and thus oxidising the carbon.

Bars were next prepared having carbons varying from 4·60 per cent. to 3·02 per cent., and silicons ranging from ·79 per cent. to ·50 per cent. On subjecting these to the process, it was found that the permanent expansion here obtained was, roughly, proportionate to the amount of silicon present. One bar in this series which did not primarily contain graphite did not expand more than A of the last series; and after considering the experiments to date, the facts were believed to be established:—

1. That alloys not containing graphite do not "grow."
2. That alloys containing graphite are, under suitable conditions, capable of "growing."

The bar A and the one which was described as behaving in a similar manner were subsequently proved not to expand until the precipitation of temper carbon began to take place, and the ultimate expansion would seem in these two cases to be chiefly due to change in volume arising from this reaction. Since the great importance of silicon would appear to have been demonstrated, a series of bars of varying silicons were produced, and the analyses are here set forth:—

Alloy.	Percentage.						
	Total Carbon.	Combined Carbon.	Graphite.	Silicon.	Manganese.	Sulphur.	Phosphorus.
N	3·98	0·64	3·34	1·07	0·25	0·010	0·013
O	3·98	0·68	3·30	1·79	0·23	0·010	0·013
P	3·79	0·30	3·49	2·96	0·25	0·010	0·012
Q	3·76	nil	3·76	4·20	0·27	0·010	0·012
R	3·79	nil	3·79	4·83	0·30	0·010	0·012
S	3·38	nil	3·38	6·14	0·30	0·010	0·013

It was considered that since the earlier members of this series would contain the carbon in combination to some extent, and the latter members would contain it as graphite, the influence of the temper carbon produced in the former could be compared with the influence of the graphite in causing the expansion.

Outerbridge has expressly stated, without giving definite reasons, that he did not consider the deposition of free carbon accounted for the "growth" of cast irons, and the following calculation taken from Rugan and Carpenter's paper will illustrate the maximum influence possible from this factor. It is assumed that for the purposes of this calculation the precipitated temper carbon has a specific gravity of 1·45, *i.e.* the lowest figure obtained for wood charcoal, and hence the maximum increase in volume is obtained.

Specific gravity of Fe_3C at 16° C. . . . 7·07
" " Fe at 16° C. . . . 7·86

	Fe_3C.	3Fe.	C.
Weight (grms.)	180	168	12
Volume (c.c.)	25·46	21·37	8·28

i.e. 25·46 cubic centimetres become 29·65.

Volume increase, 16·46 per cent.

The above represents the dissociation of the iron carbide, of which, in a white iron, there is present only from 45 per cent. to 60 per cent.; hence 8 per cent. to 10 per cent. increase in volume would be all that was possible.

As a matter of fact, the author has determined the expansion caused by the complete precipitation of the carbon in white irons, and finds that the expansion is about 3·0 per cent. This would therefore make it appear that the specific gravity of the annealing carbon is comparable with that of graphite.

The bars in the last table were subjected to the usual heat treatment, and were ultimately found to have expanded roughly in proportion to the silicon present.

The following curve (fig. 98) records the results obtained.

It will be seen that it may now be safely deduced that in some manner the silicon is responsible for the expansion, and, furthermore, it will be noticed that the expansion due to the precipitation of free carbon is rendered insignificant.

A photograph, fig. 99, of the whole of the bars of this series after the last heating is of interest; and as it illustrates, to some extent, the nature of the change, it is here reproduced.

The double-letter row are a duplicate set of bars cast to determine whether proximity to the runner had any influence upon the action. The second series were taken as far from the runner as possible. These check experiments were made as a result of earlier observations: the results, however, speak for themselves.

As a result of their experiments, the authors draw the following conclusions:—

(1) "In a series of cast irons of approximately constant carbon, the ultimate growth after repeated heatings is, broadly speaking, proportional to the silicon present. This relationship holds up to 6 per cent. of silicon."

(2) "The growth is far in excess of that which can be caused by the conversion of combined to free carbon, and is, in fact, much the largest in high silicon alloys which contain no carbon combined with iron."

(3) "The behaviour of the alloys on repeated heatings, and particularly of Q, R, and S, points to the view that two agencies are at work in their growth, viz.—

(*a*) "The internal pressure of gas which they contain in their original cast condition, and which is probably chiefly physical in its character.

(*b*) "The effect of external gas in contact with the alloys during their heat treatment, which is probably partly physical and partly chemical in its nature."

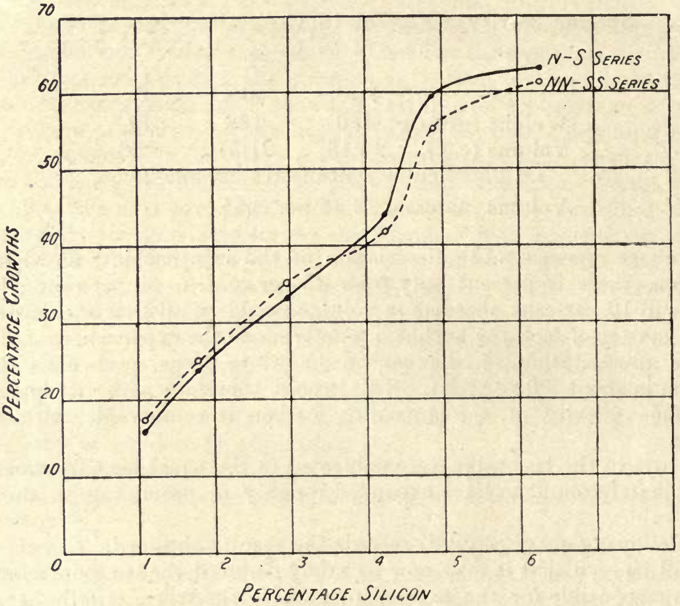

FIG. 98.—Alloys N to S. Curves illustrating the relation between percentage growth and percentage silicon.

The increase of weight, as distinct from the increase in volume, is next considered; and the authors demonstrate that the net increase in weight is in the iron and silicon oxidised minus the loss of carbon by oxidation to CO_2.

With regard to the oxidation of the silicon, accepting Guillet's suggestion that this element is present as FeSi, they show that by the oxidation of this compound to FeO and SiO_2 the increase in weight is not accounted for, and therefore they conclude that in the bars showing great expansion the free iron itself must also have become oxidised.

By an interesting set of analyses given elsewhere, they show that the carbon was oxidised to a greater extent in the irons containing least silicon, and further come to the conclusion that in the irons in which there is least combined carbon the oxidation of this element is at a minimum. This fact is interesting as supporting the author's views on this subject published in 1909.[1]

It is of interest to note the analytical method used to determine the actual oxidation of the silicon during this process of expansion. They "found, on analysing one series of the six alloys, that a sample of the original casting dissolved completely in hydrochloric acid, and that the final precipitate of silica after ignition was quite white and flocculent. Proceeding through the series, there came a point at which the hydrochloric acid failed to dissolve the

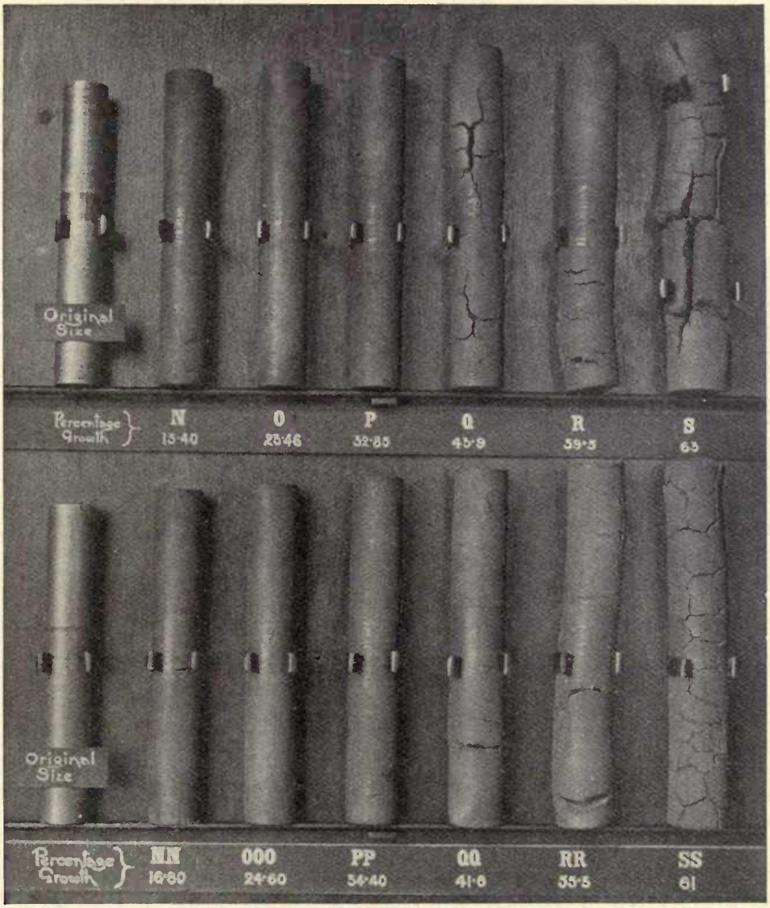

Fig. 99.—Illustrating the appearance of the alloys of the N to S series after they have reached their ultimate growth.

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[1] W. H. Hatfield, *Jour. Iron and Steel Inst.*, 1909.

entire sample, a micro-crystalline grey residue being left." They "interpret these results to indicate that in the original sample the silicon was unoxidised," and *vice versa.*

With regard to the changes observed in the microstructure, alloy P fairly represented the series, having about 3·0 per cent. of silicon present, and showing an ultimate expansion of 34 per cent.

Fig. 100 shows the structure of the original casting. A typical structure of a grey cast iron, with the graphite cutting up the matrix of ferrite (and silico-ferrite).

Fig. 101 shows the structure "of a part of the interior to which the gas has not yet penetrated after three heats. It is a most interesting photograph, because it throws light on changes that take place in the interior of the alloy before the gases penetrating from the outside have had time to make their influence felt. The three large black areas are holes, and the lines distributed through the white areas, although they doubtless correspond to original positions of graphite, no longer represent as much of it. They are," say the authors, "for the most part slits from which the graphite plates have been removed" by the gas originally dissolved in the metal. The author cannot quite accept this explanation, since the gases dissolved normally in cast iron would not, in his opinion, have this effect, being, as they are, mostly of a reducing nature, *i.e.* hydrogen, nitrogen, and carbon monoxide ; at this stage, however, he proposes merely to express the authors' views. They state, later, in their work, and the author thinks with much greater truth, that the furnace gases "penetrate to a certain depth during this period, possibly along slits existing between the graphite plates and the solid solution of silicide of iron, and through holes which exist here and there ; yet they are not actually absorbed by the solid solution until the oven is cooling. During this absorption the oxides of carbon oxidise the iron silicide," which action is, they say, accompanied by growth and incipient disintegration. They also consider that minute explosions may take place between the dissolved hydrogen and these oxidising influences which may assist in the expansion. Before considering this explana-

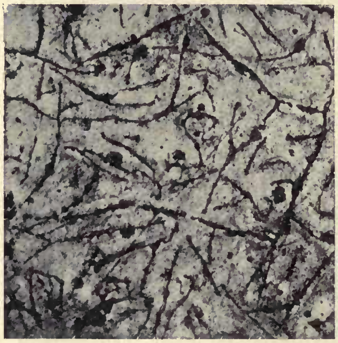

FIG. 100.—Structure of original casting. Black lines represent graphite plates. Magnified 150 diameters.

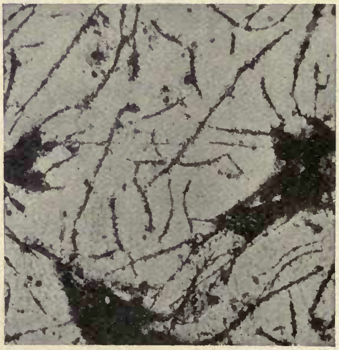

FIG. 101.—Shows development of holes in the interior to which gases have not yet penetrated. Magnified 150 diameters.

tion, however, it must be first demonstrated that the gases are actually absorbed when the metal cools down. There is no doubt that the crevices or planes of weakness developed by the graphitic plates assist in conveying the oxidising influences to the interior of the casting; and, as Saniter expressed it in the discussion, "every time it was annealed and expanded, whether by oxidation of the silicon or only a slight oxidation of the iron, the presence of those bodies again prevented it from contracting to its old size when it cooled, and that process was repeated when it was again stretched by heating." As also pointed out by Saniter, it was most interesting that a further heating and cooling was necessary to continue the expansion. He asks, with much point, "Why is it necessary to cool before continuing the heating?"

Fig. 102 shows the structure of the finally expanded metal, and illustrates how the plates of graphite have been replaced by the "blurred markings," which have, no doubt, been accounted for in the foregoing paragraph.

Fig. 102.—Typical structure after maximum growth has been reached. Magnified 150 diameters.

The authors next endeavoured to expand some iron silicon alloys not containing more than 0·20 per cent. of carbon. They met with no success, and found that it was absolutely necessary to have free carbon present before the phenomenon could be obtained.

One of the most interesting experiments, epitomised in fig. 103, was that of heating the bar S in a vacuum and also in the normal furnace atmosphere of the experiments. It was found that in vacuum it shrank, if anything, in size, whilst, as usual, it expanded in the furnace gases 67 per cent. Here is proof positive as to the influence at work.

Subsequently the occluded gases were withdrawn from one of these S bars before exposure to the normal heatings, but it still attained a permanent expansion of 67 per cent., thus showing that in this instance the occluded gases had little influence. In one bar of low silicon content (N 1·07 per cent. silicon) it must be recorded that an expansion up to 11 per cent. took place in vacuum, but this phase does not seem to have been thoroughly worked out. Suffice it that the bar did actually grow 11·10 per cent. without any recorded increase in its weight. Here would, at any rate, appear to be an instance in which the occluded gases and the precipitation of any combined carbon present were responsible for the interesting phenomenon.

Iron that will not grow.—In a later treatise[1] Carpenter, as a result of his further investigations, put forward tentatively a composition which did not grow upon exposure to high temperature. The results were obtained from alloys of the following composition:—

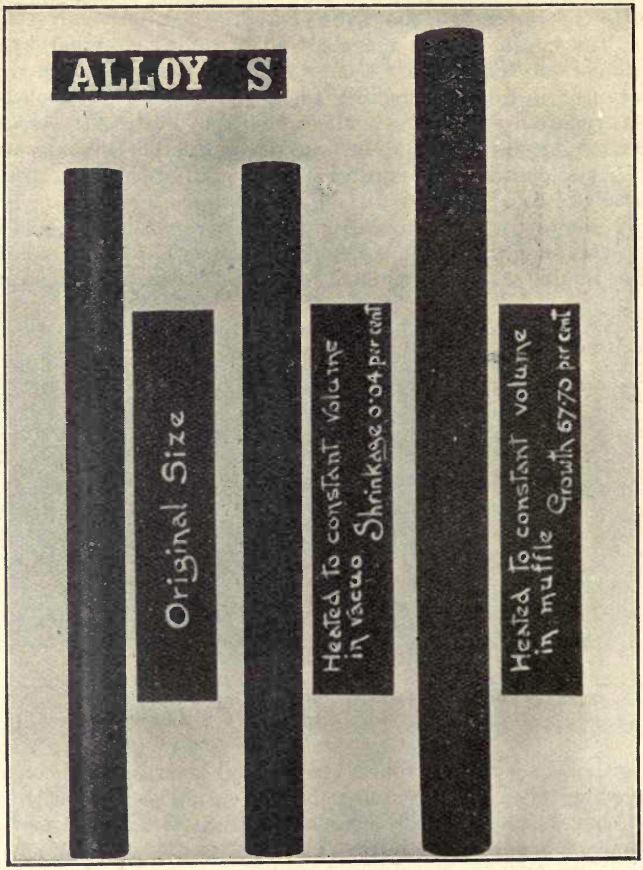

Fig. 103.—Illustrating the difference between the growth of S. (*a*) *In vacuo* at 900° C. (*b*) In a muffle in contact with gases at 900° C.

	No. 1.	No. 2.	No. 3.
	per cent.	per cent.	per cent.
Carbon	2·40	2·40	2·25
Silicon	0·485	0·471	0·406
Sulphur . . .	0·01	0·01	0·01
Phosphorus . . .	0·01	0·01	0·01
Manganese . . .	0·51	0·735	0·935

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[1] *Iron and Steel Inst.*, May 1911.

All three irons were white in fracture, and, according to Carpenter, were extremely tough. Upon the testing machine they gave the following results :—

No.	Ultimate stress. Tons per sq. in.
1	19·92
2	20·20
3	22·00

It is claimed that the increase in the manganese content is responsible for the slightly increased strength. Machined bars of each of the alloys were submitted to the usual heat treatment, *i.e.* four-hour periods at temperatures varying from 850° to 900° C. The results obtained are given in the following tables :—

No. 1.

	per cent.
Carbon	2·40
Silicon	0·485
Manganese	0·51

Length. Inches.	Diameter. Inch.	Volume. Cubic Inches.	Change per cent.	Weight. Grms.	Change per cent.	Heat No.
6·0048	0·9223	4·0124	...	486·09	...	...
6·0000	0·9225	4·0093	−0·08	485·77	−0·07	11
6·0223	0·9288	4·0789	+1·66	484·95	−0·23	27
6·0580	0·9293	4·1073	+2·36	484·58	−0·31	41
6·0800	0·9336	4·1617	+3·80	484·31	−0·37	56
6·1051	0·9378	4·2174	+5·11	483·95	−0·44	74
6·0852	0·9386	4·2097	+4·92	483·55	−0·52	100
6·0856	0·9406	4·2270	+5·35	482·93	−0·65	126
6·0694	0·9513	4·3129	+7·49	481·90	−0·86	152

No. 2.

	per cent.
Carbon	2·40
Silicon	0·471
Manganese	0·735

Length. Inches.	Diameter. Inch.	Volume. Cubic Inches.	Change per cent.	Weight. Grms.	Change per cent.	Heat No.
6·0068	0·9203	3·9970	...	479·87	...	...
6·0017	0·9204	3·9935	−0·09	479·48	−0·08	11
6·0223	0·9242	4·0391	+1·05	478·62	−0·26	27
6·0470	0·9258	4·0708	+1·85	478·23	−0·34	41
6·0625	0·9294	4·1134	+2·90	477·93	−0·40	56
6·0774	0·9334	4·1581	+4·03	477·44	−0·51	74
6·0675	0·9348	4·1629	+4·15	477·08	−0·58	100
6·0667	0·9422	4·2290	+5·80	476·52	−0·70	126
6·0560	0·9440	4·2391	+6·06	475·72	−0·87	151

No. 3.

	per cent.
Carbon	2·25
Silicon	0·406
Manganese	0·935

Length. Inches.	Diameter. Inch.	Volume. Cubic Inches.	Change per cent.	Weight. Grms.	Change per cent.	Heat No.
5·9993	0·9183	3·9727	...	478·42	...	...
5·9942	0·9177	3·9640	−0·22	478·18	−0·05	11
5·9965	0·9182	3·9691	−0·09	477·50	−0·19	27
6·0116	0·9200	3·9959	+0·58	477·08	−0·28	41
6·0241	0·9214	4·0156	+1·08	476·75	−0·35	56
6·0456	0·9213	4·0282	+1·40	476·44	−0·41	74
6·0588	0·9210	4·0369	+1·61	476·07	−0·49	100
6·0698	0·9241	4·0692	+2·43	475·54	−0·60	126
6·0748	0·9267	4·0956	+3·09	474·68	−0·78	151

A further iron of otherwise similar composition, but of 1·60 per cent. manganese, was experimented upon, and with the interesting result that the possibilities of expansion were completely eliminated. It was further demonstrated that, whereas grey irons had greatly deteriorated under these heat treatments, these particular irons retained their strength. It was, however, shown that the condition of the carbon at the end of the 151 heatings was profoundly modified, as per the following figures:—

Bar No.	Manganese per cent.	Original Bars.	Bars after 151 heats.			
		Total Carbon all combined.	Combined Carbon.	Temper Carbon.	Total Carbon.	Percentage converted.
1	0·510	2·40	0·693	1·453	2·146	67·71
2	0·735	2·40	0·956	1·134	2·090	54·26
3	0·935	2·25	1·192	1·011	2·203	45·89
4	1·640	2·66	2·367	0·251	2·618	9·60

During the discussion upon this paper, Arnold took exception to the low carbon content, and no doubt with reason, since such low carbon alloys would run somewhat sluggishly. In the author's opinion, however, the increase of the carbon to 3·0 per cent. would not materially affect the results obtained from such material, except in so far as they might render them more brittle. If, however, the sulphur and phosphorus be kept fairly low, the properties of such material would not be seriously impaired.

How is the Growth brought about?—In opening the discussion upon the paper last mentioned, Stead gave the results obtained in some experiments he had been engaged upon, which throw more light upon the manner in which the growth of cast iron takes place. His deductions from the study of a baffle plate of grey cast iron which had been placed inside a cast-iron door to prevent it burning away are fully stated.

This plate, originally square, had become considerably distorted after an exposure of 10,000 hours' heating at temperatures varying from about 800° C. at the one end and 600° C. at the other. By comparing the structure and analyses of the non-expanded end with the metal which had become expanded, together with the intermediate condition, the gradual change in the condition of the material was observed. The plate, originally 17 cm. square, had expanded at the one end to 20 cm., and the specific gravity was found to vary from 7·09 at the non-expanded end to 6·14 at the enlarged end.

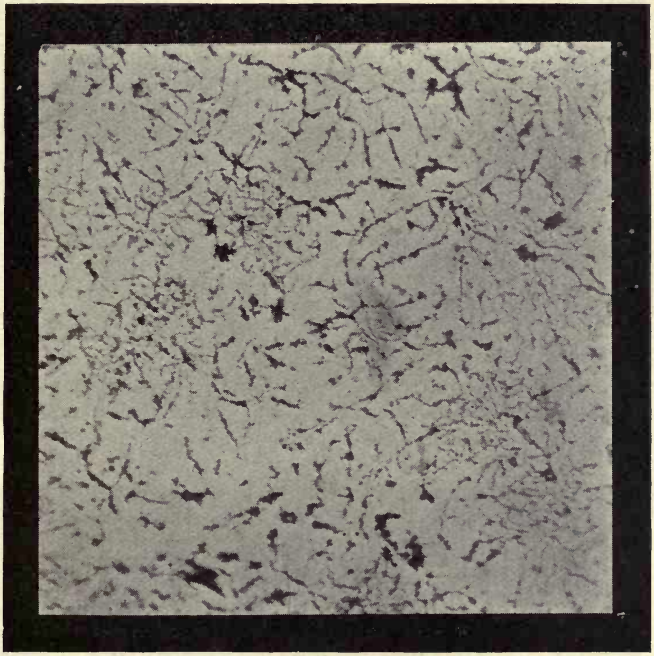

FIG. 104.—Baffle plate (original).

He gave four photomicrographs, here reproduced, which illustrate the changes in structure.

Fig. 104 is from the plate at the unchanged end; the black lines are the sections of graphitic plates.

Fig. 105, taken from 6 cm. further into the plate, shows dark lines, considered to be mixtures of graphite and oxide of iron.

Fig. 106, taken from 9 cm. further into the plate, still contains the dark lines, but these are now considered to consist entirely of oxidised metal.

Fig. 107, "metal at the extreme hot end, where only a small portion of the original metal remained sheathed in external scale. The bright irregular islands represented the remaining unoxidised metal now existing to the volume of about 30 per cent. of the original metal. The intermediate

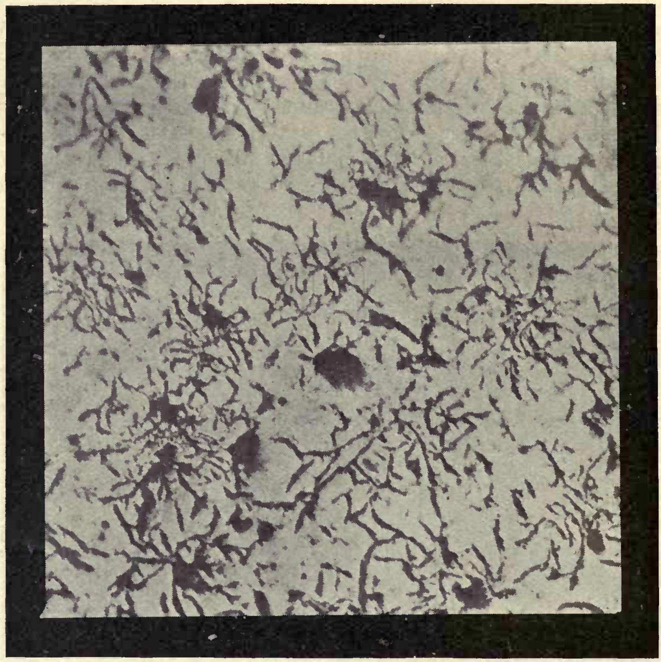

FIG. 105.—Baffle plate, heated to 800° C.

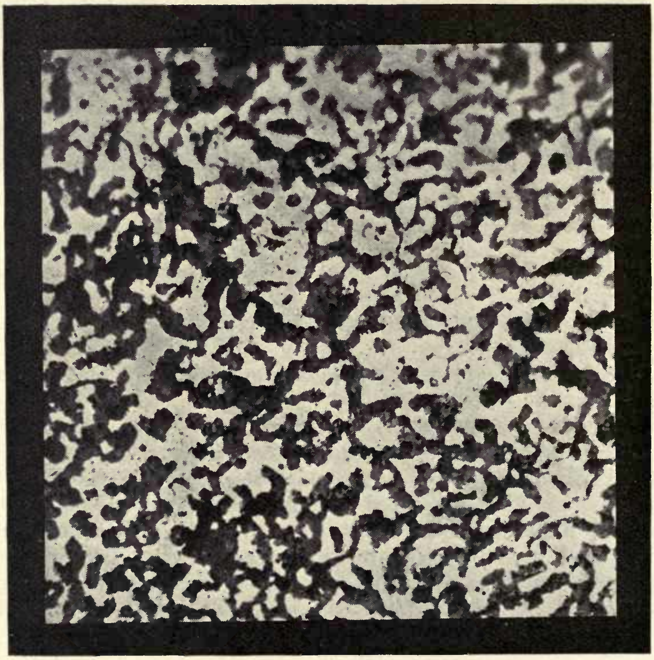

FIG. 106.—Baffle plate, heated to 850° C.

substance consisted of oxides, and it was easy to identify globules of phosphate of iron imbedded in the silicated oxide of iron."

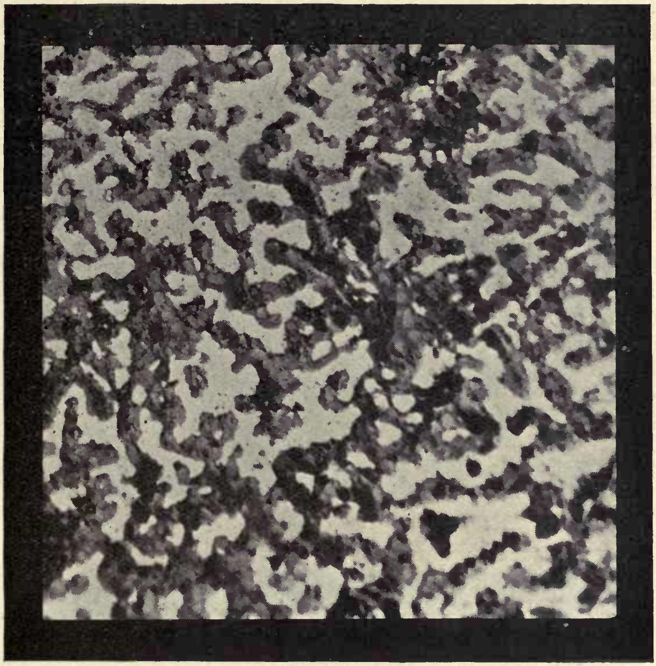

Fig. 107.—Baffle plate, heated to 900°.

The chemical analyses of the metal on drillings from the expanded and non-expanded ends are here given:—

	Unexpanded end.	Expanded end.
Iron per cent.	91·80	84·30
Combined Carbon ,,	0·05	trace
Graphite ,,	3·17	nil
Manganese ,,	0·58	0·54
Silicon ,,	1·72	1·50
Sulphur ,,	0·11	0·25
Phosphorus ,,	1·32	1·24
Oxygen, etc. ,, by difference	0·25	12·17
Total	100·00	100·00
Silicon per cent. as silica	0·01	1·13
Phosphorus per cent. as phosphoric acid	0·51	1·60

It will be seen that the oxidised portion contains 12 per cent. of oxygen. The most interesting feature revealed by this portion was that, according to Stead, the silicon oxidised to silica and phosphorus largely to phosphoric acid had escaped from the "intergraphitic metallic masses of metal." "It would be concluded from that, that both the silicon and phosphorus had diffused towards the boundaries of those metallic portions, and become oxidised to silica and phosphoric acid by the oxide of iron." It is stated, with regard to the phosphide, that after the oxidation of the combined carbon, it had been taken into solution, diffused to the boundaries, and oxidised.

Stead also describes the results obtained from his examination of a stove pipe that had been heated for six years at a practically constant temperature of about 700° C. It was found in this case that the semioxidised metal remaining consisted of small masses of metallic iron in which globules of cementite were imbedded, but which were quite free from phosphide. It is curious also to record that much of the graphite remained, and the fracture presented by the iron was similar to the original material.

Fig. 108 represents the structure of the original material. Fig. 109 illustrates the structure of the pipe after service. The iron surrounding the graphite was invariably oxidised, the graphitic plate appearing in a sheath of oxide. The black areas "correspond with oxides, graphite, and porosities." The analyses of the pipe were as follows:—

	Oxidised.	Unoxidised.
Iron per cent.	80·50	93·20
Combined Carbon ,,	0·40	trace
Graphite ,,	2·11	3·27
Manganese ,,	0·23	0·35
Silicon ,,	1·68	1·80
Sulphur ,,	0·09	0·09
Phosphorus ,,	0·88	0·90
Oxygen, etc. ,,	14·11	0·39
Total	100·00	100·00
Per cent. oxides about	45·0	...
,, metal about	55·0	...
Specific gravity	5·48	6·95

The experiments demonstrated that in iron heated to between 700° and 750° C. the graphite remained unoxidised; and it was further shown that if such oxidised iron was heated to 950° C., this graphite reduced to the metallic state much of the oxide in the surrounding sheath. It is also stated that it was found that upon exposure to 950° C., the gases, after oxidising the iron, attacked and oxidised the graphite.

The discussion upon Carpenter and Rugan's paper brought several valuable contributions from Turner, Fletcher, and Saniter, Mr Saniter's pertinent question, "Why was it necessary that the iron should be cooled and heated to make it increase so much in volume?" bringing out one of the most important phases of the action.

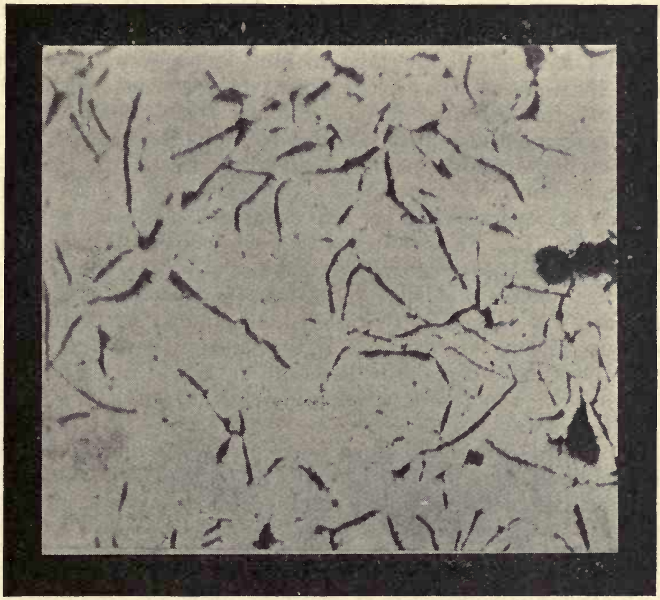

Fig. 108.—Stove pipe (original).

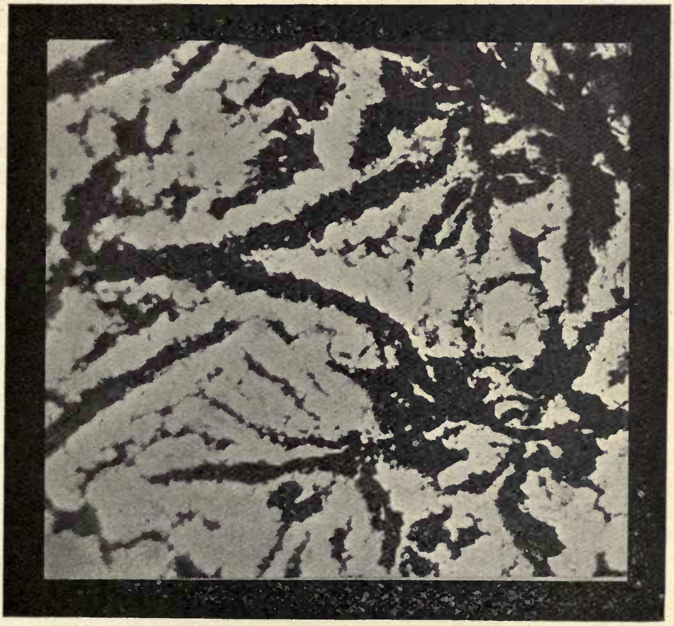

Fig. 109.—Stove pipe, heated for period at 700°–750° C.

With regard to this question, Stead considers that the extension of the iron would develop cracks (induced by the graphitic cleavages), in which films of oxide would form. "It appeared to him, as suggested by Saniter, and agreed to by the authors, that after incipient fracture on tension, when cast iron was heated, the fractured surfaces did not come together again upon cooling." The increase in growth attributable to silicon made it appear that silico-ferrite was more readily oxidised than silicon free ferrite, but an experiment of Stead's disproved that idea. He made two sheets of steel, one without silicon and one with 4·0 per cent., and exposed them for ten minutes side by side at 900° C. The result was that the non-silicon alloy oxidised at 50 times the rate of the silicon alloy. It was therefore considered evident that the physical influence of silicon was more important than the chemical influence, and it was suggested that the intergraphitic masses became, with the increase in silicon, less plastic. If this is so, it would account for the influence of silicon in causing growth, according to the theory suggested, as the incipient cracks would progressively increase in size and number as the silicon content was raised.

Such is, the author believes, an accurate presentation of some of the most interesting research work he has had the pleasure of studying. Much, no doubt, could still be done upon the subject with advantage, but at any rate we have here a mass of work which really emphasises how futile, useless, and dangerous it would be to utilise in our modern engineering practice, where factors of safety tend to become, with our increasing knowledge, less and less, this questionable method put forward by our cousins across the water, of making castings "grow until they are the proper size."

It is of interest to note that Mr Outerbridge, in discussing Rugan and Carpenter's paper, stated that, "As an indication of the practical application of the phenomena under discussion, he could instance a statement made before the Philadelphia Foundrymen's Association respecting the saving of several tons of condemned cast-iron pipe by reheating, and the similar expansion of a worn piston reported at the same time."

The author considers it is now clear that the only thing to do, if a casting is too small for the purpose intended, is to break it up and send it to be remelted.

CHAPTER X.

THE EFFECT OF SUPERHEATED STEAM ON CAST-IRON FITTINGS, ETC.

THREE interesting papers were published[1] in 1909 upon this subject. On the other side of the Atlantic the frequent failure of cast-iron fittings has led to a distrust of such material for such purposes, and the subject has therefore received considerable attention.

The effect of superheated steam at comparatively low temperatures is a very different problem to that of failure at high temperatures so ably investigated by Rugan and Carpenter, and presents several phases as yet somewhat imperfectly understood. In the author's opinion, however, it is not proved that cast iron will materially deteriorate unless exposed to higher temperatures than a "black" heat, and it is therefore proposed to consider the data at present available.

I. A. Hollis, in his paper, details the uncontrovertible facts derived from his experience. They are stated as follows:—

(*a*) Fittings have developed cracks and small changes of shape after a few months of actual service.

(*b*) Fittings exposed separately to superheated steam at a temperature exceeding 500° Fahr. have shown permanent increase in some dimensions.

(*c*) The tensile tests of pieces cut from fittings that have failed in service indicate in some cases the possibility of permanent loss of strength.

The fact (*a*) is evidently based upon observation, and therefore deserves serious consideration.

The fact (*b*) is somewhat indefinite, as "over 500° Fahr." is somewhat vague. Carpenter and Rugan found permanent expansion over 650° C., but we have no reason to believe in a similar action resulting from exposure to temperatures, say, between 300° C. and 650° C.

The fact (*c*) is certainly not conclusive; for, to be really deserving of serious consideration, the experiments should have more than proved the "possibility of permanent loss" under such conditions.

The author whose work is being discussed proceeds to state, and it is believed with good reason, that the "remainder of the evidence in the case may be classed as good guesswork, based upon some preconceived theory, as to the behaviour of the constituent parts of cast iron in a rising temperature."

Bearing, however, upon this point, some data have of late been published. H. Meyer describes interesting experiments performed upon cast-iron bars 1·18 in. dia. and 19·69 in. long. The tests were carried out upon a Krupp

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[1] Ira N. Hollis, A. S. Mann, E. F. Miller, American Society of Mech. Engineers; see *American Foundry*, Jan. 1910.

bending machine, and bars were heated in baths of oil, lead, tin, and aluminium, as necessitated by the particular temperatures. The following table gives a fair idea of this worker's results:—

Temperature, °C.	Bending strength, tons sq. in.	Bend, inch.
18	23·53	0·31
66	22·22	0·30
268	21·08	0·28
297	19·88	0·30
620	12·09	0·55
807	7·56	0·94

It will be seen that only a small increase in temperature is necessary to appreciably reduce the strength of the iron. This serious aspect of the diminution of strength during exposure to high temperatures is also supported by Cary. He, however, does not admit any chemical effect of steam upon cast iron, and considers effect must be of a physical nature. He gives the following figures:—

Temperature.	Strength.
900° F.	30·000
1100° ,,	20·000
1500° ,,	10·000

It is therefore clear that there is a possibility, if the fittings are not made sufficiently strong, that any weakness might easily be accentuated by the increase in temperature to such an extent that disaster might result. Further, iron under such circumstances, upon again reaching normal temperatures, would have a strength related to its original condition; hence mechanical tests performed before and after would hardly detect this source of failure. If, however, temperatures of any great height were met, the changes of structures obtained by Carpenter and Rugan would take place. The question which we are discussing concerns exposure to low temperatures.

The property of distortion may be found to be peculiar to certain classes of iron. For instance, the known property of some varieties of iron of developing a permanent set when subjected to stresses well below the maximum stress is known to be dependent upon a certain condition of the carbon. The author has hammered test pieces of cast iron to a considerable degree, and thus diminished the sectional thickness without producing fracture; this experience is confirmed by the recent results published in Germany. Such iron is invariably found to have a ferritic or partially ferritic matrix when examined under the microscope, and hence the possibility of "flow." If, however, the iron is hard, *i.e.* contains a suitable portion of combined carbon, it will be found that the elastic limit approximates very nearly to the maximum stress, and hence the possibility of this phase of failure is considerably lessened.

To return to the article by I. N. Hollis, he states that test bars which have been taken from fittings that have been exposed for one year or more at a temperature of 550° to 600° C. "have shown surprising irregularity of strength in the same castings," but, as he goes on to state, "there is nothing to prove that new cast-iron fittings have not a great lack of homogeneity." This would appear to substantiate the recent argument. Hollis further proceeds to detail actual observations made on the large scale for the Edison Illuminating Co., Boston, U.S.A. He describes features of the Edison Station; how the new portion is arranged in a series of complete units, each consisting of a vertical Curtis turbine and eight boilers, set in pairs. The piping extends "along the rear ends of the boilers, just beneath the brickwork, four vertical mains connecting each pair of boilers with the main line. Three of the vertical mains discharge through gate valves into T's, and a fourth at the end of a line, through a gate valve into a bend," obviously an excellent set of conditions under which to make the determinations. "The first turbine units were provided throughout with cast-iron fittings, which were ultimately replaced with steel fittings. No expansion slip joints are used. The main steam line (over 103 ft. long) is anchored at the turbine end, and is allowed to expand freely in longitudinal or horizontal direction, carrying the lower ends of the vertical mains with it. The steam pressure is 175 lb., and the superheating generally amounts to 150°, although it is not constant. The actual temperature of the steam varies from 500° to 580° F., so that the main line is changing in length from time to time, thus moving the lower ends of the vertical mains back and forward." As the worker explains, variable stresses are naturally set up, which are felt most acutely at the T's, and hence the interest of the experiments. It was not until the plant had been at work for twelve months that defects began to show, the first instance then being one of the 8 by 6 by 6 T's in proximity to the boiler, which developed cracks "near the junction of the offset with the body of the T and in the flanges." A further similar casting of like position next showed failure two months later. Tensile tests given by these and other similar castings are given in the following table:—

Description.	Condition.	Analysis.					Tensiles from various bars cut from same casting.
		Carbon.	CC.	Mn.	S.	P.	
The two tees . .	defective	3·47	1·41	3·10	0·06	0·36	27,440, 28,280, 12,646, 14,295, 27,270, 26,080.
Large tee (same service)	sound	...	...	...	...	...	23,130, 23,480, 23,875, 24,170.
Large manifold seven years' service	sound	...	...	...	...	...	16,413, 16,550, 17,000.

Apart from the irregularity which might be due to experimental error or unsoundness, there is no convincing evidence to demonstrate that the castings which failed were inferior material to those which served well; rather is the result to the contrary. The whole of this paper by Hollis is worthy of careful perusal, but the deduction the author would draw from these results is that the castings would not have developed flaws had they been, from the foundry standpoint, of correct configuration and cast sound. A properly made casting was evidently capable of being equal to the conditions which prevailed under those particular circumstances.

It is of direct interest to note that A. S. Mann, in discussing this problem, states that he has in his own experience observed many steel fittings to fail with under a year's service under similar conditions, even when such castings were "heavy, materially thicker than the commercially extra heavy cast-iron product, and had passed a right inspection." This will demonstrate that it is not cast iron alone that fails under such conditions. It would indeed appear that failures are due in these materials either to faulty moulding or to faulty configuration. It is well known that without care in design it is not even necessary to subject castings to such strains as superheated steam may produce to induce fractures. Anyone accustomed to practical foundry work will appreciate the severe internal strains that are set up in castings of certain configurations during cooling alone.

A. S. Mann, in the paper before referred to, states what is undoubtedly a fact, namely, that on this side of the Atlantic such fittings of all sizes have for many years been produced satisfactorily in cast iron. As he states, manufacturers have of necessity had to study the problem carefully, and put stock of the right composition into castings of certain ranges of strength. It is appreciated that some compositions are "fed sound" with more difficulty than others. When one walks through some of our modern ironworks and observes the obvious scientific control which exists in both the metallurgical and in engineering sides of the business, it will be seen that regular excellent products are produced with comparative ease.

One instance given by Mann is typical of what can and is being done. He describes an instance of an 8-in. valve which was perfectly tight after four years' service. The outer surface was covered with 85 per cent. magnesia insulation 4½ in. thick. Upon examination some little time ago the casting presented no internal cracks or defects under minute examination, and is still doing service under a superheat of 300°. The metal used is known in the States as "gun" iron, and was of the following composition:—

Silicon	1·72
Sulphur	0·085
Phosphorus	0·89
Manganese	0·48
Total Carbon	2·45
Combined Carbon	0·17

It will be seen that this is of such composition that it may be produced with little difficulty. The carbon in total is certainly low, but that is not, in the author's opinion, the essential feature. The silicon is fairly low, and this alone will do much to produce an iron which may be fed sound, and also give a final casting of considerable strength. It will also be noticed that the phosphorus is fairly low for foundry iron, whilst the sulphur content is balanced with a reasonable percentage of manganese.

The author would therefore conclude these remarks by expressing the opinion that properly designed fittings may be cast in cast iron provided the casting operations are well directed and the iron is of suitable composition, and that such castings may reasonably be expected under conditions of superheated steam to give satisfactory results. One point must, however, be insisted upon, and that is, that fittings of varying thickness must have the composition of the iron varied accordingly: this will be obvious from a study of the influence of varying sections upon the properties of the resulting cast iron, which subject will be found fully dealt with under another heading.

CHAPTER XI.

MALLEABLE CAST IRON.

As the result of the tremendous progress in mechanical contrivances, and the substitution of mechanical methods for human labour in almost every walk of life, there is an enormous growing demand for the small casting. It is an absolute necessity in the economical production of the machinery which displaces the drudgery of the agricultural labourer, the many fittings of our tramways and railways, in productive general machinery in shipbuilding industries, and, in fact, in almost-every sphere of modern life.

If a small casting be made of cast iron it is brittle and will not resist shock. Steel castings cannot at the present time be produced cheaply below a certain size of casting, owing to the comparative difficulty of attaining a sufficiently high temperature to cast small castings satisfactorily. Cast iron, owing to its low melting point, can, however, be melted with ease, and cast into the smallest and most intricate shapes; hence it was not to be wondered at, when it was found that some kinds of cast iron when annealed became almost as ductile and tough as wrought iron, that such a discovery became of great industrial value.

The cast-iron castings rendered ductile in this manner are the "malleable iron castings" of commerce, and their utility has been found so great that in the United States of America alone the output of this kind of casting approaches a million tons per year.

To the French savant, Réaumur, we owe the first treatise on this subject of "softening" cast iron. In *L'Art d'Adoucir le Fer Fondu*, in 1722, he states that "heating cast-iron castings imbedded in red oxide of iron softens the metal perfectly, and much more rapidly than all the other matters" which he had tried; and it is interesting to note that the bulk of malleable castings produced in Great Britain and Europe are made on much the same lines as those indicated by this Frenchman so long ago.

In 1804 Samuel Lucas, an Englishman, was able, curiously enough, to obtain a patent for this process, and from that time the method of producing malleable castings by heating with iron ore has developed. The oxygen of the ore decarburises the iron castings during the exposure to the temperatures of the annealing furnace, and this action is found to soften them. Malleable cast iron produced in this way has a fracture very similar to steel, and by fracture alone it is indeed most difficult in some instances to distinguish it from that material. The irons generally used are the white and mottled pig irons of Cumberland, which contain between 3 and 4 per cent. of carbon, 0·4 to 1·0 per cent. of silicon, and anything between 0·10 to 0·40 per cent. of sulphur, the manganese and phosphorus in such irons rarely exceeding 0·05 per cent. The pig iron is melted usually in a crucible or cupola and cast, due care being taken that the casting is "fed" so that it shall be sound. After casting, the iron will be found to be intensely hard, brittle, and white in fracture, giving a tensile strength of anything from 10 to 20 tons to the square inch. The carbon is totally in combination; and if a section be examined under the microscope, it will be seen to have a structure as shown in fig. 110.

If the casting be now packed with hematite iron ore and raised to a good yellow-red heat, the reactions which result in the final ductility take place.

Fig. 110.—White Cast Iron. Etched. Magnified 45 diameters.

It is usual in this process to maintain the annealing oven at high temperatures for a considerable time, after which it should slowly cool down. The castings are then "fettled" and "barrelled" to make them presentable for the market. The whole of this process, and the chemical physics involved, will be found fully discussed in the chapter on the Decarburisation of Cast Iron (see p. 180).

It may here be said that if this process be carefully carried out, the castings will be very tough, and give, in addition to a tensile strength of 20 to 25 tons, a very good bending angle. A section of this material examined under the microscope will present a structure most likely as shown in fig. 111. A large portion of the carbon has been eliminated, and, apart from a small percentage of 0·50 to 0·70 per cent., which is seen diffused through the matrix as laminated pearlite, the remainder is now present as small nodules of annealing carbon. The other elements would seem to be little affected by the oxidising influences, the silicon, manganese, and phosphorus being found in much the same percentage as before: the sulphur, however, in T. Turner's opinion, is slightly oxidised. Stead has published experiments which would appear to prove that some of the silicon near the surface is oxidised to SiO_2, but this should not happen if the process is carefully conducted.

In 1769 we find that Joseph Ashton of Birmingham obtained a patent for softening cast iron in a slow fire, and subsequently that in 1783 George Matthews also obtained a patent for softening large castings such as guns, etc., by this method. The latter found that the castings, after this treatment, became as tough as wrought iron. This was the germ of another process of producing malleable cast iron which ultimately developed, across the water, into the tremendous American malleable trade. Instead of depending upon the elimination of the carbon for the softening and toughening effect, this process depends on the changing of the form of the carbon from the combined to the free state. This process is sometimes described as the "Blackheart" method, and takes its name from the fact that the inner portion of the fracture is black, this black "kernel" being surrounded by a steely skin. In this process the material is melted in either the cupola, reverberatory, or open-hearth furnace, and cast as usual. The reason for using the open-hearth furnaces is a desire to keep the percentage of sulphur at a minimum, as this element tends to keep the carbon in the combined state. As cast, the properties of the material exactly resemble that of the Réaumur process

Fig. 111.

at the same stage. It is as brittle and hard, and has all its carbon in the combined state. In composition it varies only in the percentage of sulphur and manganese, the sulphur usually not exceeding 0·10 per cent. and the manganese not exceeding 0·50 per cent. The annealing process is very similar to that of the Réaumur process, with the exception that lower temperatures are used; but this question of the precipitation of carbon is fully dealt with elsewhere. The product of this system of softening, if properly made, is found to be very soft and ductile, and gives a most excellent bend, usually giving about 18 tons tensile and 5 per cent. elongation in 3 in. The author has, however, in working a similar process, produced, in conjunction with Mr J. F. Crowley, bars which have given 18 per cent. and 19 per cent. elongation in 3 in., with a maximum stress of 23 tons per sq. in. It will thus be seen that this material can actually be made to approximate to the tensile tests given for wrought iron, and hence its value is at once apparent.

FIG. 112.—Longitudinal section of Swedish Wrought Iron as seen under the microscope. Magnified 90 diameters.

FIG. 113.—Cross section of Swedish Wrought Iron as seen under the microscope. Magnified 90 diameters.

In figs. 112, 113, and 114 will be seen micrographs illustrating the structure of such a malleable casting, and that of wrought iron when seen through the microscope.

The carbon being practically all in the free state, the section only displays annealing carbon scattered through the ferrite; and if the structure of the wrought iron be compared with it, it will be seen that the only difference is that the latter has slag globules dotted about instead of the annealing carbon nodules. The author must not, however, forget to mention that the malleable casting is a casting, and not a forging; so, of course, from this point alone, the casting must always take second place. When, however, the cheapness of producing repetition castings as compared with the cost of making small forgings is considered, the approximation of the characteristics of well-prepared malleable cast iron of this type is certainly a matter of gratification to the founder.

In fig. 115 is seen a photograph of the fractures of typical samples of the two types of this product, taken from a paper[1] given by the author to the Engineers and Shipbuilders in Scotland. Fig. 116, taken from the same paper, will possibly be interesting, as showing the metallurgical position of the malleable cast irons.

Fig. 114.—Microstructure of special Malleable Cast Iron (known in America as Blackheart). Magnified 90 diameters.

All metallurgical processes must be judged by the quality of the material they produce for a given price; and it is regrettable that, owing to the carelessness and lack of knowledge of some of the earliest manufacturers of malleable cast iron, its headway was not, in this country at any rate, as rapid as it might have been, or as its properties deserve. It is nothing more than cast iron subjected to subsequent heat treatment; and obviously it depends entirely upon the skill with which it is manufactured as to whether it is equal to cast or wrought iron. In the old days when one man, melting his own iron, and with a few boys working for him, constituted a "malleable foundry," not much could be expected, as obviously the quality of the product was at the mercy of circumstances; he could not control his supply of raw materials, and, what

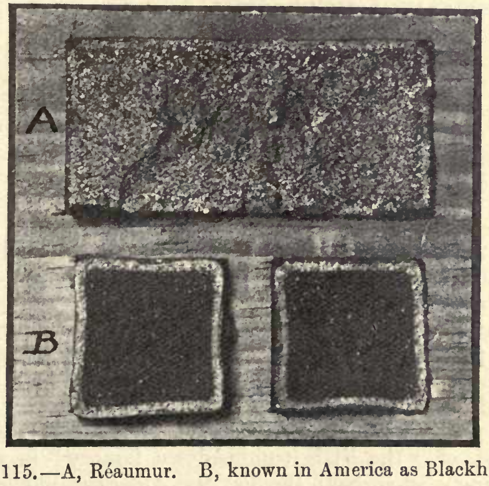

Fig. 115.—A, Réaumur. B, known in America as Blackheart.

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[1] *Jour. of the Inst. of Engineers and Shipbuilders of Scotland,* March 17, 1908.

is more, he had to "judge his temperatures" by the eye. At the present time the manufacture is being systematised, and production is being made upon a large scale in modern works supplied with all the equipment which the sciences of metallurgy and engineering can provide: the result is a regular product, which is gradually making great headway.

Apart altogether from the diminished costs of production, the quality is much improved; and for this we are no doubt indebted to a large extent to the insistence of the overseers and inspectors of the Admiralty, of various Government Institutions, and of public bodies who are now very considerable users.

The author feels that he cannot close this chapter without another reference to the United States of America. Several years ago he had the pleasure of making a tour through some of the American foundries engaged in the production of this material. Many foundries, specially equipped only for this branch of business, were found to be equal in size to some British steelworks, with outputs in proportion; and it did really seem that we in this country were considerably behind our cousins in adopting this material. The author was much interested in reading, several years ago, an article in the *Foundry Magazine* upon the growth of this industry in America, and it was almost pathetic to read of "the little tumble-down factory" in a back street of Newark, New Jersey, where Seth Boyden, the American pioneer, made his first experiments in producing this material. It is by no means claimed that he invented the process, since it is shown that he was in possession of data from the old country; still, every credit is due to him for the way in which he worked

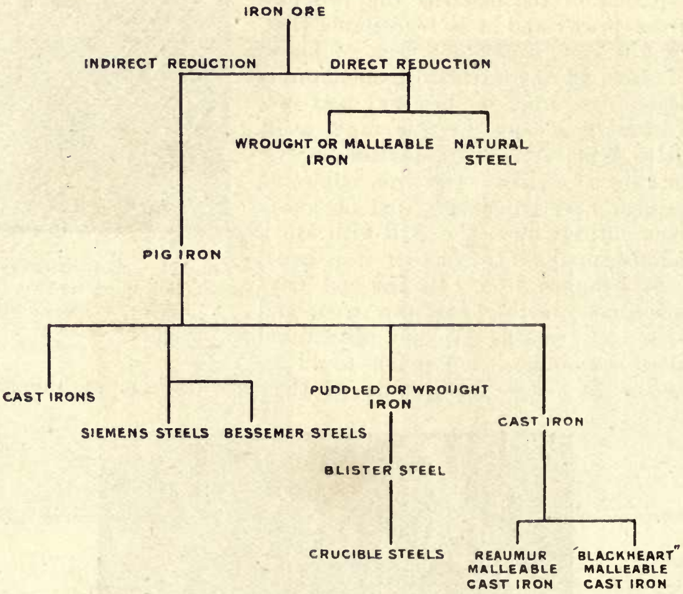

FIG. 116.

out and adapted the process to its new environment. In this first factory, manufacture was confined to small castings, and buckles and harness fittings, for which Boyden acquired a reputation. Starting to melt iron in his forging fire, as trade increased, crucibles were no longer satisfactory, and he built a "large" air furnace that could melt "a thousand pounds" at once. He had no such thing as a pyrometer, but the accuracy of his early work is shown by his recording the temperature of his annealing as the melting point of silver.

Such, then, was the beginning of one of America's triumphs in the industrial world.

CHAPTER XII.

THE HEAT TREATMENT OF CAST IRON.

The Heat Treatment of Grey Cast Iron.—The main objects in view in the annealing of grey cast-iron castings, are—

(*a*) To relieve all internal strains set up by the primary crystallisation produced during the freezing of the iron.

(*b*) To soften the casting, *i.e.* to eliminate the surplus combined carbon, which militates against normal working in the machine shop.

The annealing of grey iron inevitably leads to a weakening of such material. Grey cast iron consists of a matrix or mass of ferrite or silico-ferrite, more or less strengthened by pearlite, which is cut up and weakened by the numerous graphitic plates, not to mention the phosphide constituent usually present. If the silicon be low, or if other conducive conditions exist, cementite membranes will also be found which, in the author's opinion, strengthen the material, particularly when under compression. A comparatively short exposure between 750° and 800° C. is quite enough in foundry mixtures to precipitate any of this combined carbon, and the result then is that we merely have a silico-ferrite matrix, which is considerably weaker than the matrix existing as cast.

Longmuir has published[1] a set of results obtained from grey iron test bars as cast and annealed, which are here reproduced.

Showing the Influence of Heat Treatment on the Properties of Grey Cast Iron.

No.	Analysis.						Casting Temperature.	Condition.	Mechanical Properties.		
	CC.	Gr.	Si.	Mn.	S.	P.			Elastic Limit, tons per sq. in.	Maximum Stress tons p. sq. in.	Elongation per cent. on 2 in.
37	0·52	3·4	1·78	0·28	0·04	0·27	1400° C.	cast.	..	9·7	..
38	,,	,,	,,	,,	,,	,,	1350° C.	,,	..	14·1	..
39	,,	,,	,,	,,	,,	,,	1245° C.	,,	..	10·6	..
37 HT	not estimated		,,	,,	,,	,,	1400° C.	Heated to 940° C. and cooled in air	..	7·1	..
38 HT	,,		,,	,,	,,	,,	1350° C.		..	9·9	..
39 HT	,,		,,	,,	,,	,,	1245° C.		..	8·5	..
37 A	not estimated		,,	,,	,,	,,	1400° C.	Annealed for 48 hours in a Clinch-Jones muffle	..	6·5	..
38 A	,,		,,	,,	,,	,,	1350° C.		..	7·2	..
39 A	,,		,,	,,	,,	,,	1245° C.		..	2·6*	..
37 Q	not estimated		,,	,,	,,	,,	1400° C.	Heated to 940° C. and quenched in water	..	2·5	..
38 Q	,,		,,	,,	,,	,,	1350° C.		..	3·0	..
39 Q	,,		,,	,,	,,	,,	1245° C.		..	2·7	..

* Flaws.

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[1] *Jour. Iron and Steel Inst.*, 1909, vol. i.

The figures relating to the maximum stress per sq. in. are interesting and of considerable importance; it will be seen that by heating up to 940° C. and cooling in air the tensile strength of all three were considerably lowered. On annealing, however, the reduction in the strength of the bars is ominous.

The author[1] published a series of grey cast irons as cast and heat-treated which he considers of sufficient interest to record. The figures will be found in the following table :—

Test No.	Analysis.						Temperature.	Condition.	Maximum Stress.	Elongation.	Reduction of Area.	Fracture.
	CC.	Gr.	Si.	Mn.	S.	P.						
	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.			sq. in.	per cent.	per cent.	
G1	0·52	2·93	2·14	0·11	0·051	0·04	hot	as cast	7·01	..	..	Grey; crystalline.
H2	0·54	2·94	2·14	0·11	0·053	0·04	fair	,,	8·40	..	..	Grey; crystalline.
I3	0·54	2·96	2·14	0·11	0·051	0·04	cold	,,	12·98	..	..	Grey; crystallised, but much finer.
J1*a*	0·20	3·21	2·14	0·11	0·053	0·04	hot	heat-treated	2·82	..	..	Dry and grey crystallisation.
K2*a*	0·21	3·22	2·14	0·11	0·053	0·04	fair	,,	3·20	..	..	Dry and grey crystallisation.
L·2*a*	0·18	3·17	2·14	0·11	0·052	0·04	cold	,,	3·99	..	..	Dry and grey crystallisation.

It will be seen that the silicon content is 2·14 per cent. and that the combined carbon of 0·50 per cent. to 0·55 per cent. as cast is reduced by the annealing to about 0·20 per cent. Here the tensile strength is seen to have been reduced from 8 to 12 tons as cast to an average of 3 tons after heat treatment consisting of an exposure for several hours at 900° C., followed by a slow cooling over 48 hours.

The microstructures of these bars afford a complete explanation of this considerable reduction in tensile strength, and at the same time emphasise the detrimental influence of annealing grey irons. Figs. 117, 118, and 119 are photomicrographs of the bars as cast. All three will be seen to consist of a matrix of pearlite cut up by the graphitic plates of distinctly worm-like appearance. It must be understood that the pearlite has a similar strengthening influence in cast iron to what it has in steel, and these irons must be considered as being similar to carbon steels, with the exception that the graphite very greatly weakens the structure, just as a similar number of indiscriminate cuts or cracks would weaken it.

If we now examine figs. 120, 121, and 122, which are of sections of the heat-treated irons in exactly the same etched condition, it will be seen that the strengthening pearlite has been completely removed.

It will further be noticed that the graphite appears to be much coarser; it has apparently increased in size; and where originally it consisted of clear-cut, worm-like forms, the graphite structures would seem now to have swollen. No doubt this is due to the free carbon produced by dissociation of the carbide in the pearlite being drawn into position alongside the already existing graphitic plates.

Sufficient has now been said to demonstrate the action of annealing on the structure of grey iron; it is really the development in the annealing of white irons which has led to such a widening of the metallurgical field of cast iron.

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[1] *Jour. Iron and Steel Inst.*, 1907.

Grey Cast Iron (as Cast).

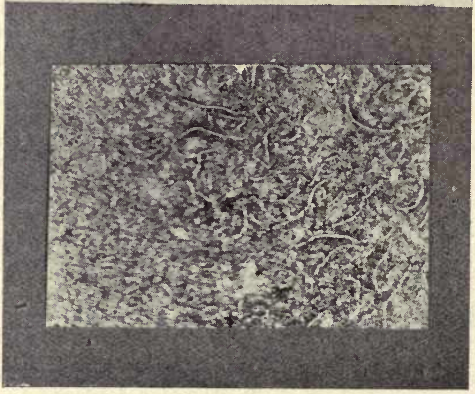

Fig. 117.—Etched (picric acid). Magnified 60 diameters.

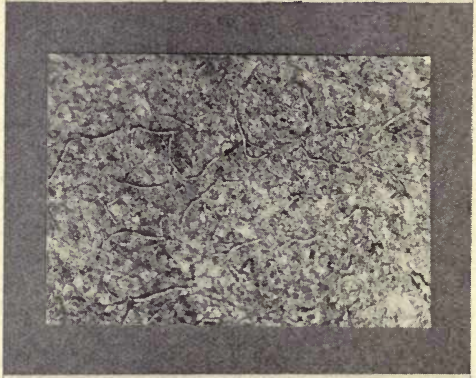

Fig. 118.—Etched (picric acid). Magnified 60 diameters.

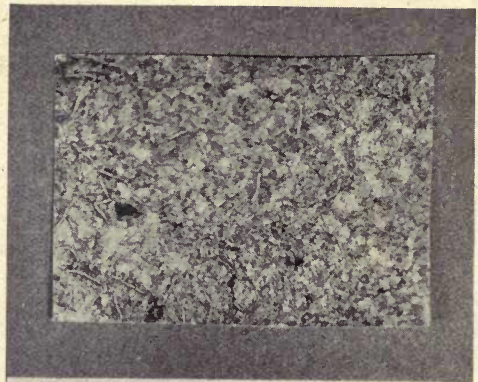

Fig. 119.—Etched (picric acid). Magnified 60 diameters.

Heat Treatment of White Irons.—One of the first important researches published upon the annealing of white cast iron is that by Charles James. In the opening of his paper he states that the data given are based not upon laboratory experiment, but upon the results of works practice, continued over a considerable period. The information to be derived, therefore, from the paper is of considerable importance, since it is from the ultimate works standpoint that all advances in our metallurgical knowledge must be judged. James was engaged in the production of malleable cast iron, and his castings, produced from iron melted in an air furnace, had an average composition of—

Combined Carbon . . .	3·02	per cent.
Graphite	0·47	,,
Silicon	0·78	,,
Manganese	0·12	,,
Sulphur	0·05	,,
Phosphorus	0·04	,,

The annealing was conducted in furnaces of a capacity of 2 to 3 tons, and the castings were either placed in the open furnace, exposed to the flame and products of combustion, or were packed in cast- or wrought-iron boxes. This latter variation in method was not found to influence the result, providing that allowance was made in the heat treatment for the altered conditions. The temperature to which the castings were heated was about 1000° C., *i.e.* between the melting points of silver and copper, and it required a period of 3½ to 10 hours' exposure at this temperature to accomplish the carbon change which he describes. In order that the nature of the change taking place during this annealing may be better understood, the following analyses are given of a casting before and after annealing:—

	Combined Carbon.	Graphite.	Silicon.	Manganese.	Sulphur.	Phosphorus.
Before annealing .	2·60	0·72	0·71	·110	·045	·39
After annealing .	0·82	2·75	0·73	·108	·04	·39

From these analyses it will be obvious that the only change of importance which has taken place is in the condition of the carbon. The greater part of the carbon which was in the combined state has been changed to graphite, or, to be more correct, "annealing carbon." It is also stated that the gradual change which takes place during the annealing is "coextensive throughout any given cross section," that is to say, that the precipitation of the free carbon takes place uniformly through the whole of the piece; and James records that in no instance does he find any inequality in the fracture, no matter at what stage the transformation has been arrested.

It was ascertained that this carbon change was directly influenced by the chemical composition. The presence of silicon James held to be absolutely essential for the change to take place; manganese, he considered, assisted, whilst his investigations as to sulphur were incomplete; phosphorus, he considered, might be dismissed, as having no influence on the change.

As an example of the action of silicon in assisting the change, the following

GREY CAST IRON (HEAT-TREATED).

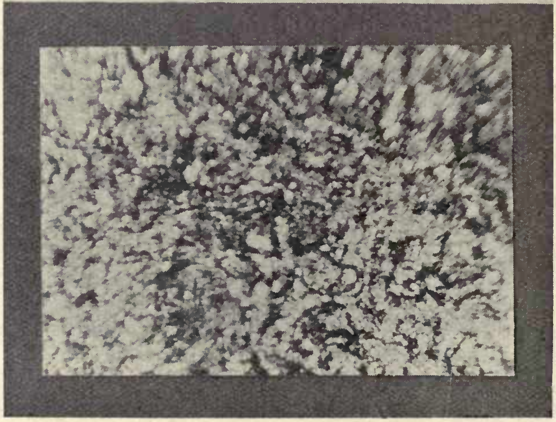

Fig. 120.—Etched (picric acid). Magnified 60 diameters.

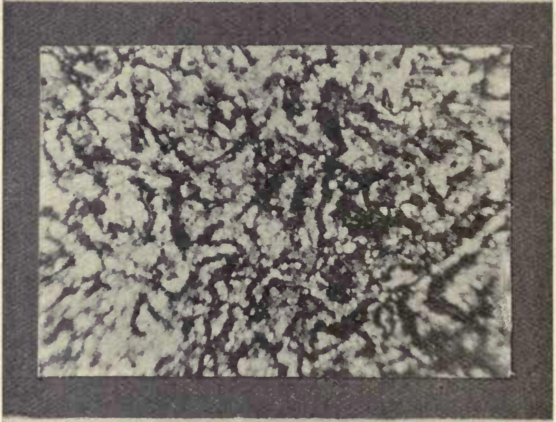

Fig. 121.—Etched (picric acid). Magnified 60 diameters.

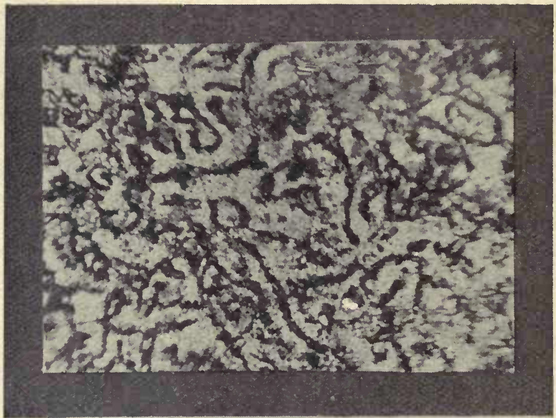

Fig. 122.—Etched (picric acid). Magnified 60 diameters.

experiment is given. Three samples, identical, apart from the silicon content, were given the same heat treatment, and the final analyses were as follows:—

Bar.	Combined Carbon.	Graphite.	Silicon.	Manganese.
No. 1	1·49	1·40	0·56	0·126
No. 2	1·57	1·33	0·45	0·130
No. 3	1·87	1·03	0·31	0·126

It will be seen that, with a gradually decreasing per cent. of silicon, the proportion of combined carbon left in the iron increased. One instance is recorded of a bar containing—

Combined Carbon . . .	2·08 per cent.
Graphite	trace
Silicon	0·42 ,,
Manganese	0·05 ,,

which, after annealing three times for 3½ hours at the annealing temperature, still retained practically the whole of the carbon in the combined state. An instance given by James of the influence of manganese is instructive, although not in the direction intended. The following analyses are of a "high" manganese bar before and after annealing for 3 hours:—

State.	Combined Carbon.	Graphite.	Silicon.	Manganese.
		per cent.	per cent.	per cent.
Before annealing . .	3·68	none	0·93	0·30
After annealing . .	none	3·62	0·95	0·31

It will be seen that there is here a complete change in the carbon, the whole of the combined carbon changing to "graphite." James attributed this to the ·30 per cent. of manganese present: it was, however, no doubt due to the high silicon and high carbon content. The influence of manganese was described as being mainly due to its protecting the silicon from oxidation at its own expense during melting, and was therefore understood to be indirect in its action. As a matter of fact, the beneficial action of manganese is mainly due to the manner in which it neutralises the sulphur.

It is only too easy to criticise early work in the light of later research, but there is no question whatever as to the marked importance of this most practical paper.

The author would here commend to the reader's notice the valuable research published by Royston. This paper, however, will not be treated in detail, owing to the difficulty in correlating that worker's temperature measurements: this observation is, however, without prejudice, since the research merits careful consideration.

One of the earliest systematic researches into the precipitation of annealing carbon in white irons is that which was published in 1902 by Charpy and Grenet.[1] They prepared a series of white cast irons of varying silicon content, the analyses of which are given in the following table:—

---

[1] *Engineering*, 1902.

No.	Carbon.	Silicon.	Manganese.	Sulphur.	Phosphorus.
1	3·60	0·07	0·03	0·01	traces
2	3·40	0·27	traces	0·02	0·02
3	3·25	0·80	,,	0·02	0·03
4	3·20	1·25	0·12	0·01	0·01
5	3·30	2·10	0·12	0·02	0·01

The carbon was retained in combination, even in the high silicon numbers, by the method employed in the preparation of the samples, *i.e.* quenching in cold water. Samples of each composition were submitted to more or less prolonged reheatings at different temperatures, and in each instance the treatment was ended by a rapid quenching at the desired moment. "The graphite was estimated, following Ledebur's process, by dissolving the metal in 1·18 per cent. nitric acid and burning the residue remaining insoluble in oxygen." The disparity, which will be occasionally noted in the total carbons of some of the series, is accounted for by the partial decarburisation during the heat treatments. From their interesting research they arrive at the following conclusions:—

(1) *Free carbon separates at a lower temperature when the silicon is high.*—Sample 1, with only traces of silicon, contained no free carbon after prolonged heating at 1100° C., and it was found necessary to heat at 1150° C. to cause a precipitation to take place. Sample 2, whilst not precipitating at lower temperatures, precipitated at 1100° C. Sample 3 contained traces of free carbon after heating at 800° C., whilst they state that samples 4 and 5 contained free carbon after an exposure to the temperature of only 650° C. No. 5 containing 2·83 per cent. of free carbon, after 6 hours' exposure at the latter temperature.

(2) *Separation of free carbon, once begun, continues at temperatures below those which repel the reaction.*—Thus, whilst a sample of No. 1, heated to 1170° C. and quenched, contained only 0·50 per cent. free carbon, another sample of the same material, heated at 1170° C. and slowly cooled to 700° C., contained 1·87 per cent. of free carbon. Similarly, a sample of No. 3, heated and quenched at 1170° C., contained 1·42 per cent. free carbon, whilst another sample of the same material, heated to 1170° C. and cooled to 700° C., contained 2·56 per cent.

(3) *At constant temperature, separation of free carbon is affected progressively more freely as the temperature is lower and the silicon is less.*—Thus, with No. 3 iron of ·80 per cent. content we get—

Period of Heating.	Temperature deg.	Graphite.	Combined Carbon.
One hour . . .	800	0·10	3·19
Four hours . .	800	0·22	3 07
One hour . . .	900	0·30	2·97
Two hours . . .	900	0·60	2·40
Four ,, . . .	900	1·58	1·14
One hour . . .	1000	0·37	2·94
Two hours . . .	1000	1·50	1·41
Four ,, . . .	1000	1·47	1·29

With No. 4 iron, containing 1·25 per cent. silicon, the following figures were obtained:—

Period of Heating.	Temperature deg.	Graphite.	Combined Carbon.
One hour . . .	700	0·06	3·42
Two hours . . .	700	0·11	3·30
Four ,, . . .	700	0·20	3·13
One hour . . .	800	0·12	3·08
Two hours . . .	800	0·51	2·47
Four ,, . . .	800	1·64	1·56
One hour . . .	900	2·28	0·90
Two hours . . .	900	2·32	0·90
Four ,, . . .	900	2·35	0·99

Whilst with No. 5 material, containing 2·10 per cent. silicon, the following respective percentages of free and combined carbon were obtained:—

Period of Heating.	Temperature deg.	Graphite.	Combined Carbon.
One hour . . .	700	1·39	1·90
Two hours . . .	700	2·09	1·19
Four ,, . . .	700	2·67	0·28
One hour . . .	800	2·36	0·78
Two hours . . .	800	2·31	0·89
Four ,, . . .	800	2·43	0·54
One hour . . .	900	2·33	0·88
Two hours . . .	900	2·32	0·90
Four ,, . . .	900	2·33	0·90

It is of considerable interest to note that these experiments indicated that whilst a constant precipitation of 2·30 per cent. free carbon is attained at 900° C. with 2·10 per cent. Si, and of 2·30 per cent. free carbon at 900° C. with 1·20 per cent. Si, only 1·5 per cent. free carbon results in the ·80 per cent. Si bar after 4 hours' exposure at 1000° C. These interesting results will be given further consideration.

(4) *The amount of combined carbon which corresponds to the equilibrium at a given temperature diminishes with the increase in silicon content.*—This deduction, whilst indicated by the foregoing series, is well confirmed by the next table, which consists of the results obtained from members of the whole series when exposed at different temperatures.

Samples.	To 1100 deg.		To 1000 deg.		To 900 deg.		To 700 deg.	
	Graphite.	Combined Carbon.	Graphite.	Combined Carbon.	Graphite.	Combined Carbon.	Graphite.	Combined Carbon.
No. 1	1·15	1·74	1·03	1·74	...	...	1·87	0·43
,, 2	1·26	1·93	1·00	1·62	...	...	...	...
,, 3	1·61	1·26	1·60	1·52	1·67	1·17	2·56	0·38
,, 4	2·10	1·02	2·20	0·98	2·32	0·90	...	...
,, 5	2·18	1·00	2·10	0·93	2·33	0·90	2·67	0·28

(5) *The amount of combined carbon which corresponds to the equilibrium diminishes as the temperature decreases.*—Again, it will be noticed, the preceding table gives excellent support to this last conclusion, but another series of experiments now given can be considered conclusively to prove the deduction. Samples of No. 1 silicon content ·07 per cent., and samples of No. 3 silicon content 0·80 per cent., were heated to 1170° C. in charcoal, and allowed to cool slowly until the desired temperature was reached. After maintaining at this desired temperature for two hours, the sample was quenched. These experiments were done under excellent conditions, and are most important. The results will be found in the following table:—

Temperatures.	Sample No. 1.		Sample No. 3.	
	Graphite.	Combined Carbon.	Graphite.	Combined Carbon.
deg. 1170	0·50	2·61	1·42	1·69
1100	1·15	1·74	1·49	1·48
1000	1·03	1·74	1·35	1·55
900	...	...	1·91	0·90
800	1·15	1·31	2·09	0·43
700	1·87	0·43	2·56	0·88

The publication of the results of the foregoing experiments constituted what may justly be considered the commencement of a proper appreciation of the fundamental principles underlying the successful heat treatment of white irons, and led to rapid development in this field of metallurgical research. Before concluding the survey of Charpy and Grenet's research, their thermal data must be recorded. A most interesting heating and cooling curve of a low silicon white iron which they publish indicated that both the pearlite change and the carbide austenite eutectic change take place at an appreciably higher temperature in heating than in cooling, and it will further be noticed that the intensity of these two critical ranges is reversed. The curve, fig. 123, is here reproduced.

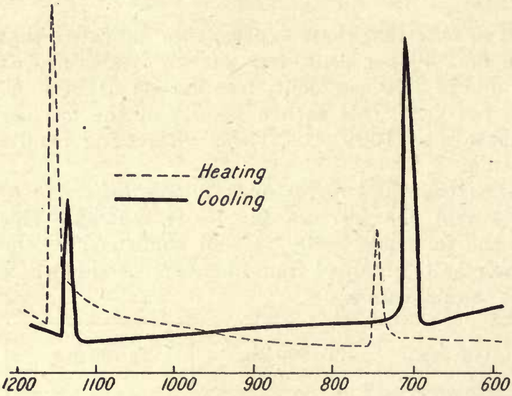

Fig. 123.

At the time of the publication of this research the investigators stated that they had not determined whether the higher critical point was due to the resolution of the "martensite-graphite eutectic mixture" or to the "martensite-cementite eutectic mixture." It has, however, since been demonstrated to be the resolution of the eutectic into carbide and austenite. The critical points obtained in the whole of the series of the irons experimented upon were as follows:—

Sample.	Heating.	Cooling.
No. 1	1140	1120
,, 2	1165	1145
,, 3	1137	1130
,, 4	1165	1137
,, 5	1165	1145

The micrographic examination of the series indicated—

(1) That the structure of the temper carbon varied with the temperature at which it was produced.

(2) That the precipitation was more complete in certain regions, and appeared to proceed from various centres.

(3) That the ultimate stable phases of the alloys were ferrite and free carbon.

Influence of Condition of Free Carbide upon the Precipitation.—The structures of these irons as cast are reported to be those which would be expected from white irons, but this the author can hardly accept, since, as the following experiment will show, the amount of cementite present in these quenched irons must have been low, a large quantity, no doubt, being in solution in the austenite matrix. The one disturbing feature is probably the fact that the balance, even under these conditions, would be varied by the varying composition of the iron. The following experiment[1] was performed by the author to determine the influence of the size of the structurally free carbide upon the size of the annealing carbon nodules.

Two test bars were cast of white cast iron of the following composition:—

Silicon	0·70 per cent.
Manganese	0·30 ,,
Sulphur	0·04 ,,
Phosphorus	0·11 ,,
Carbon	3·40 ,,

One bar, A, was cooled normally, *i.e.* allowed to cool down in the green sand mould in which it was cast, and its microstructure will be found illustrated in fig. 124.

Fig. 125 represents the structure presented by the other bar, B, which was quenched when it had cooled down to 1000° C. It will be observed that whereas the normally cooled bar has the free carbide in large thick membranes, the carbide in the quenched sample is apparently in less quantity of much smaller structure. The latter fact is explained by the austenite retaining in solution the missing carbide: this feature is still more accentuated with an increasingly higher quenching temperature.

The samples, A and B, were heated to 1050° C., maintained at the temperatures for 45 minutes, and quenched from 1030° C. The

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[1] *Royal Society*, A, vol. lxxxv., 1911.

FIG. 124.—Etched. Magnified 52 diameters.

FIG. 125.—Etched. Magnified 52 diameters.

FIG. 126.—Etched. Magnified 52 diameters

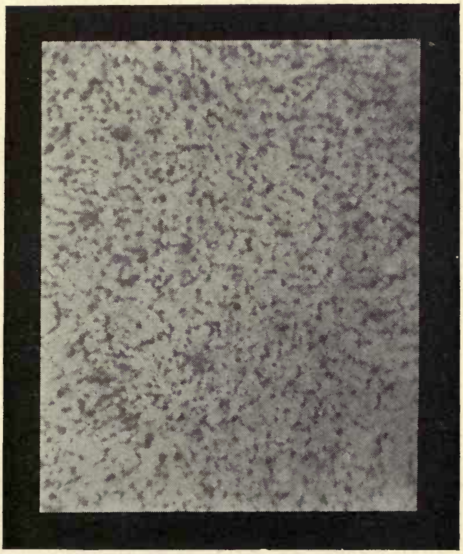

FIG. 127.—Etched. Magnified 52 diameters.

microstructures presented by the two heat-treated bars will be seen in figs. 126 and 127; it will be seen that the free carbon liberated in A materially conforms to the size of the original cementite membranes, which would appear to have decomposed *in situ.*

With regard to the sample B, it will be seen that the free carbon is present in very small nodules, which also compare with the size of the original free carbide. Perhaps the most important observation to be recorded in considering this experiment is the fact revealed by examination at high power, that all the free carbide was broken up in the quenched sample, whereas much remained unchanged in the normally cooled one. This experiment would also indicate that it is not necessary for the carbide to ball up before dissociation, which is contrary to the view expressed by a recent worker[1] upon this question; it will also be appreciated that in considering Charpy and Grenet's important memoir, the actual condition of the bars subjected to heat treatment must not be overlooked.

Influence of Varying Composition upon the Purity of the Structurally Free Carbide in White Cast Irons.—E. H. Saniter[2] has published interesting experiments made with a view to studying the properties of the free carbide Fe_3C. By the Arnold and Read electrolytic method he separated the carbide from cemented bar and subjected it to varying heat treatments.

His results are summarised in the following table:—

Treatment.	Graphite per cent.
When heated to about 800° C. and slowly cooled . .	0·40
When heated to about 1000° C. and chilled . . .	0·56
When heated to about 1000° C. and slowly cooled . .	2·45
When fused at about 1400° C. and slowly cooled . .	3·05

It will thus be seen that the carbide was proved to be unstable at high temperatures, and further proved that upon fusion only 4·27 per cent. carbon (the eutectic per cent.) remained in the iron.

Mylius, Foerster, and Schoene publish the results of a similar investigation, but their carbides had not the same degree of purity, and hence their results are not strictly comparable.

James, Charpy, and Grenet had emphasised the important influence exerted by silicon upon the precipitation of free carbon, and the author made a series of experiments[3] to determine, if possible, how the influence of this element, and also that of sulphur and manganese, was brought to bear. Four white irons were chosen, of which the microstructures will be found in figs. 128, 129, 130, and 131, and the analyses are given in the following table:—

	CC.	Gr.	Si.	Mn.	S.	P.
A	3·62	nil	1·20	·18	·011	·041
B	3·2	nil	·81	·14	·010	·04
C	3·4	nil	·85	2·66	·012	·041
D	3·16	nil	·97	·04	·45	·04

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[1] Levy, *Jour. Iron and Steel Inst.*, ii. 1908.

[2] *Jour. Iron and Steel Inst.*, 1897.

[3] *Royal Society*, A, vol. lxxxv., 1911.

Fig. 128.—Etched. Magnified 52 diameters.

Fig. 129.—Etched. Magnified 52 diameters.

FIG. 130.—Etched. Magnified 52 diameters.

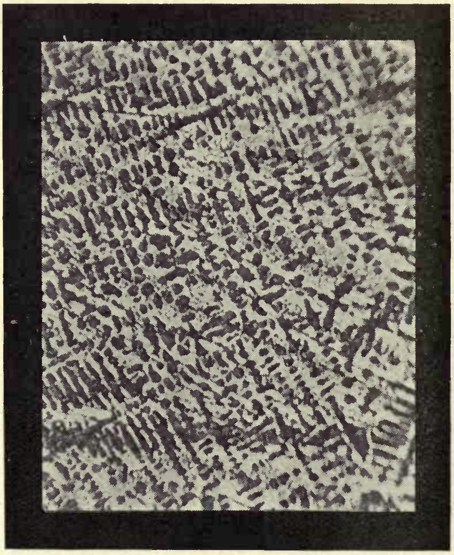

FIG. 131.—Etched. Magnified 52 diameters.

Since it was believed that the influence resulted from some modification of the composition of the carbide, it was considered that the analysis of the isolated carbide in each case might throw much light on the subject. Quantities of carbide from each of the four samples were therefore carefully prepared by Arnold's galvanic method, and were, after careful washing and drying, submitted to analysis. The carbide gave the following interesting figures:—

Bar.	Si per cent.	Mn per cent.	C per cent.
A	1·09	0·19	6·79
B	·61	0·16	6·40
C	·15	3·74	7·20
D	·37	traces	6·60

It is important to record that the whole of the silicon, apart from that found in the carbide, was found in perfect solution in the cold dilute hydrochloric acid (1·02 s.g.) used in the experiments. The exposure of the material in the acid bath was in each instance for 48 hours. The bars used were, in this first experiment, hardened just above *Ar* 1.2.3, in an endeavour only to obtain the carbide of supersaturation, it being considered that the carbon in the hardenite or solid solution would be given off as hydrocarbons. A second set of experiments performed upon the bars in the unhardened condition gave vastly different results; and since the figures may ultimately prove of value, they are here given:—

Bar.	Si.	Mn.
A	2·15	0·28
B	1·01	0·19
C	1·45	3·62
D	0·49	traces

It will be noticed that the silicon in this series did not enter into solution in the HCl, but remained with the carbide residue. As, however, at the temperatures at which the dissociation of the carbide takes place, the pearlite areas are in the hardenite condition, this latter question will not now be discussed. The author claims that the following deductions may safely be made from these experiments:—

(1) That the silicon is not uniformly distributed through the material, but that the carbide, whilst not containing as much silicon as the matrix, still contains an appreciable quantity corresponding to some extent to the total percentage.

(2) That the manganese is in combination in the carbide, to the exclusion of the silicon.

(3) In the case of high sulphur irons the silicon in the carbide will be low; but although the sulphur was not found, it is responsible, in some manner, for the comparative absence of the silicon.

Influence of the Composition of the White Iron upon the Precipitation of the Annealing Carbon.—Dr Wüst has shown that a perfectly

Fig. 132.—Etched. Magnified 52 diameters.

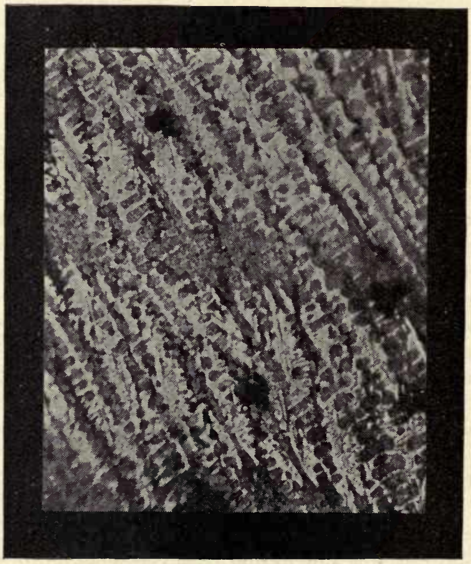

Fig. 133.—Etched. Magnified 52 diameters.

pure non-carbon alloy of eutectic composition may be made to throw its carbon content completely out of solution, but to accomplish this it is necessary to cool it very slowly from above the eutectic freezing point. Our immediate concern, however, is the behaviour of white cast irons under the heat-treatment ranges to which they are likely to be subjected in works practice. To determine the influence of varying composition, the four bars A, B, C, and D, recently dealt with, were put through various heat treatments.

In one experiment the bars, the original microstructures of which are given in figs. 128–131, were placed in a Clinch-Jones muffle, standing at 920° C., maintained at that temperature, and then carefully quenched in acid brine.

Sections were prepared from these quenched bars, and micrographs of the structures presented after etching will be found in figs. 132, 133, 134, and 135.

In each case it will be seen that the cementite is beginning to disappear, *i.e.* to be dissolved in the austenitic matrix. In the instance of A it will also be seen that some of the remaining cementite had decomposed *in situ*. The area of the annealing carbon being approximately equal with that of the cementite, it will therefore be obvious that these dark areas are not free carbon, but consist of the products of the dissociation of the carbide. The micrograph of B indicates that there has been a similar dissociation, but not to such a large extent as in the former case. It will be noticed that in the case of both C and D, whilst the austenite has commenced to dissolve the free carbide, none of the latter has decomposed.

A second experiment was performed with the same bars, but in this latter instance they were maintained for an hour at 1050° C., and then quenched in precisely the same manner. Figs. 136, 137, 138, and 139 indicate the microstructure of the etched sections prepared from these bars.

In the case of A, all the free carbide has disappeared; it is either dissolved in the austenite or has broken down with the liberation of the annealing carbon. An examination of the structure in the case of B will show that the same transformation has taken place; there is only one noticeable difference, and that is the size of the annealing carbon nodules. An explanation of this difference will possibly be found in the original disposition of the free carbide.

Even in C the free carbide is practically either in solution or is decomposed, only traces of the carbide being observed. Considering the high percentage of manganese in this particular bar, this is of additional interest.

In the case of D, much undissociated carbide still persists; but many peculiarly well-rounded nodules of annealing carbon also appear in the austenitic matrix.

The following table will be of interest, as indicating the amount of free carbon present in these particular bars after the treatment at this higher temperature:—

	CC per cent.	Free Carbon.	Carbon per cent. in Austenite.
A	1·55	2·07	1·55
B	1·71	1·49	1·71
C	2·26	1·12	2·26
D	2·46	0·70	?

FIG. 134.—Etched. Magnified 52 diameters.

FIG. 135.—Etched. Magnified 52 diameters.

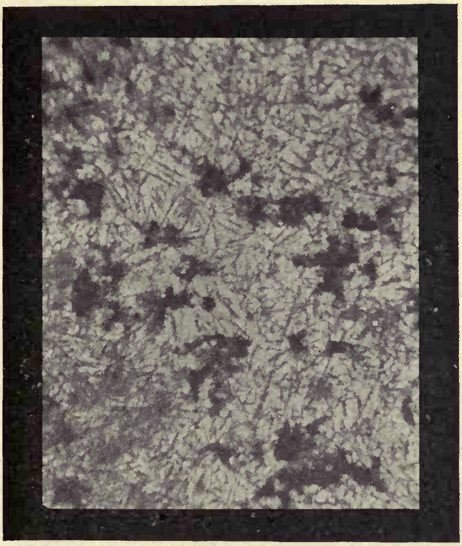

FIG. 136.—Etched. Magnified 52 diameters.

FIG. 137.—Etched. Magnified 52 diameters.

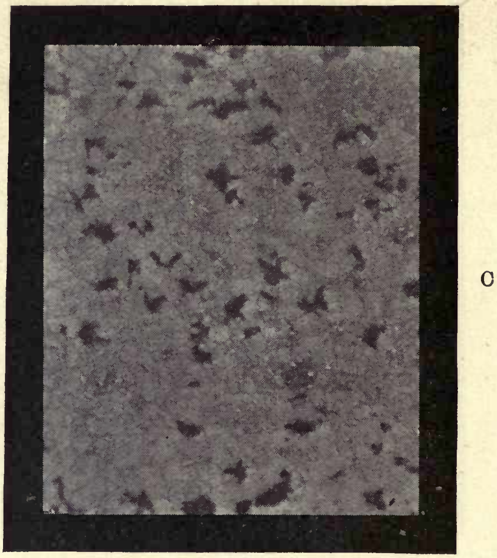

FIG. 138.—Etched. Magnified 52 diameters.

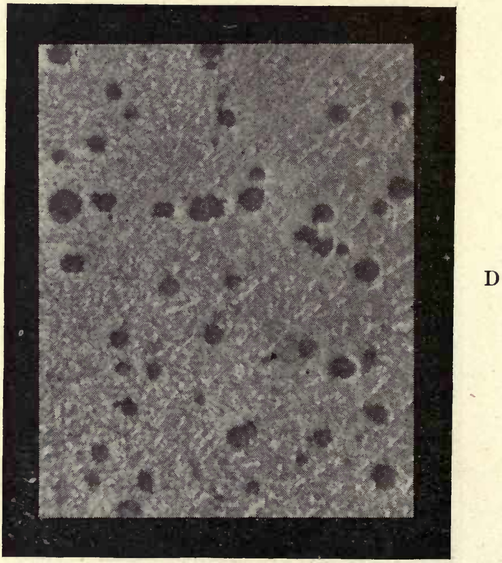

FIG. 139.—Etched. Magnified 52 diameters.

It would appear from these experiments that the presence of silicon renders the carbide less stable; that manganese and sulphur have the opposite effect, rendering it more stable; 3·0 per cent. of manganese and 0·45 per cent. of sulphur, under these particular conditions, have not been able, however, to render the carbide completely immune from dissociation.

It is thus considered that these elements affect the precipitation in two ways:—

(1) By modifying the composition of the cementite, they render it more or less difficult to dissociate at a given temperature.

(2) By altering the solubility of the carbide in the austenite, more or less is left free, and so liable to decomposition at a particular temperature.

An experiment made by the author to determine the actual manner in which the carbon is precipitated in white irons under works conditions may be of interest.[1] The intention was to determine the regions of temperature in which the precipitation took place. The bars used were all cast in the same moulding box from the same ladle of iron, and under the same conditions, and were allowed to cool down to normal temperatures in the same.

The heat treatment was done in an annealing oven of considerable size and the bars were all placed in juxtaposition; the transformation of the internal structure of the bars was arrested at different temperatures in this instance by rapidly cooling in a current of cold air. The structures thus obtained, whilst not strictly representing the conditions prevalent at the high temperatures, have by much experiment been found practically to represent very nearly the balance of the constituents at the particular stage of the heat treatment, the main error being in the condition of the pearlite, which naturally would be, at the temperatures of the experiment, in the condition of hardenite.

The samples submitted to microscopical examinations were six in number, and the time at which each particular sample was taken is given in the following table:—

No. 1. Material as cast.
No. 2. Material after attaining a heat of 780° C.
No. 3. The same upon reaching 820° C.
No. 4 is the material when 860° C. is reached.
No. 5. Without exceeding 900° C., the material has now cooled during a period of 24 hours to 750° C.
No. 6. After a further 24 hours, cooled to 650° C.

Microsections were prepared of each of the samples thus obtained, and the microstructures are given in figs. 140, 141, 142, 143, 144, 145, and 146.

Fig. 140 illustrates the structure of the original white iron. It will be seen to consist of pearlite and cementite, the cementite existing as normally found in white irons.

Fig. 141 presents a somewhat changed structure; and although no free carbon is as yet discernible, a change has taken place in the structure of the cementite. It would appear that the matrix has already begun to dissolve the cementite, and had, upon cooling down, thrown out of solution again the carbide thus dissolved.

Fig. 142 contains evidence of the precipitation of free carbon, several nodules of annealing carbon now being observed.

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[1] *Jour. Iron and Steel Inst.*, 1907, vol. ii.

ILLUSTRATING THE DISSOCIATION OF THE CARBIDES.

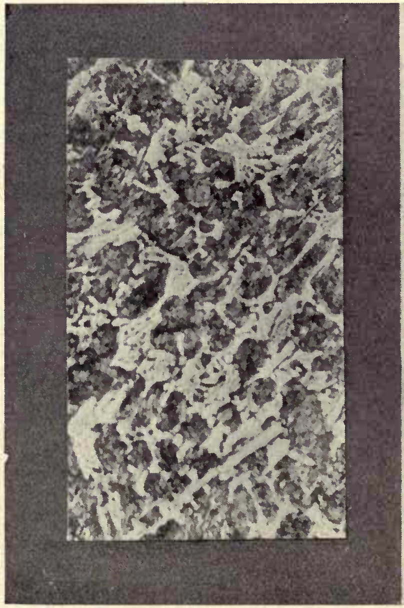

FIG. 140.—Etched (picric acid).
Magnified 120 diameters.

FIG. 141.—Etched (picric acid).
Magnified 120 diameters.

FIG. 142.—Etched (picric acid).
Magnified 120 diameters.

ILLUSTRATING THE DISSOCIATION OF THE CARBIDES.

FIG. 143.—Etched (picric acid). Magnified 120 diameters.

FIG. 144.—Etched (picric acid). Magnified 120 diameters.

FIG. 145.—Etched (picric acid). Magnified 120 diameters.

Fig. 143 indicates that the dissociation of the carbide is progressively taking place, with the result that the bulk of the free carbide (cementite) is now broken up.

Fig. 144 represents the structure after an appreciable lowering of the temperature (to 750° C.). It will be seen to consist of a matrix of pearlite, in which are to be observed areas of ferrite, surrounding in instances the annealing carbon nodules. The author is of the opinion that, had the bar been cooled with a theoretically perfect rapidity, the ferrite would have been absent, and the structure have presented a matrix with carbon in solution up to saturation, containing the annealing carbon nodules.

Fig. 145, which is a micrograph of the material when it has cooled to 650° C., will now be seen to consist of annealing carbon nodules in a purely ferritic matrix.

"OCCURRENCE" IN HEAT-TREATED WHITE CAST IRON.

FIG. 146.—Etched (picric acid). Magnified 60 diameters.

FIG. 147.—Etched (picric acid). Magnified 60 diameters.

It will be of interest to state that samples quenched at the temperatures as described during the foregoing experiment showed practically no difference in either the amount or distribution of the free carbon, and it is therefore considered safe to deduce—

(1) That the free carbide was broken up into free carbon and iron between the temperature of 800° C. and 900° C.

(2) That the carbide resulting from the resolution of the hardenite decomposed between 650° C. and 750° C., *i.e.* immediately after or during the hardenite-pearlite change.

The analyses of the material used was comparable with the materials used by Charpy and Grenet, and would be between their samples 3 and 4.

Combined Carbon	3·40	per cent.
Graphite	nil	
Manganese	0·14	,,
Silicon	1·10	,,
Sulphur	0·06	,,
Phosphorus	0·20	,,

The author has, during his experiments in the heat treatment of cast irons occasionally,[1] in the treated bar, noticed peculiarly bright areas of the section, which to the naked eye appeared unattacked by the acid medium (HNO^3). The microstructures of the edges and centres of such areas are given in figs. 146 and 147. These areas would seem to consist of a soft ferrite-like constituent, cut up by thin bands of a constituent which is distinctly affected by the acid. Annealing carbon will be seen dotted through the area. The author considers these occurrences worth recording.

It will thus be seen that by simple heat treatments a most valuable product can be obtained which is essentially the equivalent of wrought iron, in which, instead of the slag inclusions, are found the precipitated free carbon nodules. Here we have that product which is so largely produced in America under the name of malleable iron: in this country it has taken to itself the appellation of "special" and sometimes "blackheart" malleable cast iron, as distinctive from the Réaumur or European malleable cast iron, which will be found treated in the following chapter.

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[1] *Jour. Iron and Steel Inst.*, 1907, vol. ii.

CHAPTER XIII.

THE CHEMICAL PHYSICS INVOLVED IN THE DECARBURISATION OF CAST IRON WITHOUT FURTHER FUSION.

Attempts made to explain the process of the decarburisation of cast iron without further fusion have until recently met with little success, as the attempts to explain the phenomena of cementation, and the correct theory of the process, for a very long time remained undetermined. It is the recent developments in the manufacture of malleable cast iron, and the attendant research work involved, which have ultimately led to a probable solution of the problem.

At the May meeting of the Iron and Steel Institute, 1909, the author read a paper upon some experiments which he had made to determine the accuracy of the theory recently propounded by Wüst in an admirable paper in *Metallurgie.* Since in both papers there is a considerable amount of careful experimental work, the author proposes to reproduce them in some detail, so that the reader may form his own opinion as to the accuracy of the opposing theories.

Ledebur originally explained the process of decarburisation somewhat as follows:—

"The decarburisation is not only confined to the surface of the glowing piece of iron, but also penetrates to the inmost parts. As long as the heating is carried on sufficiently and the temperature is high enough, a circulation of the carbon takes place. When the amount of carbon diminishes on the surface of the piece of iron, the carbon flows from the inside, so that an equalisation takes place."

He further explains "that one could get a conception of the process by imagining that the carbon is given off from molecule to molecule as soon as one molecule becomes poorer in carbon than another."

When Ledebur propounded the foregoing theory he had not the advantage of the later work which has been done in the higher regions of the iron carbon diagram, but yet, in the author's opinion, his views remain substantially correct.

Wüst says that this idea of the reactions cannot be accepted, since "an equalisation of carbon as here represented can only take place where carbon is in solution, while the carbon, separated out as free carbon, can in nowise travel from molecule to molecule in the solid iron." He is absolutely correct in saying that carbon can only diffuse when in solution (or in combination), and it is on this very point where the author considers that Wüst's argument is proved untenable. This will be referred to later.

James, Charpy and Grenet, Forquignon, Ledebur, Royston, Watanabe, Levy, Wüst, and the author have demonstrated that to a great extent it is upon the precipitation of free carbon that the successful production of malleable cast iron depends, and, in the author's opinion, the subject of the decarburisation becomes somewhat involved, since Wüst does not treat separately—

(1) The actual elimination of carbon.

(2) The precipitation of the annealing carbon.

This chapter is merely treating with the *decarburisation* of cast iron, and not with the production of *malleable cast iron*, which will be found treated under another heading.

The experiments performed by Wüst will now be described. In an earlier work (*Stahl und Eisen*, 1903, s. 1136), he says he had demonstrated that the production of malleable cast iron takes place in two distinct phases:—

(1) Annealing carbon is produced according to formula—

Cementite = ferrite + annealing carbon.

(2) The annealing carbon thus produced is converted into gas and then the tempering begins.

"Since," he says, "motion of the free carbon cannot take place in the solid irons, and equalisation of this free carbon, molecule to molecule, is impossible to conceive of, it must be conclusively accepted that the former conception of the processes during 'tempering' is untenable. The conversion of the annealing carbon into gas could only take place where it was separated out. Thus it takes place not only at the points of contact between the iron ore and the heated iron, but it must distribute itself over the entire cross section of the piece. The carbon does not move towards the oxidising agent, but *vice versa*; the oxidising agent, beginning its activity at the surface, gradually penetrates, and in this manner reaches the annealing carbon which has not yet been oxidised. Accordingly," Wüst explains, "the oxidising agent can only be a gas giving off oxygen, and the oxide of iron used to carry on the process of elimination only thus indirectly effects the conversion of the carbon into gas.

To prove his theory, Wüst and his pupil Schulte-Kemp carried out the following experiments.

Swedish charcoal pig iron of the following composition was used, Mn 0·18 per cent., P 0·02 per cent., Si 0·014 per cent. With the addition of ferro-silicon, the pulverised pig iron was melted in a blacklead crucible and cast into chill moulds, producing rods 10 mm. in diameter. The fractures of the bars were white, and they analysed as follows:—

Total Carbon	4·17 per cent.
Graphitic Carbon . . .	traces
Silicon	1·01 ,,
Manganese	1·18 ,,
Silicon	0·01 ,,
Phosphorus	0·02 ,,

Fig. 148 shows the structure of this white iron. As was to be expected, it only, in Wüst's words, "shows the structure of the solidified eutectic enlarged 70 times."

In order to separate the annealing carbon, the bars were heated for two hours at 950° C. in a vacuum oven. The analysis of the annealed samples showed that 3·45 per cent. of the carbon had been precipitated as annealing carbon. A cross section of the sample, magnified 150 dias., is shown in fig. 149. The "nest-like" appearance of the temper carbon surrounded by ferrite is here plainly shown.

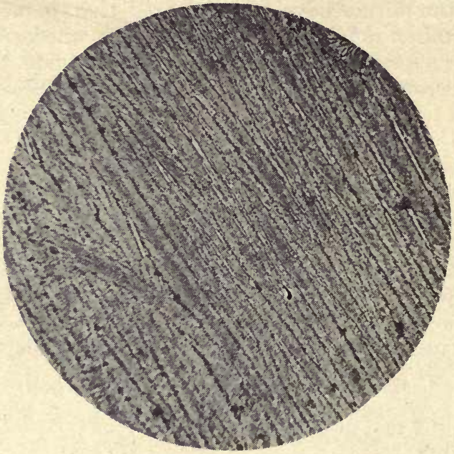

Fig. 148.—Etched. Magnified 70 diameters.

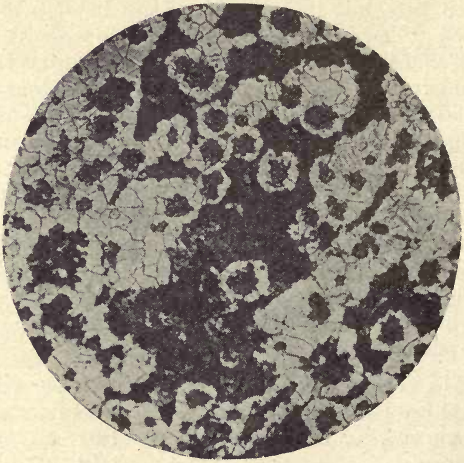

Fig. 149.—Etched. Magnified 150 diameters.

For the elimination, that is, for the execution of the second phase of the process, an excellently designed apparatus was used. "On the left is an automatically operated mercury air-pump which serves to exhaust the air out of the oven, which is held in a horizontal position in a framework. On the right of the oven an air-tight tube is attached for observing the conditions during heat treatment. On the side of the tube there is a three-way cock connecting a burette, so that it is possible to take samples of gas during the experiment."

One of the first experiments was to place two porcelain vessels in the porcelain tube of the oven; one of them contained the heat-treated sample containing 3·45 per cent. of annealing carbon, the other contained pure oxide of iron, dried at 130° C. The proportions of the materials entering into the reaction were ascertained by weighing before and after the experiments. After the oven had been pre-heated to about 450° C., the porcelain vessels were put in, the air exhausted and the temperature was rapidly raised to between 900° and 960° C., at about which temperature it was usually maintained for from 20 to 25 hours. The glazed porcelain tube proved to be completely air-tight, even at 1000° C.

As soon as the temperature reached 600° C., the mercury in the gauge began to fall rapidly, and after a while continued to fall more slowly and uniformly, until after 20 to 23 hours the pressure within the tube was atmospheric. The results obtained in this way are arranged in the following table:—

Number of Test.	Temperature in °C.	No. of Hours heated.	Amount of Fe_2O_3.	Loss in Weight of Fe_2O_3.	Per cent. of Oxygen lost.	Amount before.		Amount after.		Loss.		
						Total C.	Annealing C.	Total C.	Annealing C.	Total C.	Annealing C.	Per cent. Total C.
I.	900	20	uncert.	uncert.	uncert.	4·17	3·45	3·46	2·76	0·71	0·69	17·
II.	920	20	3·2008	0·2220	23·11	4·17	3·45	3·43	2·74	0·74	0·71	17·1
III.	940	24	3·0031	0·3353	37·22	4·17	3·45	3·28	2·58	0·91	0·87	21·8
IV.	960	26	3·0542	0·4000	43·66	4·17	3·45	3·01	2·29	1·16	1·16	27·8
V.	1000–940	26	3·3321	0·6926	69·28	4·17	3·45	1·84	1·10	2·33	2·35	55·9
VI.	1000	21	3·1673	0·3730	39·26	4·17	0·00	3·21	2·75	0·96	un.	23·02
VII.	960	24	uncert.	uncert.	uncert.	4·17	0·00	2·98	2·52	1·19	un.	28·5
VIII.	960	20	packed in iron oxide			4·17	0·00	3·46	2·49	0·71	un.	17·
IX.	960	44	5·2770	0·4614	uncert.	4·17	0·00	3·12	2·52	1·05	un.	25·2
X.	940	110	one-half packed in oxide			4·17	0·00	2·52	2·02	1·65	un.	39·5
XI.	...	50	uncert.	uncert.	uncert.	4·17	3·45	2·59	1·90	1·58	1·55	37·9
XII.	...	52	uncert.	uncert.	uncert.	4·17	3·45	2·29	1·52	1·88	1·93	45·1

In experiments I. to V. cast iron in which the annealing carbon had already been separated was used, whilst in experiments VI. to X. the cast iron used was in the as-cast condition, so that the annealing carbon had to form during the heat treatment. In experiment VIII. the iron to be heat treated was packed in the iron oxide: similarly in experiment IX.; but in the latter case four parts of used oxide to one part of new oxide composed the oxidising mixture, and in experiment X. only half the material was packed in the oxide. Wüst truly states that in all these experiments, as will be seen from the Table I., is shown a decrease in carbon irrespective of the proximity or otherwise of the iron oxide.

It is, he says, clearly evident from the first five experiments that the elimination is confined to the annealing carbon, since the analyses show that that has diminished whilst the combined carbon has remained constant; and a further fact which he considers requiring explanation is that no further precipitation of annealing carbon has taken place. The author will discuss these points later, and for the present proposes to state Wüst's case, as he presents it, as fully as possible. It is next claimed by him that, since the microscopic investigation of No. V. revealed annealing carbon in gradually increasing proportion towards the centre of the piece, it is proved that the oxidising gas has first attacked the annealing carbon precipitated on the outside portion of the bar.

The material of experiment No. X. shows on examination more and larger annealing carbon nodules towards the centre of the bar. It is, he says, remarkable that in this instance the extreme outer edge of ferrite (completely decarburised iron) is succeeded by a band of pearlite, which in turn gives way to the ferrite of the interior. This he mentions again later in the work.

The iron oxide was found after the experiments to have become black and to have lost considerably in weight in each case. It was found by analysis that as much as 70 per cent. of the oxygen had escaped, and that part of the iron oxide had been reduced to metallic iron. This reduction to the metallic state was proved by the fact that hydrogen was given off when treated with hydrochloric acid, and when treated with copper sulphate metallic copper separated out.

By means of the three-way cock before described, samples of gas were taken during the experiments, and the results are grouped in the table below.

Number of Test.	Gas drawn off after — hours.	Amount of CO_2 per cent.	Amount of CO per cent.
III.	20	26·0	74·0
IV.	20	27·3	72·7
V.	18	26·0	74·0
VI.	14	37·3	62·7
	20	32·1	67·9
	2	31·1	68·9
VII.	25	31·0	69·0
VIII.	40	68·0	32·0
	20	31·0	69·0
IX.	4	62·6	37·4
	18	40·8	59·2
	27	34·5	65·5
	43	28·0	72·0
X.	16	31·0	69·0
	40	28·2	71·8
	42	28·0	72·0
	45	27·0	73·0
	63	12·9	87·1
	65·5	16·3	83·7
	110	11·0	89·0
XII.	18	32·0	68·0
	24	27·5	72·5

From an examination of the results in this table, it will be seen that carbon-dioxide CO_2 is the gas which actually accomplishes the elimination, according, says Wüst, to the equation—

$$CO_2 + C = 2CO.$$

This explains the observations made, namely, that the CO_2 diminishes and the CO increases as each experiment proceeds, this action being particularly emphasised in the case of experiment No. X.

"If," says Wüst, "we now seek to explain the presence of CO_2 and CO, we find the solution to be comparatively simple. It is known that iron oxide gives off part of its oxygen at higher temperatures, and this has also been proven experimentally by one of my scholars, Bergen." Bergen's results are given in the following curve, fig. 150.

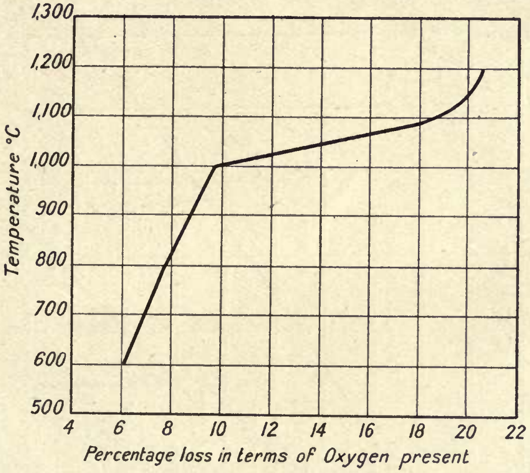

FIG. 150.

It is evident that at 600° C. the evolution of oxygen from the oxide commences.

The iron oxide was found to dissociate as follows:—

at 1050° C. into Fe_2O_3 FeO (Fe_3O_4)
at 1100° C. into Fe_2O_3 2FeO (Fe_4O_5)
at 1200° C. into Fe_2O_3 3FeO (Fe_5O_6)

This oxygen is said to combine with the free precipitated annealing carbon, with the production of the gas CO_2; "and as soon as the oxygen has thus been used up, the process is kept up by the CO_2 combining with the annealing carbon to form CO. The CO reacts with the iron oxide and completely reduces same to iron protoxide, and finally to metallic iron, by which action the CO_2 is again generated. The ratio of the CO_2 and CO depends upon the proportional weights of iron oxide used and the material which is being decarburised."

The rise in pressure obtained by heating reaches its maximum when equilibrium between partial pressure of the oxygen and the pressure of dissociation of the iron oxide begins.

The curves, fig. 151, illustrate the pressure from heating pure iron oxide compared with the variations of pressure obtained in experiments II. and III. The rise in pressure in these experiments is attributed to the increase in volume produced by the formation of CO according to the equation—

$$CO_2 + C = 2CO.$$

Experiment X. is most interesting: in this instance the heating was continued for 110 hours, and successive samples of gas were taken. It will be seen on reference to the table that the CO_2 decreases and the CO increases, but, it is stated, a decrease in pressure was noted. It is argued that this is only made possible by means of the reaction expressed in the following equation,

$$3Fe + 2CO = Fe_3C + CO_2,$$

during which two volumes of CO produce one of CO_2.

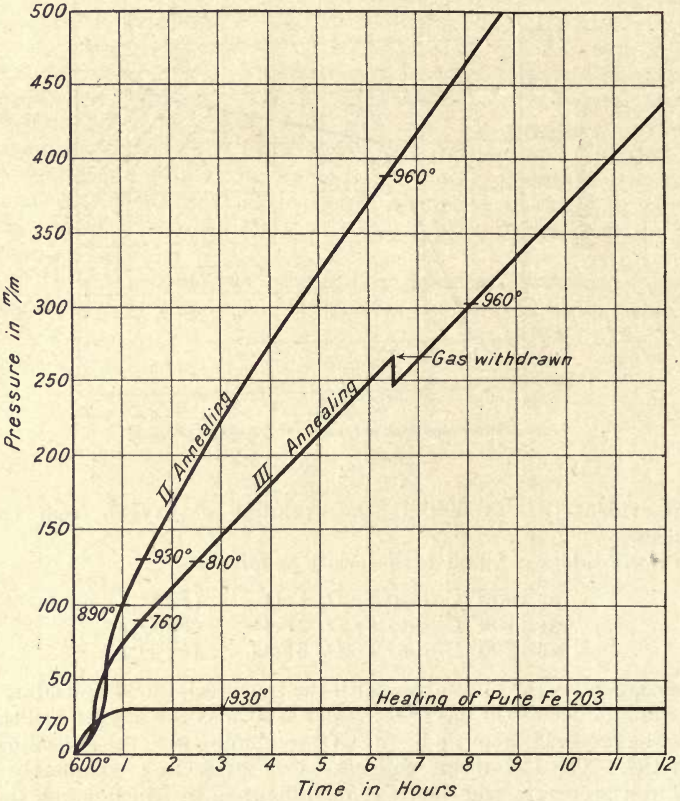

Fig. 151.

Fig. 152 shows, in Wüst's opinion, how the process of elimination has become one of cementation, owing to the substitution of CO for CO_2. "The sample shows a ferritic surface, next to that is a ring of pearlite, and in the middle there is ferrite with annealing carbon. The outer two bands on the surface, one black and one white, can be accounted for by light reflections, and have nothing to do with the structures. It can be seen that this band of pearlite owes its existence to the reversal of the annealing process into the cementation process. The CO increases to such an extent that it could neither have any oxidising influence or remain neutral, but, according to the equation given, produced an increase in carbon, the iron taking up the carbon given off from the CO."

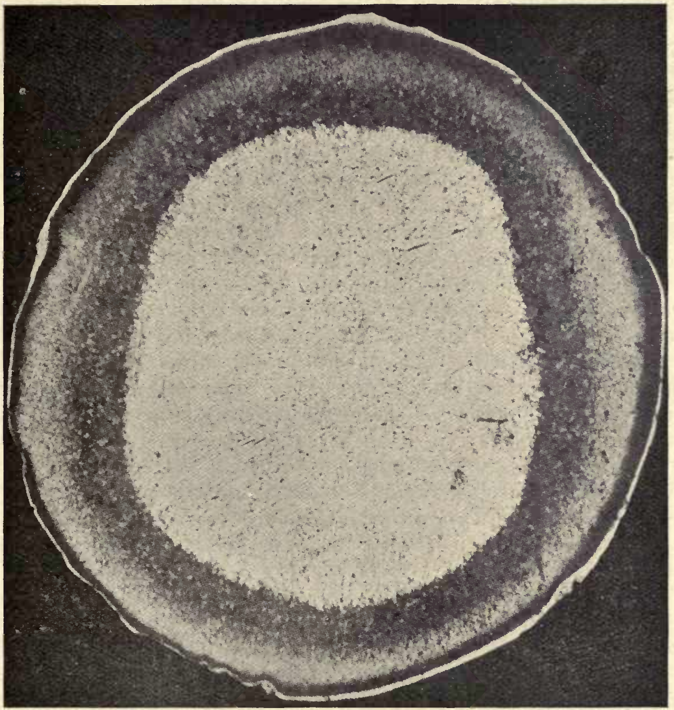

Fig. 152.—Etched. Magnified 15 diameters.

The analyses are given, and claim to confirm the theory above quoted. The author will later put forward his theory of the matter, but in the meantime here are the analyses :—

	Surface.	Middle.
Total Carbon . . .	1·07 per cent.	3·98 per cent.
Annealing Carbon . .	·21 „	3·86 „
Combined Carbon . .	·86 „	0·12 „

The sample resulting from experiment VII. was analysed in a similar manner, and the results obtained are here given :—

	Surface.	Middle.
Total Carbon . . .	2·02 per cent.	3·97 per cent.
Annealing Carbon . .	1·54 „	3·50 „
Combined Carbon . .	0·48 „	0·47 „

Since in this instance the combined carbon is practically the same throughout, it is considered by Wüst that, as the conditions were different, his ingenious theory is proved. Wüst summarises his results as follows:—

1. The process of elimination is caused by oxygen which forms CO_2 with the annealing carbon produced during that treatment.

2. The CO_2 penetrates into the glowing iron and forms CO with the annealing carbon.

3. The CO_2 is again generated when the CO reduces the iron ore into iron protoxide and metallic iron respectively.

4. If there is a lack of oxygen in the ore, the regeneration of CO_2 does not occur, and the CO content in the gas mixture can increase to such an extent that through the decomposition of the CO the piece is decarburised.

Such are Wüst's valuable experiments and deductions upon this question of decarburisation, and obviously, according to his view, the carbon must be precipitated as annealing carbon before it can be eliminated.

In the English translation of his *Einfuhrung in die Metallographie* Goerens would seem to accept the same theory, since he says, speaking of a heat-treated white iron, "the previously glass-hard material may now be easily filed in accordance with its composition (temper carbon, ferrite, and pearlite). If the temper carbon produced in this way is removed by some means, *e.g.* by oxidation, an iron remains consisting of ferrite and pearlite only, and is, in consequence, malleable." To make a malleable casting, as pointed out elsewhere, it is not necessary to eliminate the carbon, but only to precipitate it, and it would seem that the two actions are being somewhat confused.

The author takes exception to the German theory on two grounds:—

(1) Carbon can and is every day eliminated without it being first precipitated in the free state.

(2) At the temperature of 960° C., such as used by Wüst, much of the temper carbon would recombine with the iron.

With regard to the first point, in any mill or forge, unless the greatest skill is used, the surface of the billet or ingot becomes decarburised on exposure to the furnace gases, and this happens in steels in which the occurrence of free carbon is unheard of. In the old English process of producing malleable cast iron, as the author will later show, decarburisation takes place independently of the precipitation. Many samples of this material have been studied which, whilst possessing a decarburised exterior, have still retained the carbon in the combined condition. When the carbon precipitates in white cast iron it usually does so uniformly through the mass, and hence, if it be precipitated in the outer portions of the casting, the same action should take place completely through the bar; hence, it may reasonably be argued, that since the interior is still in the combined state, the outer decarburised portions never had the carbon precipitated. The carbon has, most likely, in such instances been eliminated from the carbide according to the equations—

$$\begin{aligned} 2Fe_3C + 2CO_2 &= 3Fe_2 + 4CO \\ 2CO + O_2 &= 2CO_2 \\ 2CO_2 + 2Fe_3C &= 3Fe_2 + 4CO \end{aligned}$$

continuously, and not according to Wüst's equations—

$$\begin{aligned} Fe_3C &= Fe_3 + C \\ C + CO_2 &= 2CO \\ 2CO + 2O &= 2CO_2 \\ C + CO_2 &= 2CO \quad \text{continuous.} \end{aligned}$$

With regard to the second point, it is now firmly established that the precipitated free carbon returns, upon the reheating of the material to a high temperature, to a considerable extent, to the combined state. Hadfield, some years ago, in discussing a paper before the Iron and Steel Institute, described how he obtained a material of glass-scratching hardness by quenching a sample of American blackheart malleable cast iron. Arnold and McWilliam, speaking of black tool steel, state that "in heating this steel to bright redness for a short time, it has been demonstrated, both practically and scientifically, that nearly the whole of the amorphous graphite combines with the iron, forming Fe_3C, and that on quenching such steel it is found to be fully hardened, but of inferior quality."

The process of cementation itself depends, of course, upon this solubility of carbon or its compounds at high temperatures. Data is now available upon this particular point from results of experiments published during recent years, and it would therefore seem that, instead of deducing from Wüst's figures that, since the combined carbon is constant before and after the experiment, and the annealing carbon is much lower after than before the experiment, the carbon must have been eliminated from the annealing carbon portion, Wüst should have considered, in formulating his theory, the actual condition and equilibrium of the carbon at the particular temperatures of the experiment.

The author will now describe the experiments[1] which he made to determine the actual principles involved in decarburisation, and to find whether it really was necessary to precipitate the carbon as "annealing" carbon before it could be eliminated.

For the first experiments a pure Swedish blister steel was used. Owing to its composition, it was unlikely that free carbon would be precipitated at the temperature at which it was decided to work. The material had the following composition :—

Total Carbon	1·64 per cent.
Combined Carbon . . .	1·64 ,,
Silicon	0·03 ,,
Manganese	trace
Sulphur	0·01 ,,
Phosphorus	0·01 ,,

Upon microscopic examination the bar was seen to consist of cementite in a ferritic matrix, and the structure is reproduced in fig. 153.

The laminated pearlite usually present in such material had, by very slow cooling, been separated into cementite and ferrite, and the carbon of supersaturation was present in thick membranes, as shown in the photomicrograph. Three test bars were cut from the same portion of the same bar, and measured each 3 in. by ½ in. square. One of them, *A*, was packed in wood charcoal. This was to form the standard. It was considered that oxidation would be prevented by the presence of the charcoal, and, if possible, further absorption of carbon might take place. If precipitation of free carbon did take place in the experiment, it should have been found in this bar.

One bar, B, was packed in pulverised quartz sand, so that simple heat treatment might be observed.

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[1] *Jour. Iron and Steel Inst.*, 1909, vol. i.

The third and most important bar was packed in hematite iron ore, similar to that invariably used for annealing malleable castings by the old Réaumur process.

The pots containing the bars were placed together in an annealing oven and subjected to the heat treatment shown in fig. 154, the temperatures being ascertained by means of a thermo-couple. It will be seen that after 3 days' firing a temperature of 890° C. had been attained, and, after well soaking at this temperature, the bars were raised to Wüst's general temperature of 960° C. After being maintained at this temperature for 48 hours, the bars were allowed slowly to cool down until just cold enough to handle. It would be well to consider the condition of the materials whilst exposed at the highest temperature during this experiment. After passing through the first critical point the matrix became saturated with carbide, and with the increasing temperature the remaining cementite would be gradually taken into solution, until at 960° C. it is probable that very little cementite would be left structurally free. The samples then, it may be presumed, presented most likely a molecularly homogeneous condition to the varying influences for a period of 48 hours. The examination of the bars after the treatment was most interesting. A, presented a crystalline fracture not unlike that of the original blister steel.

FIG. 153.—Cemented bar before treatment. Magnified 130 diameters. Etched HNO_3.

B, treated in sand, was fairly tough, and broke with a steely fracture, whilst

C, which had been treated in ore, actually bent considerably and its fracture showed what appeared to be a mass of ferrite crystals.

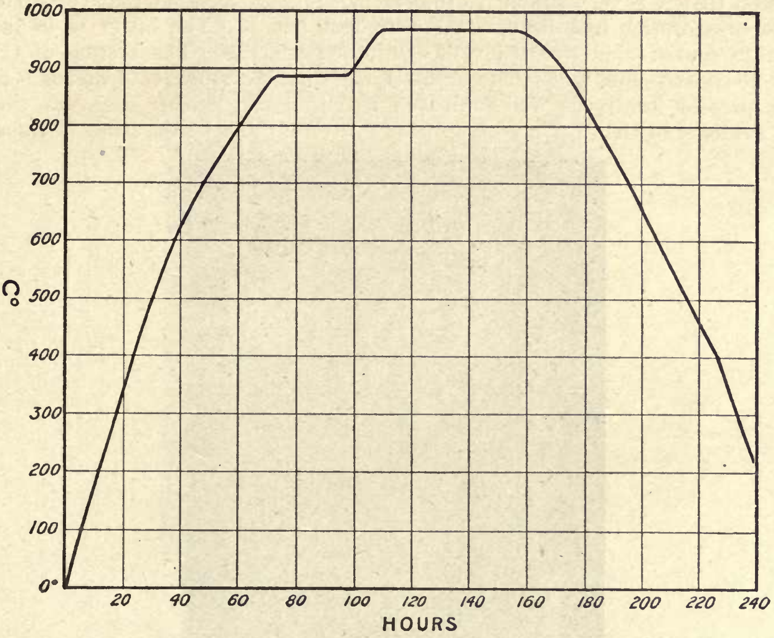


FIG. 154.

Samples thoroughly representing the materials gave on analysis the following compositions:—

Sample.	Total Carbon.	Combined Carbon.	Silicon.	Manganese.	Sulphur.	Phosphorus.
	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.
A in carbon	1·63	1·63	0·03	traces	0·01	0·01
B in sand.	0·75	0·74	0·03	traces	0·01	0·01
C in ore	0·15	0·13	0·03	traces	0·01	0·01

It will be seen that, in spite of A being packed in charcoal, no further absorption of carbon had taken place, and, what is more, all the carbon present was in the combined state, as no free carbon was noticed during the analysis.

Sample B, it will be seen, has lost a great deal of its carbon, and this is attributable to the furnace gases permeating the sand, and thus conveying the oxidising influences, which disposed of more than half of its carbon.

Sample C has lost all its carbon but 0·15 per cent., and this is the explanation of its ductility.

Sections prepared from the samples were examined under the microscope, and the structures presented are shown in figs. 155, 156, and 157. It will be seen that A is very similar to the original blister steel, but that the carbon of supersaturation has disappeared from test bar B. The latter is, in fact, seen to consist almost entirely of laminated pearlite. The section of C is seen to consist chiefly of ferrite crystals, the small percentages of carbon being only present locally as well-laminated pearlite. In neither case was there any evidence of the presence of annealing carbon; and hence, since obviously the carbon has in B been partially removed, and in C almost totally removed, the author considers that it established that carbon is eliminated without previous precipitation.

Fig. 155.—Cemented bar after heat treatment in charcoal. Magnified 130 diameters. Etched HNO_3.

It may now be of interest to reproduce an experiment made to trace, by means of the microscope, the actual process of the elimination of the carbon during the conducting of the English Réaumur malleableising process. Samples of fairly representative composition were taken for the purpose, and will be recognised by anyone familiar with the process.

They analysed as follows:—

Combined Carbon . . .	3·5 per cent.
Graphite	nil
Manganese	traces
Silicon	0·50 per cent.
Sulphur	0·35 „
Phosphorus	0·05 „

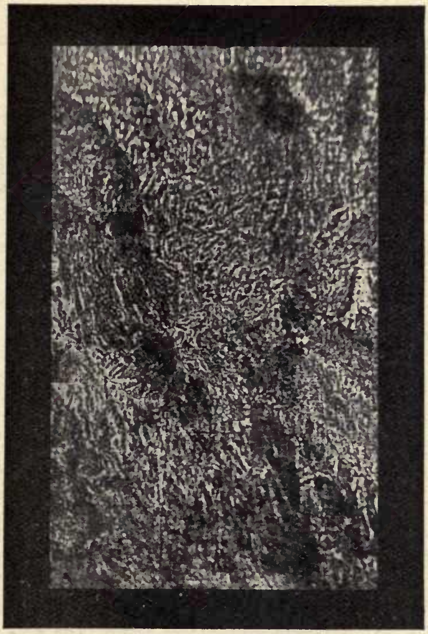


FIG. 156.—Cemented bar after heat treatment in sand. Magnified 130 diameters. Etched HNO_3.

FIG. 157.—Cemented bar after heat treatment in iron ore. Magnified 130 diameters. Etched HNO_3.

The following curve, fig. 158, illustrates the heat treatment to which this material was subjected.

The packing used was hematite ore, 3 parts old and 1 part new. It will be seen that the curve is marked at different places by the letters A to J. At these points samples were taken from the oven and cooled rapidly in air. Microsections were examined from each sample with the following results:—

Sample A.—Already the oxidation had commenced, resulting in a very thin skin of ferrite and pearlite. The remainder of the casting was of the cementite pearlite structure of white iron.

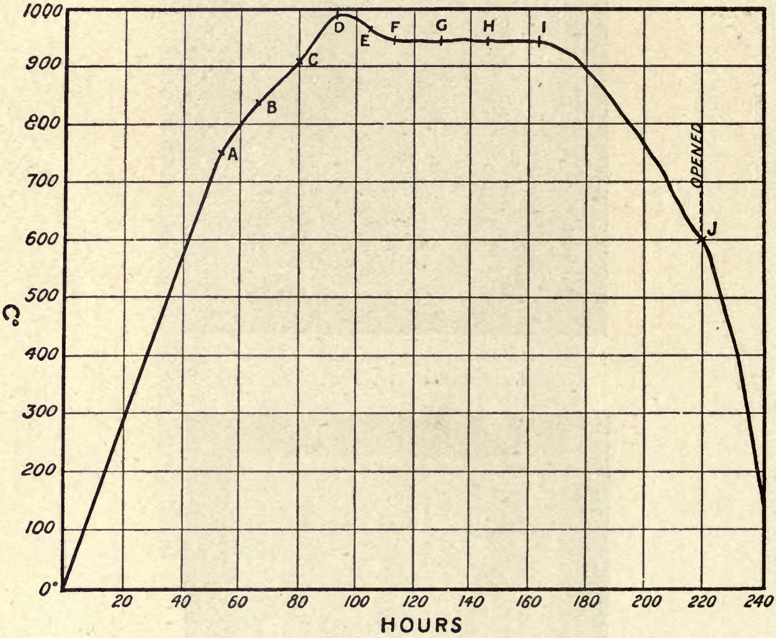


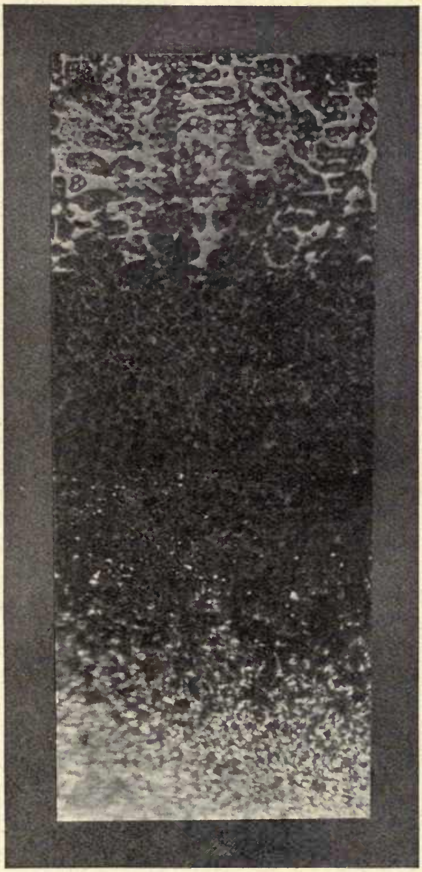
FIG. 158.

Sample B.—The skin has now increased in thickness, but otherwise the centre still remained hard.

Sample C.—The skin is now much increased in thickness, and consists of ferrite with pearlite increasing towards the still intact cementitic centre.

Sample D.—The skin is thicker still. The decarburisation has at least penetrated $\frac{3}{16}$ of an inch, but the microstructure varies little from the last, the white cementite centre being still practically unchanged.

In fig. 159 will be seen a photomicrograph clearly illustrating the nature of the skin. It also throws some light upon the nature of the action by which the carbon is removed. No free annealing carbon is noticeable. "The upper portion, which is in continuity with the centre of the casting, is obviously the unchanged cementitic structure of white iron. If the photomicrograph is traced downward this cementitic structure abruptly terminates, giving place to a structure similar to that of slightly supersaturated steel, which in turn is replaced by a purely pearlitic range, and then ferrite crystals begin to appear, which are ultimately traceable to the ferritic outer skin."



Cementite-pearlite structure of white iron: combined carbon per cent., 3·00.

Carbon equal to slightly supersaturated steel.

Saturation 0·80 to 0·90 per cent.

Pearlite with ferrite increasing.

Skin of ferrite.

Fig. 159.—Illustrating the decarburisation of White Iron. Magnified 130 diameters. Etched HNO_3.

Sample E.—The hard centre is now broken down and the skin merges imperceptibly into the centre, which consists of a structure similar to high carbon steel, but containing much precipitated annealing carbon.

Samples F to I show little changes, except that the annealing carbon nodules would appear to grow less and the decarburised skin to increase in depth.

Sample J presented the structure of the finished material, and was a really good sample of English Réaumur malleable cast iron. It consisted mainly of well-laminated pearlite, in which was immersed the remaining annealing carbon, with a skin of well-developed ferrite.

The analysis of the finished casting may be of interest, and is therefore given:—

Combined Carbon	0·65 per cent.
Sulphur	0·35 „
Phosphorus	0·05 „
Temper Carbon	1·10 „

A careful examination of these microsections clearly demonstrated that the process of malleableising presented two phases:—

(1) Elimination of carbon from the outer portions of the casting.

(2) Softening of the iron by precipitation of the annealing carbon.

It will, however, be noticed that the elimination was in no way dependent upon the precipitation. The foregoing experiment may be summed up as follows, and fairly represents, in the author's opinion, the changes taking place during this process.

At the temperature of 750° C. the oxidation of the carbon has commenced; and since there is no evidence of free carbon being present at this stage, the carbide itself must have been attacked. The activity of this reaction increased with the temperature, until a temperature is reached at which the precipitation of annealing carbon takes place until equilibrium for the particular temperature and composition is attained. The later stages simply consist of further elimination of carbon from the outer portion, to which carbon is replaced by diffusion with carbon as carbide from the inside of the piece, the latter being also replaced by the precipitated annealing carbon being taken back into solution, and thus preserving the equilibrium for the temperature.

Such is the author's view of these reactions; and it will be observed how much they are in keeping with Ledebur's original theory. It may here be said that Wüst is further investigating this interesting subject, and in some future edition of this work it will be a pleasure to put forward any new experiments he may have been pleased to publish.

Rugan and Carpenter, in a paper elsewhere referred to, published since those by Wüst and the author, described some experiments which, although not intended to deal with this particular subject, appear to throw light upon it. A number of cast-iron bars of varying silicon content were heated in a muffle for 4 hours at 900° C. and allowed to cool. They were then submitted to this treatment twenty-five times, and at the end of the twenty-fifth treatment were analysed to determine the loss of carbon. The results are given in the following table:—

Alloy.	Si.	Per cent. of Carbon in original Alloy.	Per cent. of Carbon after twenty-five heats.	Percentage Loss.
N	1·07	3·98	2·45	38·4
O	1·79	3·98	2·40	39·7
P	2·96	3·79	2·60	31·4
Q	4·20	3·76	2·77	26·3
R	4·83	3·79	3·25	14·3
S	6·14	3·38	3·44	nil

The authors say, "The loss is greatest in N and O, which is only to be expected, as these contain the greatest amount of combined carbon, a more easily oxidised form than graphite. It diminishes with rising silicon, until in S it is nil." Here is interesting proof that free carbon does not oxidise unless it has first recombined with the iron. Silicon reduces the solubility of carbon, and hence the fact that with increasing silicon content the loss of carbon decreased.

The Carbon Content of the Skin of Decarburised Cast Iron.—In Wüst's research, already referred to, an important feature described is the microstructure of the actual outer edges of several of the "tempered" castings of which he makes particular mention. Fig. 152 illustrates the character of this structure.

This is a phenomenon with which the author is quite familiar, and one he has frequently met with in practice. The explanation which he would give is, however, somewhat different to the German one (see p. 186). It is certainly plausible that if the carbon monoxide preponderates a recarburisation might take place, but the fact is that this outer ring of pearlite is frequently met in annealed castings that have had throughout their heat treatment an oxidising atmosphere.

What, then, is the cause of this layer of pearlite being sandwiched between layers of ferrite? The author would tentatively put forward the following explanation:—

The condition of each region of the section must be studied individually. Now, if we consider the conditions at the highest temperatures, we shall find that the bulk of the centre is extremely high in combined carbon; and on gradually cooling down, the carbon of supersaturation is precipitated, as one would expect in an alloy of that composition. In such compositions the presence of some annealing carbon seems to induce an almost complete precipitation of the carbon, resulting in ferrite and annealing carbon. The extreme outer layer, which is decarburised, in cooling down merely develops the crystalline structure of ferrite, but the intermediate layer, which is the subject of our immediate consideration, is a material just about equivalent to a saturated steel, having lost by diffusion and oxidation most of its carbon. The result is, that it simply behaves like a steel during the cooling down; and as the carbon is not high enough for precipitation to take place, it remains in combination as pearlite. This explanation would, of course, lead one to suppose that the occurrence was to be expected; and, in the author's opinion, it will indeed be found that such a layer of pearlite does generally occur in a greater or lesser degree in all blackheart malleable castings, in which category Wüst's heat-treated irons must be placed.

CHAPTER XIV.

MECHANICAL PROPERTIES OF CAST AND MALLEABLE CAST IRON.

Cast Iron.

Cast iron, generally considered, holds its present important position in the mechanical arts mainly to the ease with which it may be melted and cast into any requisite shape. It may with ease be cast "sound," *i.e.* free from blowholes and shrinkage faults, by skilled workmen in the foundry; and further (and this is very important), it presents a smooth skin and a generally good appearance. Judging from its performance upon the testing machine, its mechanical properties are, however, somewhat indifferent and variable. Its ultimate tensile strength is low; but then it is not usual, except in cylinders and kindred castings, to make parts in such material required to stand tension. In compression the opposite result is to be found, and it is still held to be an excellent material for use where the compressive strain predominates, and hence its adoption for such conditions. In the transverse tests very fair results are obtained, but under impact the results are poor. When tested under either steam or water pressure the material stands well. W. A. Scoble[1] discusses the strength and behaviour of cast iron under combined stress, and his other work[2] is also deserving of attention to students interested in these questions. The whole of the properties of a casting are extremely sensitive to the manner in which the material is produced. It has been shown in other chapters how important are the influences of composition, size of casting, and casting temperature; and it has also been shown how all these influences affect the iron by modifying the condition of the carbon. The material contains normally 3 per cent. to 4 per cent. of carbon, all or none of which may be in the combined state; should it exist in the combined condition, the greater part of the casting consists of the intensely hard carbide of iron, Fe_3C, and the hard white fracture typical of such material results. If the whole of the carbon be present in the free states the material consists mainly of ferrite, and the well-known grey fracture is presented.

The influence of the rate of cooling, and incidentally of the size of section, is admirably illustrated in an experiment described by F. J. Cook.[3] He cast a wedge of comparatively low silicon iron (as shown in fig. 160). The

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[1] *Proceedings of the Physical Society of London*, vol. xx. p.453.

[2] *Ibid.*, vol. xx. p. 533, and vol. xxii. p. 115.

[3] *Jour. Staffordshire Iron and Steel Inst.*, 1909-10.

chemical analysis, apart from the condition of the carbon, showed no variation; and yet, when hardness tests were taken by the drill method, it was found that the numbers recorded varied from 70 at the point to 40 when near the heaviest section. This variation was microscopically proved to be due to the chilling action producing white iron at the extreme point, whereas the heat retained in the thicker portion allowed the breaking down of the carbide to take place. This aspect emphasises the importance of R. Buchanan's remarks to the effect that test bars are not as strong when cast on the casting as when cast separately. He also gives an instance in which there was 20 per cent. variation in transverse strength, and the combined carbon was lowered from 0·49 per cent. in the test bar to 0·101 per cent. in the heaviest part of the casting.

The ultimate Tensile Strength and Elastic Limit considered.—Like all the other tests for cast iron, the maximum stress is determined by the condition of the carbon; and as this particular test is generally considered of first importance, great care should be taken to ensure that the structure of the bar truly represents that of the castings.

The influence of the size of the bar is a feature which merits careful attention, and this will be emphasised by the following results

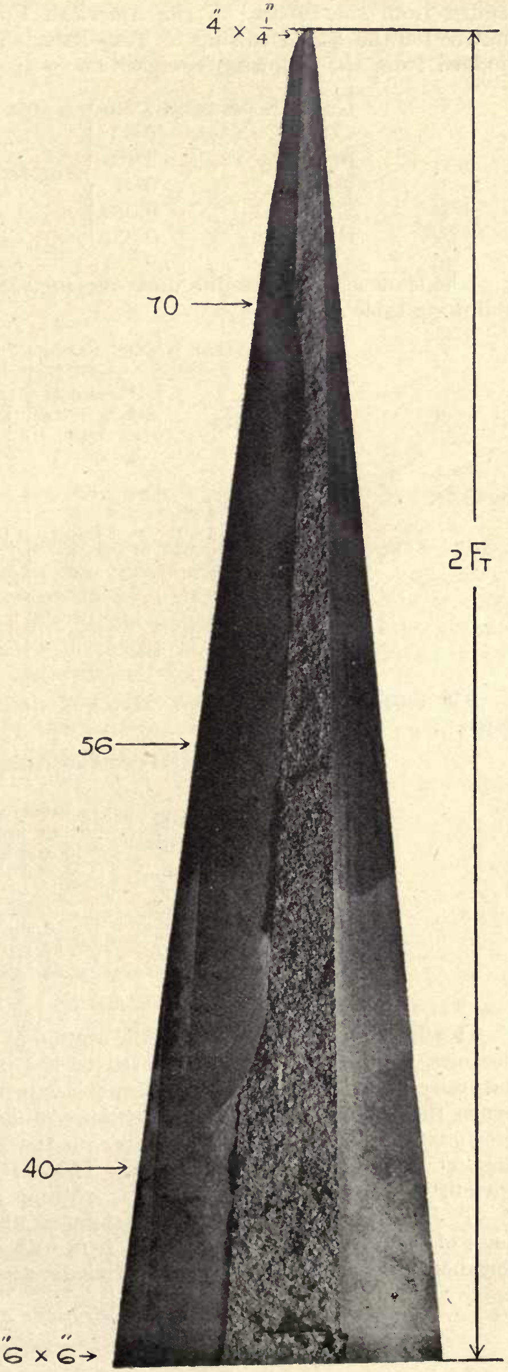

FIG. 160.

culled from the report[1] of the American Foundrymen's Association Committee for the Standardising of Test Bars. The type of iron used will be judged from the following composition:—

Graphite	per cent.	2·99	Analysis of a 1 in. sq. bar.
CC	,,	0·40	
Si	,,	2·49	
Mn	,,	0·47	
S	,,	0·084	
P	,,	0·839	

The transverse test results upon varying sections of bar are given in the following table:—

TRANSVERSE (GREEN SAND, NOT MACHINED).

Section of Bar.	Breaking Strain in lbs. on section.	Deflection.
·49 × ·49	380	·14
1·10 × 1·00	2·400	·14
1·50 × 1·50	5·990	·13
2·04 × 2·03	15·300	·14
2·51 × 2·51	23·970	·11
3·00 × 2 99	41·610	·10
3·52 × 3·51	64·150	·08
4·04 × 4·03	74·170	·08

The tensile results upon the varying sections of bars are given in the next table.

TENSILE TESTS (GREEN SAND BARS, NOT MACHINED).

Approx. section of Bar.	Area of section.	Breaking Strain in lbs. on section.	Max. Stress, tons per sq. in.
0·5″ × 0·5″	0·26	4·830	18·580
1″ × 1″	1·04	17·900	17·000
1·5″ × 1·5″	2·29	34·470	15·050
2″ × 2″	4·04	59·710	14·780

It will be seen that the larger the section of the bar the weaker the iron becomes, and this is to be attributed to the fact that the speed of cooling naturally becomes slower with each increase in the sectional area of the bar; hence the conditions come into existence which favour the more complete precipitation of the carbon, and also at the same time assist in the production of coarser graphitic plates. The strength of the smaller bars is obviously then due to a comparative chilling action.

T. J. Cook has published some figures which are of interest from this point of view. He cast a number of bars with chills of gradually increasing thickness, and the results of his experiments are here given:—

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[1] *Jour. American Foundrymen's Assoc.*, vol. ix.

Iron used.	Analysis.					Thickness of Chill.	Max. Stress, tons per sq. in.
	CC per cent.	Gr per cent.	Si per cent.	Mn per cent.	S per cent.		
Tough	0·23	2·80	1·96	0·50	0·11	0	11·6
,,	,,	,,	,,	,,	,,	⅛″	15·15
,,	,,	,,	,,	,,	,,	¼″	15·6
,,	,,	,,	,,	,,	,,	⅜″	white iron
Engineers mix	0·10	3·16	2·52	0·28	...	0	9·8
,,	,,	,,	,,	,,	...	⅛″	11·2
,,	,,	,,	,,	,,	...	¼″	13·2
,,	,,	,,	,,	,,	...	½″	15·2
No. 3 Foundry Iron	0·09	3·19	3·36	0·23	...	0	8·1
,,	,,	,,	,,	,,	...	⅛″	11·9
,,	,,	,,	,,	,,	...	¼″	12·1
,,	,,	,,	,,	,,	...	⅜″	15·2

The phosphorus contents of the irons were 1·1 per cent., 1·3 per cent., and 1·52 per cent. respectively.

It is of interest to note, when considering the section of test bar most suitable for tensile testing, that Sulzer Bros.,[1] after numerous tests, came to the conclusion that rectangular bars were hardly as good as those of circular section, and in this conclusion the author considers that they have general support. These workers also show that with rapid cooling the strength of the iron becomes greater whilst its resistance to shock diminishes.

Numerous figures have been given from time to time as indicating the maximum tensile stress given by this material, and the figures generally are well summarised by Professor Unwin in the following table :—

Experimenter.	No. of Tests.	Section of Bars. in sq. in.	Tenacity in tons per sq. in.			Probable No. of Fusion.	Condition of test Bars.	
			Highest.	Lowest.	Mean.			
Minard and Desormes .	13	0·23 to 0·5	9·08	5·09	7·19	..	rough	1815. Lowe, *Résistance de la Fonte.*
Hodgkinson and Fairbairn	..	1 to 4	9·76	6·00	7·37	2nd	rough	1837. *Brit. Assoc. Rep.*, vi.
,, ,, ,,	81	3 to 4½	10·5	4·9	6·83	2nd	rough	1849. *Report on App. Iron.*
Woolwich	53	..	15·3	4·2	10·4	2nd & 3rd	?	1856. *Report of* 1858.
Wade	6	..	..	..	13·7*	..	..	1856. *Report on Metal for Cannon.*
,, ...	4	..	..	..	9·1†	..	..	1856. *Report on Metal for Cannon.*
Turner ‡	..	1·0	15·7	4·75	..	2nd	rough	1885. *Jour. of Chem. Soc.*
Rosebank Foundry . .	23	..	18·2	6·5	15·3§	..	..	*Industries*, April 1887.
Unwin	6	0·75	..	..	13·7	2nd	turned	..
,, ...	3	1·0	17·3	14·9	15·7	2nd	turned	..
Wade	..	..	20·5‖	..	..	..	..	..

* Selected as good iron. † Selected as bad iron.
‡ Special series of experimental test bars, with varying proportion of silicon.
§ Mean of ten best specimens. ‖ Highest result obtained.

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[1] *International Assoc. for Testing Materials Report*, 1909.

It is, however, now claimed that consistent tonnages may be obtained in good works practice of over 12 tons to the square inch, and the following table[1] will give a fair idea of what may be expected when using normal foundry mixtures. The complete analyses are given, and it will be noted that the combined carbon is present in sufficient amount to practically constitute a pearlitic matrix.

Analysis.							Diameter of Test Bars at fracture.	Tensile Strength per sq. in.
TC.	GC.	CC.	Si.	S.	P.	Mn.		
per cent.	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.	in.	
3·56	2·98	0·58	1·53	0· 11	1·19	0·90	¾	13·75
3·57	3·04	0·53	1·67	0·106	1·20	0·85	,,	14·88
3·56	3·00	0·56	1·65	0·075	1·20	0·87	,,	15·44
3·58	2·99	0·59	1·88	0·106	1·17	0·80	,,	14·88
3·57	2·98	0·57	2·00	0· 09	1·17	0·81	,,	15·47
3·56	2·98	0·58	1·30	0·077	0·59	0·68	,,	15 62
3·59	3·05	0·54	1·46	0·073	0 84	0·65	,,	14·57
3·56	3·02	0·54	1·72	0·072	0·78	0·66	,,	14·64
3·56	3·00	0·58	1·86	0·076	0·70	0·65	,,	13·74

This series of tests, it will be seen, emphasises the fact that, providing the correct condition of the carbon is obtained, considerable variation in the content of silicon, phosphorus, and manganese is permissible.

Very different opinions have been expressed as to what ratio of combined carbon to graphitic carbon gives the highest tensile. The author, however, is of opinion that the higher the combined carbon, the higher the maximum stress. The actual physical condition of the carbides has a great influence than must not be overlooked, and results have been obtained from perfectly white irons varying from 10 tons to 22·8 tons per square inch. Here and there in this volume will be found figures illustrating the different conditions which are responsible for this variation (see, for instance, p. 37). For works practice it is considered that the best results are obtained from irons containing as much combined carbon as is compatible with the work to be done in the machine shop. Fig. 161 diagrammatically illustrates the varying results likely to be obtained from commercial irons under ordinary works conditions.[2] The two series were of similar analyses, but were produced from different brands of iron. The variations in this instance were attributed to the varying condition of the free carbon.

In a paper recently published,[3] a plea has been made for low carbon and low silicon as a means of raising the strength. The result of such a composition would most likely lead to a high combined carbon content which would, in excess, impair the utility of the iron in the machine shop. The tests given in the paper, although unfortunately not accompanied by analyses, are of interest, and are to be found in the following table. Mixture (1) is stated to be composed of "hot-blast pig iron, cold-blast pig iron, and scrap"; mixture (2) is stated to be composed of "coke hot-blast pig and scrap."

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[1] Adamson, *Jour. Iron and Steel Inst.*, 1909, vol. ii.

[2] F. J. Cook, *Jour. Staff. Iron and Steel Inst.*, 1909–10.

[3] *Scotch Branch*, *British Foundrymen's Assoc.*, Dec. 1910.

	Specimen No.	Tensile Tons per sq. in.	Transverse. (Standard Bar.)		Specific Weight (water).
			Breaking Load, tons.	Deflection, in.	
Mixture No. 1. Tensile strength, average 16·40 tons. Transverse „ „ 1·85 „	1	15·14*	...	...	7·237
	2	18·39	...	...	7·230
	3	...	...	...	7·240
	4	...	...	...	7·225
	5	...	...	...	7·227
	6	...	...	...	7·215
	7	16·26	1·76	0·35	...
	8	17·60	1·89	0·38	...
	9	15·27	1·90	0·40	...
	10	...	1·854	0·437	...
	11	...	1·870	0·468	...
	12	...	1·825	0·406	...
	13	16·34	...	...	...
	14	16·83	...	...	...
	15	16·60	...	...	...
	16	15·86	...	...	...
	17	15·53	...	...	...
Mixture No. 2. Average tensile strength, 15·943.	1	16·10	...	...	7·240
	2	14·36	...	...	7·214
	3	...	...	...	7·303
	4	...	...	...	7·207
	5	...	...	...	7·207
	6	...	...	...	7·198
	7	15·48*	1·24	0·25	...
	8	16·76	1·77	0·40	...
	9	14·93	1·54	0·32	...
	10	16·62	...	...	7·217
	11	17·35	...	...	7·206
	12	...	...	...	7·250
	13	...	...	...	7·221
	14	...	...	...	7·244
	15	...	...	...	7·212

* Unsound.

Tests made by R. H. H. Stanger, Westminster Testing Laboratories.

The elastic limit of cast iron naturally varies with the amount of combined carbon. When all the carbon is in the combined condition, the range of proportionality continues practically up to the point of fracture; this is indeed so even if the matrix consist of pearlite. With irons containing practically the whole of the carbon as graphite, we obtain, however, a weak ferritic matrix, and obviously the elastic limit will be low; it has been stated that such material possesses no elastic limit. Dr Unwin[1] gives an interesting set of figures showing the extensions obtained in bars made from ordinary foundry iron, which is reproduced on p. 205. Such iron, it is to be presumed, would have the greater part of its carbon present as graphite, and no greater percentage of combined carbon than would allow of normal working in the machine shop.

The elastic limit in the cast irons of commerce may safely be assumed to synchronise with the breaking load, there being no readable elongation or reduction of area. C. Frémont,[2] however, states that as a result of 110 static

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[1] *Bull. Soc. d'encouragement Nat. Ind.*, May 1909.

[2] *Ibid.*

bending tests of various cast irons, he found the modulus of elasticity to vary from $\frac{1}{5}$ to $\frac{3}{5}$ of that of steel. The elastic limit, he found, in his bending tests to occur at 0·45 to 0·80 per cent. of the ultimate load. Ira N. Hollis[1] states that cast iron has no well-defined elastic limit and modulus of elasticity,

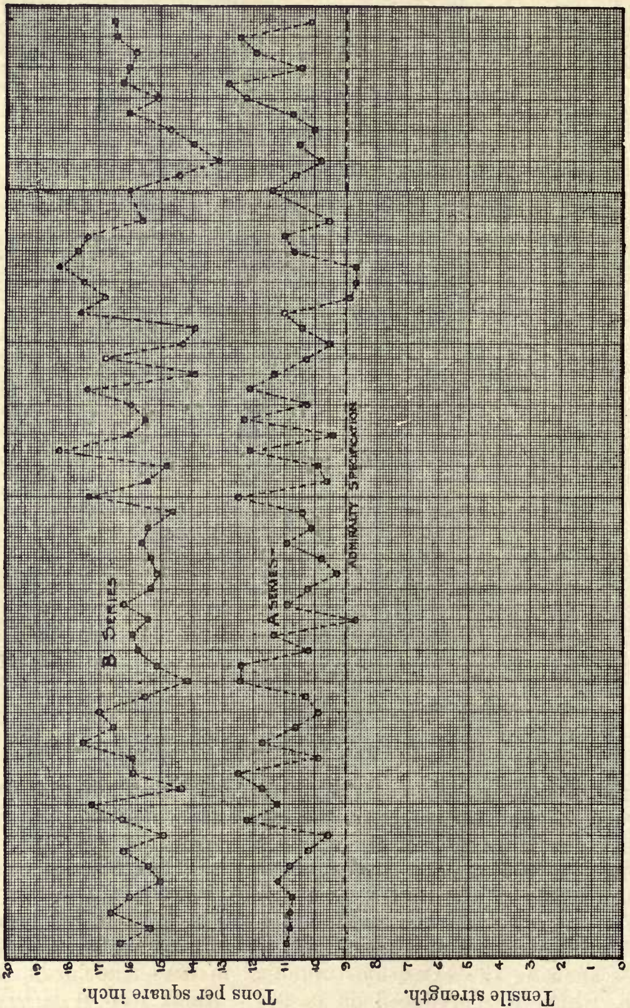

Fig. 161.

and states that a permanent set in cast-iron test bars is noticed when the material is subject to very moderate tensile stress. It is, however, to be regretted that most workers have omitted to state the condition of the carbon in the bars upon which the experiments were performed, and hence the value of the figures obtained is somewhat diminished.

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[1] *American Foundry*, 1910.

Extensions of Cast-Iron Bars.

(Extensions in 8 in., measured by touch micrometer. Bars screwed at ends and fixed in nuts with spherical seatings.)

Load in tons.	Diam. 1·0005	1·005	·999	1·000	·999	·993
	Area ·7862	·7862	·7832	·7854	·7832	·7743
	Extensions in 8 in., in ins.					
2·5	·0043	·0036	·0034	·0037	·0039	·0034
4·5	·0073	·0069	·0062	·0069	·0074	·0061
5·5	·0093	·0087	·0080	·0089	·0096	·0083
6·5	·0114	·0107	·0105	·0112	·0116	·0104
7·5	·0139	·0132	·0134	·0142	·0147	·0131
8·5	·0168	...	...	...	...	..
9·5	·0215	...	...	...	...	...
	Extensions per ton in 8 in., in ins.					
2·5	·00172	·00144	·00136	·00148	·00156	·00136
4·5	·00162	·00153	·00138	·00153	·00165	·00136
5·5	·00169	·00158	·00145	·00162	·00175	·00151
6·5	·00175	·00165	·00162	·00172	·00178	·00160
7·5	·00185	·00176	·00178	·00189	·00196	·00175
8·5	·00196	...	...	...	...	...
9·5	·00226	...	...	...	...	...
Breaking weight in tons per sq. in.	12·94	14·37	13·87	13·04	14·21	13·90

The Transverse Test.—This test is the simplest, and perhaps the one by which cast iron is most generally judged. In this country the size of bar used in the standard test is 2 in. by 1 in. by 40 in. long. The bar is supported upon two knife-edges 36 in. apart, and the pressure is exerted from above by a third knife-edge midway between the other two until the bar breaks. Good, average cast iron should give a breaking load of 26 to 30 cwt., but readings exceeding 40 cwt. are not uncommon. As typical of what may be obtained in practice the following figures[1] are of service:—

TRANSVERSE TESTS.

Analysis.							Transverse, 3 ft. 0 in. Centres.	Deflection.	Moment of Resistance.
TC.	GC.	CC.	Si.	S.	P.	Mn.			
per cent.	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.	cwt.	in.	
3·56	2·98	0·58	1·53	0·110	1·19	0·90	34·75	0·336	20·283
3·56	3·03	0·53	1·65	0·098	1·19	0·85	38·5	0·386	20·430
3·57	3·04	0·53	1·67	0·106	1·20	0·85	36·5	0·329	19·725
3·56	3·00	0·56	1·65	0·075	1·20	0·87	35·0	0·329	19·523
3·58	2·99	0·59	1·88	0·10	1·17	0·80	36·5	0·359	20·796
3·57	2·98	0·57	2·00	0·09	1·17	0·81	30·0	0·314	17·078
3·56	2·98	0·58	1·30	0·077	0·59	0·68	31·5	0·329	19·125
3·59	3·05	0·54	1·46	0·073	0·84	0·65	28·5	0·347	17·569
3·56	3·02	0·54	1·72	0·072	0·78	0·66	29·5	0·350	17·813
3·56	3·00	0·58	1·86	0·072	0·70	0·65	27·5	0·321	16·588

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[1] Adamson, *Jour. Iron and Steel Inst.*, 1909, vol. ii.

The Crushing Strength of Cast Iron.—The behaviour of cast iron under the crushing test is one of its most valuable properties. Dr Arnold considers 40 tons per sq. in. a fair result, but at the same time records such high figures as 60 tons per sq. in. The shape and size of the test piece naturally materially influences the value of the figure obtained. As pointed out by Professor Unwin, the ratio of the diameter to the height of the piece seriously modifies the result, and he cites Hodgkinson's experiments on cylinders $\frac{1}{2}$ in. in diameter.

Height of cylinder	$\frac{1}{8}$.	$\frac{1}{4}$.	$\frac{3}{8}$.	$\frac{1}{2}$.	$\frac{3}{4}$.	$1\frac{1}{2}$.	2.	$3\frac{3}{4}$.
Crushing strength in tons per sq. in.	69·3	63·5	60·0	55·0	53·3	53·3	49·6	34·4

He considers that so long as the height does not exceed three diameters the strength is fairly uniform. He also records the fact that the common form of fracture under this test "is shearing at an oblique plane making an angle of about 56° with the axis."

It must be emphasised that with regard to this test also the condition of the carbon is the determining factor, the compressive strength being greater as the combined carbon increases.

Coe[1] has also shown that, other conditions being equal, a considerable increase in the manganese content will raise the crushing strength, as evinced by the following figures:—

Bar.	Manganese.	Height.	Thickness.	Area.	Breaking Load.
	per cent.	in.	in.		tons per sq. in.
B	1·00	1·25	0·633	0·395	37·34
E	2·65	1·25	0·635	0·398	43·27
F	3·45	1·25	0·638	0·404	46·91

With regard to the relative behaviour of cast iron and steel under compression, the data given by A. Victorin[2] is of interest. He describes experiments made with a view to determining the necessary width of rocker required to carry the load of 800,000 lb. of a disappearing gun carriage. The work was done with two blocks, of which the lower one had a flat surface and the upper one was curved to a radius of 144 in. The steel casting used had a tensile of 75,000 lb. per sq. in. and an elastic limit of 35,000 lb., whilst the cast iron had a tenacity of 30,000 lb., with an elastic limit approximating to the same figure. With a load of 400,000 lb. placed upon a rocker 12 in. wide the elastic compression amounts to ·0047 in. for cast iron and ·0037 for steel. There was no disintegration or permanent set in either case.

Hardness.—The hardness of cast iron is controlled by the condition of the carbon, the maximum hardness being obtained with all the carbon in the combined state. As a matter of fact, however, the exterior of a casting generally contains rather more combined carbon than the interior, owing to the chilling produced by contact with the mould; and this effect is accentuated considerably in low silicon irons. It will thus been seen that the hardness

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[1] *Jour. Iron and Steel Inst.*, 1910, vol. ii.

[2] *Ibid.*, vol. i., 1902, p. 62.

determination made upon the surface of the casting will probably not truly represent the bulk of the material. This fact must not, however, depreciate too unduly the value of this test, as it is the degree of hardness possessed by the material which determines the ease with which it may be machined. When manufacturing chilled iron castings, it is also necessary to have some method of measuring the hardness obtained, and in this field alone it may probably be found that further research will prove productive.

Hardness is a property possessed by metals in varying degree and kind, and the term is hardly possible of definition. The Nomenclature Committee of the Iron and Steel Institute, however, give in their report a concise summary of this property which merits careful attention (see p. 233). Of late several valuable contributions[1] to the literature of the subject have appeared, and this form of test is obviously now being recognised to be of more importance than formerly. The hardness of cast iron is mainly considered from one of two standpoints, — (1) that of the machine shop; (2) the capacity of wearing, *i.e.* abrasive hardness.

The importance of tests which will accurately give an index of these values naturally needs no emphasis.

Professor Turner's recent paper, to which reference has already been made, constitutes an excellent epitome of the work already done in the development of this subject, Turner himself having done a considerable share. Of the methods of determining the hardness now in vogue, those of Turner, Shore, Keep, and Brinell are the most typical.

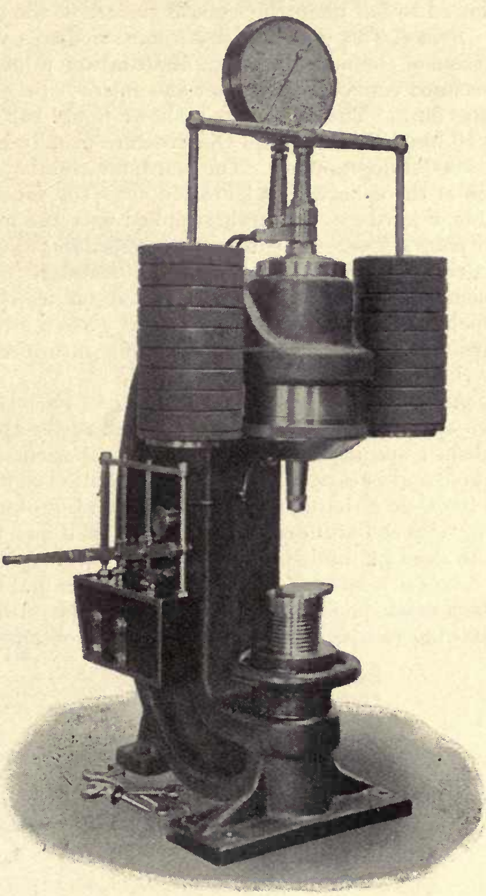

FIG. 162.—Brinell ball test machine.

Turner's Sclerometer.[2]—In this form of test a weighted diamond point is

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[1] Professor Turner, *Jour. Iron and Steel Inst.*, vol. i., 1909. Mather, *British Foundrymen's Assoc. Report*, 1910.

[2] *Birm. Phil. Soc.*, Dec. 1886.

drawn once forward and once backward over the smooth surface of the material upon which the test is being made. It is required to produce a standard scratch, and the weight in grammes required to do this constitutes Turner's hardness number.

Shore's Scleroscope.—In this test the hardness is determined by the height of rebound of a small steel cylinder with a hardened point when allowed to fall upon the smooth surface of the material under test.

Brinell Test.—In this test a hardened steel ball is pressed into the smooth surface of the metal until an indentation is obtained sufficiently large to be measured conveniently under the microscope. This test is perhaps the most important. The apparatus is shown in fig. 162. The steel ball is standardised at 10 mm. diameter, and the pressure usually employed is equal to a weight of 3000 kilogrammes. The hardness number is obtained by dividing the area of the spherical indentation into the pressure and comparing it with a table of hardness numerals supplied with the machine.

Keep's Test.—This test is of considerable value, and is practically a form of drill, the tool of which makes a standard number of revolutions under a constant force. The hardness is automatically recorded on a diagram upon which a perfectly dead soft material gives a straight line, whilst a material as hard as the drill gives a vertical line, intermediate hardness being indicated by the varying angles obtained.

As Turner truly says, each test has its advantages and limitations. His own apparatus is cheap, portable, and easily applied, but can only be used for polished specimens, and even then experience is necessary. Shore's test is simple and is carried out with ease, while the data obtained applies not only to the type of hardness under consideration, but appears to give an index of the "elastic hardness" also. The Brinell and Keep tests are of such a nature as to need no discussion.

Actual readings.—There is very little published data available, but that which exists is quite sufficient to show the utility of the hardness test. The following results[1] indicate the numbers obtainable from the Brinell test:—

Dia. of Ball 10 mm. Pressure 3000 kilos.	Average Hardness No.
Glazed iron	143
No. 1 ,,	104
No. 3 ,,	112
No. 4 foundry	156
No. 4 forge	160
Hard forge	197
White iron	418
Pure Swedish wrought iron	87
Hard face of chilled casting	445
Middle (mottled) of chilled casting	350
Grey back of chilled casting	207

Records of a few tests performed with the Brinell machine and the Shore sclerometer will be found upon p. 209.

A series of grey irons tested by the Shore scleroscope gave the following results[2]:—

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[1] Stead and Jones, *Pro. Cleveland Inst. of Engineers*, 1906–7.

[2] R. Mather, *British Foundrymen's Assoc. Report*, 1901.

Sample No.	Hardness No.	Deflection.	Breaking Load.	Graphite.	Combined Carbon.	Silicon.	Manganese.	Sulphur.	Phosphorus.
		in.	cwt.						
963	38	0·36	31	2·88	0·49	1·77	0·37	0·083	1·26
920	37	0·35	29¾	2·80	0·52	1·82	0·56	0·083	1·16
943	36	0·35	29¼	2·65	0·53	1·96	0·34	0·090	1·25
1114*	36	...	...	2·99	trace	2·70	0·35	0·060	1·6
956	35	0·35	28¼	2·89	0·24	2·64	0·32	0·112	1·6
955	33	0·35	27¼	2·91	0·21	2·55	0·29	0·114	1·6
915	31	0·34	29	3·01	0·15	1·99	0·54	0·075	1·6
897	30	0·37	28½	2·92	0·34	2·15	0·35	0·071	1·6

* This sample was a portion of a casting, and not from a test bar.

As an index of the comparative results obtained by the different methods, the results given by Turner will be found of interest.

Metal.	Turner's Sclerometer.	Shone's Sclerometer.	Brinell's figure divided by 6.	Keep.
Lead	1·0	1·0	1·0	Angles varying from 0° to 90°.
Tin	2·5	3·0	2·5	
Zinc	6·0	7·0	7·5	
Copper (soft)	8·0	8·0	...	
Copper (hard)	...	12·0	12·0	
Softest Iron	15·0	...	14·5	
Mild Steel	21·0	22·0	16 to 24	
Soft Cast Iron	21 to 24	24·0	24·0	
Rail Steel	24·0	27·0	26 to 35	
Hard Cast Iron	36·0	40·0	35·0	
Hard White Iron	72·0	70·0	75·0	
Hardened Steel	...	95·0	93·0	

Impact Testing.—With regard to the behaviour of cast iron under this test, very little work has apparently been done. Although very good results are not likely to be obtained from ordinary cast irons, the author considers that, particularly in connection with heat-treated material, more work might be done with advantage.

Of all the machines designed for impact testing, Izod's is equal to any. It consists of a pendulum of known mass swinging from a known height. At the bottom of the swing the pendulum strikes the notched test piece, which is securely gripped in such a manner that the notch faces the blow. It is essential that the notch be perfectly standardised, so that the tests from a number of specimens may be strictly comparative. This is ensured by means of a suitable gauge. The resistance offered by the specimen to the swing of the pendulum reduces its momentum, and the interesting feature of the machine is that it directly measures the energy dissipated in this manner. Fig. 163 gives an idea of the form of machine.

Malleable Cast Iron.

The mechanical properties of this variety of cast iron are admirably described by the old appellation of "malleable." If such castings are properly made, they are malleable, ductile, and tough. In the early days, before the introduction of scientific control in its manufacture, the product was most unreliable, being frequently either too hard or over-annealed. Thanks to the researches of recent years, the principles underlying the various processes of "softening" are recognised, and it is now not sufficient that the annealed casting be malleable only, but it is also insisted upon by engineers that the usual mechanical tests be complied with. Possibly no more conclusive evidence as to the progress made in this field can be obtained than by examining the results obtained upon the testing machine. Professor Unwin, F.R.S., in his classical work upon the "Testing of Materials of Construction" gives figures (p. 264) which are always in danger of being accepted as typical of this material. They are here reproduced.

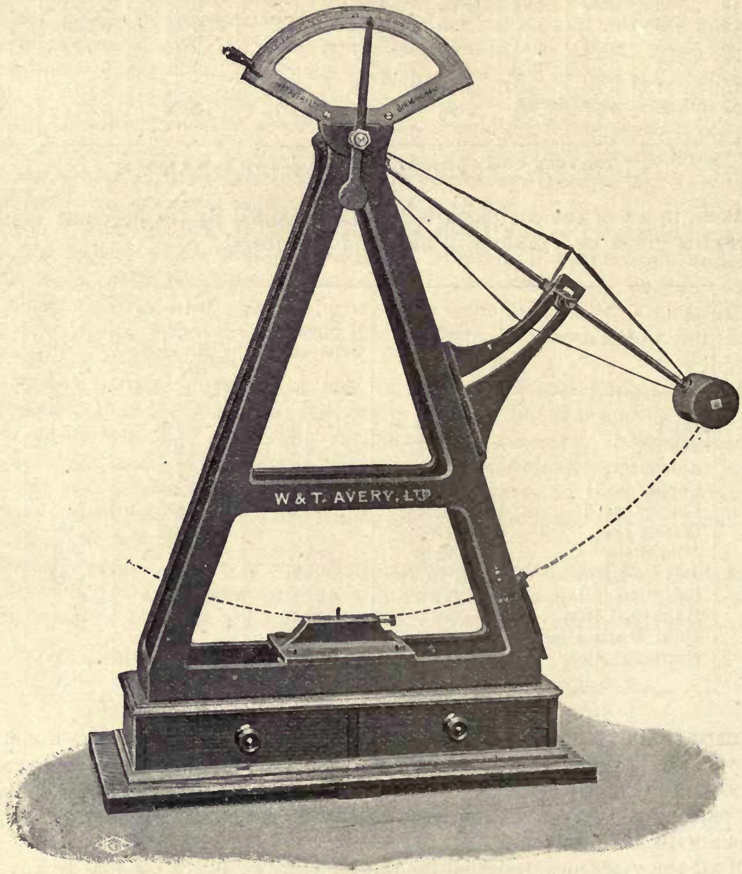

Fig. 163.

TENSILE STRENGTH OF MALLEABLE CAST IRON.

Form of Bars.	Approximate Size.	Mean Elastic Limit in tons per sq. in.	Tenacity in tons per sq. in.			Elongation per cent.	Contraction per cent.
			Highest.	Lowest.	Mean.		
Square . . 1- 8	$\frac{3}{4} \times \frac{3}{4}$	0·45	19·7	16·1	17·8	5·6	6·9
,, . . 11-14	,,	1·01	...	...	14·5	2·0	4·7
Rectangular . 1- 7	$1 \times \frac{3}{8}$	1·33	16·5	14·6	15·3	2·4	6·6
Circular . . 1- 9	$\frac{1}{2}$ diam.	1·02	19·8	16·1	17·4	3·5	10·0
,, . . 1-13	$\frac{3}{4}$,,	·65	18·2	12·8	15·2	1·7	4·3
,, . . 1- 8	$\frac{3}{4}$,,	...	...	...	13·4*	0·8	3·5

* Skin turned off.

It will be seen that the bars made, for instance, to the Admiralty section 1 in. by $\frac{3}{8}$ in. give a tensile strength of 15·3 tons per sq. in., accompanied by an elongation of 2·4 per cent. One would almost be justified in accepting these figures as representing malleable cast iron of a decade ago.

It has been previously pointed out that there are now two distinct types of malleable cast iron, one having its origin in Europe (Réaumur) and the other being of American origin (sometimes known as Blackheart). It is safe to say that it is by the development of the latter type that the best results have been obtained in the mechanical testing laboratories.

European (or Réaumur) Malleable Cast Iron.—With regard to the old European type, an abstract of a paper read before the Scandinavian Society may be of interest. The tensile strength is given as between 40,000 to 50,000 lb. per sq. in., the elongation varying with different samples from 1 to 6 per cent., with a reduction of area at the breaking point of from $\frac{3}{4}$ to 3 per cent. It is then stated that the ordinary grade of cast iron having a tensile strength of 20,000 to 30,000 lb. per sq. in. is but half so strong as malleable cast iron, although its compressive strength is much higher. This statement somewhat represents the results obtained, but it should be pointed out that when the elongation is below 3 per cent., the material is likely to be brittle. A few figures of the tests obtained by the author from this type of malleable cast iron in actual works practice (Meadow Hall Ironworks) may be of interest.

Test No.	Maximum Stress, tons per sq. in.	Elongation per cent. in 2 in.	Reduction of Area per cent.
1	23·0	6	5
2	21·3	4·5	4·5
3	19·97	4·2	5·0
4	23·20	6·5	3·5
5	27·07	3·5	4·0
6	20·93	4·2	5·2
7	25·60	5·0	4·6
8	26·80	4·6	3·6
9	23·72	5·2	4·1
10	21·08	4·7	3·8
11	19·78	3·9	4·7
12	22·42	4·9	6·0

Such material has an elastic limit of from 12 to 15 tons per sq. in., and, as seen by the figures given, has comparatively little elongation. It should, however, be stated that the material is very malleable and tough, and wears well. With regard to bending tests, the angles obtained with the 1 in. by $\frac{3}{8}$ in. bar vary from 45° to 90° over a 1 in. radius.

Special Malleable Cast Iron—(sometimes known as Blackheart, as previously explained, p. 149).—This type is structurally very different from the former kind, and this difference is particularly emphasised by the variation in fractures (see p. 151). The matrix, as revealed by the microscope, consists of ferrite, and from this standpoint the material is in the same category as wrought iron. It will therefore be appreciated that here was a material which careful study might reasonably be expected to improve. The author has spent much time in this field, and has obtained results which may prove of interest. Bending and twisting tests are those chiefly used in the daily process of checking, and such tests enable our people in the works to judge the quality of the product. Fig. 164 will not only show the manner of test usually applied, but will also give some idea of the behaviour of the material. It will be seen that such iron is capable of fulfilling many useful functions. With regard to the figures obtained from tensile tests upon bars 1 in. by $\frac{3}{8}$ in., the selection on p. 213, which represent works practice, will be found useful.

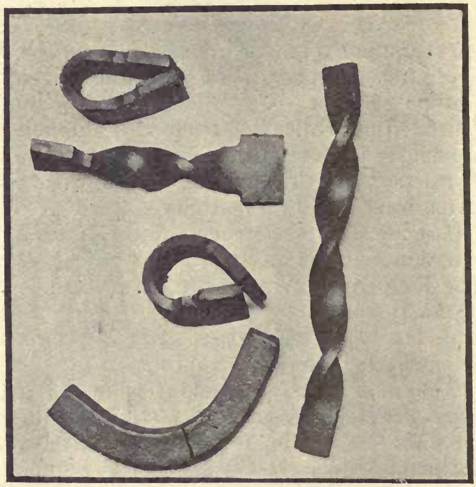

Fig. 164.

The elastic limit of such material will be found to be from 12 to 16 tons per sq. in., whilst the bending angles given by the standard 1 in. by $\frac{3}{8}$ in. section bar will be found to exceed considerably the results obtained from similar bars of Réaumur malleable cast iron. There is little difficulty in exceeding a 90° bend, and with good practice 180° can be obtained over the 1 in. radius.

Test No.	Maximum Stress in tons per sq. in.	Elongation per cent. in 3 in.	Reduction of Area.
1	20·99	10·0	9·1
2	21·67	14·0	10·5
3	22·85	10·0	8·5
4	21·06	11·3	7·9
5	20·70	11·3	12·8
6	21·13	15·3	17·5
7	21·03	10·5	11·5
8	19·97	11·0	7·8
9	21·53	11·5	9·2
10	20·55	10·0	8·3
11	20·10	11·0	7·7
12	19·41	11·0	7·8
13	22·33	10·0	12·5
14	21·60	13·0	11·0

If attempts are made to increase the maximum stress obtained from such iron, the elongation would appear to have to be sacrificed, and to a considerable degree. In illustration of this, the following records are given :—

	Maximum Stress, tons per sq. in.	Elongation per cent. in 2 in.	Reduction of Area per cent.
1	18·9	12	9
2	21·1	13	8
3	24·0	9	8
4	26·5	7	5
5	27·8	5·5	3·5
6	29·0	5·0	4·2
7	34·3	3·0	2·5

The cause of the increase in tonnage is the retention of increasing proportions of combined carbon. This combined carbon stiffens the material and incidentally reduces its ductility.

Torsion Tests.—With regard to the behaviour of malleable cast iron under this test, there is very little published data.

It may be recorded, however, that 1 in. diameter samples submitted by the author's firm were found to undergo no apparent deformation under a stress of 500 lb. at 7 in. leverage (equalling a twisting moment of 3500 in lbs.).

CHAPTER XV.

FURNACES AND SLAGS.

Pig iron is remelted in furnaces which come under (generally speaking) one of the four following types:—

(1) Crucible furnaces,
(2) Cupola furnaces,
(3) Open-hearth (regenerative or reverberatory) furnaces, and
(4) Electric furnaces.

Crucible Melting.—The crucible furnace is perhaps the simplest form, but presents several points worthy of discussion. If iron is melted in a crucible very little oxidation takes place, and the iron may be expected to pour off at very nearly the same composition as the mixture charged. One exception must be pointed out, and that is the percentage of sulphur. It is generally known and appreciated that the sulphur from the fuel contaminates the iron, sometimes to a marked degree. It has been shown in a most interesting paper by Arnold and Knowles[1] that the walls of a crucible in no way exclude the gases of the fire. In an ordinary clay crucible, such as is used in the Sheffield steel-melting industry, they melted Swedish iron of the following composition:—

Combined Carbon	0·04	per cent.
Silicon	0·02	,,
Manganese	0·06	,,
Sulphur	0·01	,,
Phosphorus	0·02	,,
Iron	99·85	,,

Varying weights of aluminium were added to the molten metal, and the ingots thus produced were remelted.

In one instance 12 oz. of aluminium were added to a 25-lb. ingot. The resulting analyses are of interest:—

	CC.	Al.	Si.	Mn.	S.	P.
	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.
First melting	0·06	2·25	0·03	traces	·02	·02
Second melting	1·02	0·20	0·04	traces	·03	·02

It will be seen that the alloy as prepared contained 0·06 per cent. of carbon and 2·25 per cent. of aluminium, whereas after remelting it contained 1·02 per cent. of carbon and only 0·20 per cent. of aluminium, the constitution

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[1] *Jour. Iron and Steel Inst.*, 1897, vol. i.

of the material being thus profoundly modified. How was this change brought about? As the authors state, it could only have been brought about in one way, *i.e.* by the action of the aluminium in reducing the furnace gases passing into the crucible (the lid was sealed on), according to the following equation :—

$$2Al + 3CO = Al_2O_3 + 3C.$$

It will thus be seen that the aluminium as Al_2O_3 passed into the slag lying upon the top of the metal, whilst the liberated carbon, as shown by the analysis, entered the alloy. It may be calculated from these figures, as shown by Arnold and Knowles, how large a volume of gas must have permeated the crucible. It is important to note also, that although the coke used was of the best steel-melting quality, an increase of 0·01 per cent. of sulphur was obtained for each melting. This sulphur passed in with the other gases from the fire. This experiment illustrates one bad feature of crucible melting, and that is, the permeability of the crucible by the furnace gases. Otherwise the process does not materially alter the composition. The small output possible, coupled with the large fuel consumption, however, preclude this method of melting excepting in special cases.

Cupola Melting.—This method is undoubtedly the cheapest for melting iron, and owing to its extensive, and indeed almost its universal use, merits careful discussion. The cupola bears great resemblance, both in design and manner of working, to the blast furnace, but there is one essential difference, viz. that whereas in the latter furnace the coke is responsible for the reduction of the ore, in the cupola its only function is that of fusing the pig iron. The actual calculation of the proportions of the charge is adequately dealt with elsewhere, and it is therefore only proposed now to deal with the metallurgical reactions involved.

The coke is burnt to CO_2, hence the intense local heat of the fusion zone. This CO_2, however, in its upward progress through the overlying charges, becomes converted into carbon monoxide (CO), and in this form makes its exit from the cupola. In this way much useful energy is lost, and unfortunately the intermittent working of the cupola militates against its useful application. Analyses (by volume) of the gases leaving the cupola have recently been published by Bradley Stoughton,[1] and selections are here given as being of particular interest.

	Time elapsed since blowing commenced.	Oxygen per cent.	CO_2 per cent.	CO per cent.	N per cent.
A ×	10 minutes	0·0	13·8	9·9	76·3
	73 ,,	0·0	9·5	16·9	73·6
	173 ,,	0·4	9·2	16·6	73·8
	193 ,,	0·0	6·7	21·7	71·6
	255 ,,	0·1	7·8	22·3	69·8
B ×	45 minutes	0·0	13·0	12·6	74·4
	100 ,,	0·0	13·0	11·2	75·8
	100 ,,	0·0	8·2	20·0	71·8
	230 ,,	0·4	6·0	22·1	71·5
	283 ,,	1·2	5·1	21·2	72·5

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[1] *The Foundry*, Oct. 1907.

It will be seen that all the oxygen is burnt up, and that the gases leaving the cupola consist of nitrogen, together with carbon dioxide and carbon monoxide, the ratio of the latter increasing as the blowing continues. The function of the cupola is to bring down the iron as quickly as possible, but however efficient the melting operation may be, the metal is in direct contact with the fuel and furnace gases. Considerable modification of the composition of the charge takes place.

The chief alterations are a loss of manganese and silicon by oxidation and an increase of sulphur. The carbon contents tend to be lowered, but not materially. The losses of manganese and silicon are usually allowed for in calculating the composition of the charge, whilst the proportion of sulphur absorbed from the coke may be to some extent controlled by a judicious proportion of a suitable flux. The flux is necessary to render fluid the refractory ash from the coke, and the sand from the pig and scrap. A fusible silicate has to be produced that will freely run from the cupola. Just enough flux must be added to combine with the impurities charged: an excess must not be used, otherwise the linings of the cupola will be attacked. The cheapest and possibly one of the most efficient fluxes is limestone.

Limestone as Flux in the Cupola.—Limestone in suitable proportions, judged by the particular nature of the charge, is usually employed. The data recently published by Wüst[1] is of interest. As a rule in normal works practice, even when suitable additions of limestone are made, some additional sulphur is taken up by the metal from the coke. Wüst showed that this need not be so. He discusses the function of limestone, and clearly demonstrates that the absorption of sulphur may be checked. His experiments indicated that for his particular conditions 3·3 per cent. of the weight of the coke in limestone yielded an iron containing ·156 per cent. sulphur, whereas when he increased the limestone to 30 per cent. of the weight of the coke the iron only contained 0·08 per cent. S. It is further of interest to record that further additions of limestone did not cause a further decrease, but were responsible for an increase.

The author would, however, point out that the small percentages of sulphur introduced in cupola melting are, as shown in Chapter IV., of little moment in ordinary foundry practice, and it will be found that the quantity of limestone needed to eliminate sulphur is too large a quantity for works conditions. Just enough should be added to produce a slag of suitable consistency.

When the limestone falls through the length of the cupola, it loses its carbonic acid and becomes lime (CaO), and this lime unites with the silica in its vicinity, thus producing that important constituent of cupola slags known as calcium silicate.

Oxide of Manganese as a Flux in the Cupola.—Several bases have been proposed as possible constituents of the slag with a view to eliminating sulphur. Of these, manganous oxide is of interest; and although the addition has not come widely into vogue, some experiments published by P. Reusch[2] are worth describing. His experiments were made in a small cupola 20 in. dia., and in each case an excess of coke was used, with a view to rendering possible the introduction of the maximum amount of sulphur. Besides vary-

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[1] Wüst, *Stahl und Eisen*, vol. xxiv. pp. 28–32.

[2] *Jour. Iron and Steel Inst.*, 1902, vol. i. p. 560.

ing proportions of limestone, he added in several cases gradually increasing percentages of manganiferous clay slate of the following compositions:—

FeO	4·1 per cent.
MnO	38·48 „
Al_2O_3	3·27 „
CoO	6·71 „
MgO	2·76 „
SO_3	0·99 „

The following table contains the results of his experiments:—

	Pig Iron used.	I.	II.	III.	IV.	V.	VI.
	percent.	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.
Limestone added	...	...	2·0	4·0	2·0	4·0	6·0
Manganiferous ore added	...	...	...	...	1·0	2·0	3·0
Carbon per cent.	3·81	3·58	3·18	3·55	3·44	3·72	3·57
Silicon per cent.	1·93	2·04	2·07	2·09	2·12	1·91	1·88
Manganese per cent.	·92	0·79	0·70	0·75	0·82	0·77	1·02
Phosphorus per cent.	·18	0·22	0·22	0·23	0·23	0·21	0·21
Sulphur per cent.	·006	0·05	0·07	0·06	0·007	trace	traces

These experiments clearly indicate that the addition of manganous oxide will effectively reduce the sulphur content in cupola practice.

Fluor Spar in Cupola Practice.—Fluor spar is a flux which seems to have gained much favour in America, but to have made very little progress in this country. Possibly the reason is not far to seek, and no doubt lies in the fact that limestone, under the conditions we are discussing, is equally efficacious. In the presence of a considerable excess of base such as lime, etc. (as in the basic open-hearth process), it assists in the elimination of sulphur, but, under the conditions prevalent in cupola practice, it acts similarly to limestone. Its action would appear to be one of simply lowering the melting point of the slag by forming, as Swinden points out, a solution of fluoride in the silicates. Roberts-Austen found the fluor spar as CaF_2 unchanged in the slag. In a similar manner to lime, under like conditions, it assists in the elimination of phosphorus, but this aspect of its action is of no service in cupola practice.

Cupola Slags in general.—T. Swinden, in a recent paper,[1] published some important data upon this subject; and in the table following will be found the analyses and descriptions of slags produced in cupola practice under varying conditions.

The slags I. to VI. were produced whilst melting hematite iron of the following composition:—

Combined Carbon	0·50
Graphitic Carbon	3·50
Silicon	2·25
Manganese	0·80
Sulphur	0·035
Phosphorus	0·045

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[1] *British Foundrymen's Assoc.*, Aug. 1910.

In normal working, 1¾ per cent. of the weight of iron was added in limestone. Sample I. was obtained when the slag ran thick, II. when of medium viscosity, and sample III. when it was running thin, the latter state being obtained by increasing the limestone to 3·0 per cent. Slags IV., V., and VI. form a supplementary series, produced when working upon a mixed charge of hematite irons for Bessemer blowing. The coke used during these experiments was Oswaldtwistle, and had the following composition :—

Ash	6·35
Sulphur	1·11
Moisture	1·30
Fixed carbon	91·24

The blast pressure was 14 in. of water.

In Swinden's words, it will be seen upon reference to the table (p. 219) "that as the slag is thinner, so the iron content increases, silica tends to fall, whilst lime also is lower in the sample, in spite of the fact that more limestone is charged. The alumina steadily increases. The explanation would appear to be that in I., either there was insufficient limestone or the temperature was too low for the lime to react and form with alumina and iron oxide a very fluid slag." The thin slag is described as being like black "obsidian" glass in appearance.

The numbers VII. to IX. in the table were produced during the melting of spiegeleisen in an acid-lined cupola. The spiegel used had the following composition :—

Carbon	4·50
Manganese	11·50
Silicon	0·75

The limestone used varied from 2·0 to 3·0 per cent., and it is observed that when the cupola was not working well the slag was "brown, heavy, and inclined to be stony" (see No. VII.). The manganous oxide in this slag will be seen to be 39·06 per cent., which is abnormally high. No. VIII. is the slag produced later with an increase in limestone, and obviously is much improved. Slag IX. was considered ideal, and the metal produced along with it gave a manganese content of 10·0 per cent.

Slags X. and XI. are of interest, as being produced during the melting of similar materials in basic-lined cupola. The flux in this case was limestone with a little fluor spar. Much better results were obtained than in the acid cupola, the content of FeO and CaO in the slag being increased, and the percentage of MnO running much lower. The manganese content of the melted spiegel was also appreciably increased. Here, then, the presence of excess of other bases have saved the manganese in the spiegel.

Slag XII. was obtained during the melting of silico-spiegel with an acid lining, and the increase of silica in the slag is the most noticeable feature.

Swinden has added slag XIII. to the table, as being of special interest. This sample was found, after working, in a basic cupola, and was very infusible. It was bright green and stony in appearance, and fell to powder shortly after the cupola was worked out.

Swinden has studied the value of colour in cupola slags as a guide to their composition, and his observations are of such wide interest as to merit being given somewhat fully :—

Iron oxide (FeO), in the first stages grass green, changing through greyish green to brown, and finally almost to black.

METAL SLAGS.

Sample No.	Melting.	Analysis.							Silicate grade.	Appearance.*	Streak (or colour of powder).
		SiO_2.	Al_2O_3.	FeO.	MnO.	CaO.	CaS.	MgO.			
I.	Thick	50·05	4·68	14·97	2·23	27·42	0·110	0·43	1·90	Hard crystalline stony centre. Glassy exterior. In glassy, dark greenish brown.	Dirty greenish brown.
II.	Medium	44·0	5·01	15·55	3·07	31·92	0·120	0·36	1·49	Slightly spongy on top. Dense, glassy, of brownish green tint.	Light brownish green.
III.	Thin	44·6	5·52	21·51	2·67	24·53	0·110	0·43	1·49	Dense, glassy. Easily splintered. Dark olive green.	Brighter green.
IV.	Thick	54·36	7·32	5·76	7·20	23·60	0·031	0·81	2·17	In transmitted light deep brown. Interior shows bluish green.	Light greyish brown.
V.	Medium	62·50	7·02	12·97	8·37	7·98	0·033	0·89	2·84	Dark olive green in transmitted light. Direct shows mixture dark brown and dark olive green.	Light greenish brown.
VI.	Thin	51·40	8·36	20·84	7·56	11·18	0·030	0·44	2·14	In transmitted light greenish brown. Direct light shows interior rather dark olive green.	Dark greenish brown.
VII.	..	41·00	6·19	1·75	39·06	11·62	0·58	..	1·40	Dark brown, heavy, inclined to be stony, crystalline, of light greenish brown tint. Exterior deep chocolate brown.	Light brown.
VIII.	..	44·60	6·27	2·84	29·46	16·80	0·58	..	1·62	Very much lighter in colour. Very spongy.	Very pale brown.
IX.	..	50·05	10·80	0·62	22·86	15·10	0·414	..	1·80	Light, porous, and almost pure meerschaum colour.	Pure creamy white.
X.	..	33·00	5·85	6·05	16·56	36·45	1·45	0·80	0·94	Heavy stony crystalline. Deep chocolate brown.	Brown.
XI.	..	34·60	5·68	6·23	10·70	38·59	3·25	0·82	0·93	Denser than X. Colour more greyish tint. Surface shows "manganese brown."	Greyish brown.
XII.	..	47·30	10·20	2·54	29·02	9·60	1·45	..	1·66	Very similar to VIII.	Very pale brown.
XIII.	..	23·70	0·04	0·50	32·36	42·32	..	..	0·64	Brilliant green. Stony crystalline until decrepitation.	Bright grass green.

* Samples caught and cooled in iron mould giving sample 3 in. by 2 in. by 2 in.

Manganous oxide (MnO), yellow to brownish green, changing to yellowish brown. When very high, deep brown.

Alumina (Al_2O_3) tends in excess to produce to opalescence, and to keep a slag vitreous.

Lime (CaO), by virtue of its basic nature, tends to give a dull stony colour when very high.

Vanadic oxide is said to produce a bluish slag.

Titanic acid in stony slags gives a peculiar purplish grey, whilst in glassy it may be brown or violet.

Sulphides of manganese and iron behave similarly to the oxides of these metals.

It will perhaps be suggested that the slags are of such a complex nature that colour is discounted. To some extent this may be true, but the author can support Swinden's statements, and considers that the practical man can with profit study the colours of his slags.

Enough has been written to disclose and to emphasise the fact that the ultimate modification of the composition of his molten iron is largely the result of careful or otherwise manipulation of the composition of the slag. Not only is the percentage of sulphur thus affected, but the degree to which the other oxidisable constituents are affected is determined.

Open-hearth Melting.—Open-hearth practice is necessarily upon a much higher plane than cupola practice. The initial cost of the plant, however, together with the fact that the cost both of fuel and labour are higher, limit its application. The most valuable feature of this method is the fact that both the metallic bath and the superimposed slag is possible of complete control, and hence for special work such furnaces are unsurpassed. The regenerative furnace has many advantages over the old reverberatory furnace, chief of which are lower fuel consumption and quicker melting. The reactions, however, are similar in either case. The iron is charged upon the hearth or bottom and melted. During the melting, considerable oxidation takes place, resulting in the production of a slag by a union of the oxide of iron produced from the charge with the sand, and also of a proportion of silicon in the charge, oxidised during the melting operations. Essentially, then, the slag is primarily a silicate of iron, and if left unaltered upon the surface of the molten metal, would so react upon it that in a very short time it would become neutral and protect the charge from further oxidation. McWilliam and the author[1] have indeed shown that under such conditions it may even add to the silicon (and manganese) content of the bath by the action of the carbon contained therein reducing the silicates. Enough has been said to show the value of this type of furnace when the capital expenditure and cost of maintenance are justified.

The Electric Furnace.—The electric furnace has undoubtedly come to stay, and where the cost of power is sufficiently low, it is the furnace *par excellence.* In the open-hearth furnaces, worked either with solid fuel, as in the reverberatory, or with gaseous fuel, as in the regenerative type, there is invariably a more or less oxidising atmosphere in the furnace. In the electric furnace this phase disappears, since, as no air is necessary to burn the fuel, there are no products of combustion to interact with the slag, or if it be uncovered, with the metal. The author therefore looks forward to the successful development of this type of furnace: in such a furnace not only is the temperature controlled, but the material, carefully produced under such conditions, may prove superior to present products.

Scientific Balancing of the Constituents in Slags general.—Much good work has of late been done upon the constitution of slags, and

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[1] *Jour. Iron and Steel Inst.*, 1902, vol. i.

perhaps no subject will be found more profitable to the young student to study than this. As Ledebur originally pointed out, slags must be considered as solutions of variable composition, the solvent being in each case the predominant constituent. For instance, in an acid slag the silicates carry in solution, at the temperatures of the furnace, the bases present. In a basic slag, the bases carry in solution the silicate present.

It is, of course, necessary, before considering the balance of the constituents, first to decide which are the bases and which the acids, the bases and acids through chemical affinity satisfying each other, with the production, in the slags, of either silicates or phosphates as the case may be.

As a rule, the base is the oxide of a metal, *i.e.* oxide of iron, oxide of manganese, oxides of calcium, aluminium, magnesium, sodium, etc.; whilst the acid is the oxide of a non-metal, *i.e.* silicon, sulphur, phosphorus, etc.

TABLE I.

Nature of Slag.	Grade.	Ratio.		Proportion.	Range.	General appearance.	Fusibility.
		Oxygen in acid.	Oxygen in base.				
Basic .	sub-silicate .	1	2	½	0·5 – 0·75	stony . .	Easily fused. Limpid slag.
Neutral	mono-silicate	1	1	1	0·75 1·25	stony; crystalline	Less easily fused.
,,	sesqui-silicate	3	2	1½	1·25 – 1·75	crystalline	Still less easily fused.
,,	bi-silicate .	2	1	2	1·75 – 2·5	glassy . .	Difficult to fuse. Forms viscous mass; draws out into threads.
Acid .	tri-silicate .	3	1	3	2·5 – 3·5	glassy; enamel	Very difficult to fuse.

As before stated, one of the two types present in the small proportion becomes neutralised by chemical affinity, and thus it is that the entire character of the slag is determined. For instance, if the bases are in excess, the slag is capable of taking into its composition more of the acid, *i.e.* a slag containing an excess of CaO or FeO will combine readily with acids such as silica, SO_2, phosphoric acid, P_2O_5, or sulphuric acid, SO_3. Hence this is the type of slag desired in "basic" practice. If acids predominate, as in a highly siliceous slag, the slag absolutely fails to remove either sulphur, silicon, or phosphorus, as it is already saturated with acid oxides. It will thus be seen how important is the careful manipulation of the slags in metallurgical processes.

Some compounds are found in slags which are neither acid or basic, and these, as a rule, will be found to be compounds whose chemical affinity is clearly satisfied, such as the sulphides, fluorides, and chlorides. These substances, however, play a useful part, as, by solution in the slag, they are sometimes found favourably to modify its melting point.

One constituent, however, has been the subject of much discussion, and that is alumina, Al_2O_3. Sometimes this compound takes the rôle of base and sometimes that of acid. In blast-furnace practice it is usual, if the SiO_2 (silica) is high, to treat it as a base, whilst if the silica is low, it is usual to consider it an acid, and the reactions of the blast furnace are, according to the best authorities, found to justify this procedure.

In acid-cupola or open-hearth practice this constituent must therefore be considered as a base, whilst in basic-furnace practice it is safe to count it an acid.

TABLE II.

Silicate grade.	Silica required by one part of				Pure Calcium Carbonate required by one part of		
	MnO.	MgO.	CaO.	FeO.	SiO_2.	TiO_2.	Al_2O_3.
0·5	0·21	0·37	0·27	0·21	6·66	5·00	3·91
0·6	0·26	0·44	0·32	0·25	5·52	4·17	3·24
0·7	0·30	0·52	0·38	0·29	4·73	3·57	2·79
0·8	0·34	0·60	0·43	0·34	4·14	3·12	2·44
0·9	0·39	0·67	0·49	0·38	3·68	2·78	2·17
1·0	0·43	0·74	0·54	0·42	3·33	2·50	1·95
1·1	0·47	0·82	0·60	0·46	3·00	2·27	1·77
1·2	0·54	0·90	0·65	0·50	2·76	2·08	1·60
1·3	0·56	0·97	0·71	0·54	2·57	1·92	1·51
1·4	0·60	1·04	0·76	0·58	2·36	1·78	1·40
1·5	0·64	1·12	0·81	0·62	2·22	1·67	1·30
1·6	0·68	1·20	0·86	0·67	2·07	1·56	1·22
1·7	0·73	1·27	0·92	0·71	1·95	1·47	1·15
1·8	0·77	1·34	0·97	0·76	1·84	1·39	1·08
1·9	1·81	1·42	1·03	0·80	1·74	1·32	1·02
2·0	0·85	1·50	1·08	0·83	1·67	1·25	0·98
2·1	0·90	1·57	1·14	0·87	1·58	1·20	0·93
2·2	0·94	1·64	1·20	0·92	1·51	1·14	0·89
2·3	0·98	1·72	1·25	0·96	1·44	1·09	0·85
2·4	1·03	1·80	1·30	1·00	1·38	1·04	0·81
2·5	1·07	1·87	1·36	1·04	1·32	1·00	0·78
2·6	1·11	1·94	1·42	1·08	1·27	0·96	0·75
2·7	1·15	2·02	1·46	1·12	1·23	0·93	0·72
2·8	1·20	2·10	1·52	1·16	1·18	0·89	0·69
2·9	1·24	2·17	1·57	1·20	1·14	0·86	0·67
3·0	1·28	2·24	1·62	1·24	1·11	0·83	0·65
3·1	1·33	2·32	1·67	1·30	1·07	0·81	0·63
3·2	1·37	2·40	1·72	1·34	1·03	0·78	0·61
3·3	1·41	2·47	1·77	1·38	1·00	0·76	0·59
3·4	1·45	2·54	1·83	1·42	0·97	0·74	0·57
3·5	1·50	2·62	1·88	1·47	0·94	0·72	0·55

Swinden,[1] in the paper to which reference has already been made, carefully discusses the principles underlying scientific control of the slag. As he states, "much work has been done in determining exactly how these acids and bases combine, the temperature of fusion of the resulting compound, and other problems of direct bearing on the practical working of fluxes and slags. The published data of the different groups of acids and bases is, however, too large to consider in detail; moreover, notwithstanding the value of the numerous curves, say, for the lime-silica, magnesia-silica, lime-alumina-silica, and other compounds, the influence of small quantities of, say, iron oxide, manganese oxide, or especially fluor spar, is so profound as to render a direct application of the data rather difficult." It will therefore be seen how complex is the question before us, since, to do justice to it, a whole volume would be necessary. It is therefore proposed to confine the remarks following to main principles on the lines of the paper quoted.

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[1] *British Foundrymen's Assoc.*, 1910.

TABLE III.

Substance.	Factor for Oxygen content.	1 part of substance requires following weight of Silica for			
		Mono-Silicate.	Sesqui-Silicate.	Bi-Silicate.	Tri-Silicate.
CaO	0·285	0·536	0·803	1·07	1·60
$CaCO_3$	0·160	...	...	...	...
MgO	0·400	0·750	1·125	1·50	2·25
$MgCO_3$	0·190	...	...	...	...
Al_2O_3	0·466	0·873	1·310	1·75	2·62
FeO	0·222	0·417	0·625	0·83	1·25
MnO	0·225	0·422	0·633	0·84	1·27
		Calcium Carbonate required.			
SiO_2	0·533	3·33	2·22	1·67	1·11

TABLE IV.

For ascertaining the necessary amounts of Bases to convert given amounts of Silica into Slag.		For ascertaining the necessary amounts of Silica to convert given amounts of Bases into Slag.	
One part by weight of Silica requires	Parts by weight of Bases.	One part by weight of Base requires	Parts by weight of Silica.
For Mono-silicates—		For Mono-silicates—	
Lime	1·86	Lime	0·535
Magnesia	1·33	Magnesia	0·750
Alumina	1·14	Alumina	0·873
Ferrous oxide	2·40	Ferrous oxide	0·416
Manganous oxide	2·36	Manganous oxide	0·422
For Bi-silicates—		For Bi-silicates—	
Lime	0·93	Lime	1·070
Magnesia	0·66	Magnesia	1·500
Alumina	0·57	Alumina	1·747
Ferrous oxide	1·20	Ferrous oxide	0·833
Manganous oxide	1·18	Manganous oxide	0·845
For Sesqui-silicates—		For Sesqui-silicates—	
Lime	1·24	Lime	0·803
Magnesia	0·88	Magnesia	1·125
Alumina	0·76	Alumina	1·310
Ferrous oxide	1·60	Ferrous oxide	0·625
Manganous oxide	1·57	Manganous oxide	0·633

In considering the adjustment of the components of slags, the general method is to compare the oxygen present in the respective acids and bases, as in this way their relative strengths may be judged. The slags are named according to this ratio, and in Table I.,[1] a classification of the siliceous slags is given in this manner, together with statements as to their properties. The last two columns were added as a "rough guide in considering cupola- and blast-furnace slags."

To save time in calculating oxygen equivalents, these tables have been prepared giving equivalent weights of the more common acids and bases required to satisfy each other, and also to form any grade of slag.

Tables II. and III. were compiled by Wiborg.[2] Table IV. by Balling.[3]

The following typical calculation of the silicate grade of slag, cited by Swinden, is here included :—

Composition.	Per cent. Oxygen content.	
SiO_2 . .	54·36 × 0·533 = 28·97	28·97 acid
Al_2O_3 .	7·32 × 0·466 = 3·41	
CaO . .	23·60 × 0·285 = 6·72	
MgO . .	0·81 × 0·400 = 0·32	
MnO .	7·20 × 0·225 = 1·62	
FeO . .	5·76 × 0·222 = 1·28	13·35 basic

$$\text{Silicate Grade} = \frac{28{\cdot}97}{13{\cdot}35} = 2{\cdot}17 \text{ or Bi-silicate.}$$

The process is stated as follows :—

(1) Ascertain the silica required for each base (to form the particular grade of slag).

(2) Multiply by the percentage of the bases in the average ore charge.

(3) Add up the silica values and deduct from the silica already present in the charge.

(4) From tables, convert this excess silica into lime or limestone necessary from fluxing.

Ordinary limestone is safely taken at 80 to 85 per cent. of the active $CaCO_3$. The relation of acids to bases has been considered, but there still remains an all-important consideration from a practical point of view, viz. the most fusible proportion in each class of combination. As has been previously noted, this is a very important subject, but a brief summary may be helpful when considering slags more fully. The following notes are taken from Wiborg's *Metallurgy*, and are the work of R. Åkerman, published in 1886.

Silicates with one base :—

Lime Silicate.—1·5. Three silicates are most fusible. Below one, very difficult to fuse.

Magnesia Silicate.—All extremely difficult to melt.

Alumina Silicate.—Practically infusible.

Iron Oxide (FeO) *Silicate.*—Easily fusible, particularly the more basic silicates. Mono-silicate most fusible.

Iron Oxide (Fe_2O_3) *Silicate.*—Much less fusible than FeO silicates ; only tri-silicate anywhere near fusible.

Manganous Silicate.—Rather less fusible than corresponding FeO silicates, but easily fusible.

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[1] Swinden.

[2] Wiborg, *Jour. Metallurgie*, 1904, p. 470.

Balling, *Compendium der Metallurgischen Chemie*, 1882.

The difference between the two iron oxides, ferrous (FeO) and ferric (Fe_2O_3), is very interesting.

Silicates with several bases:—

Lime-Magnesia Silicates.

Silicate grade:—

1:5—most fusible lime: Magnesia—7:3.

2:0—most fusible lime: Magnesia—7:3, and with this ratio is more fusible than corresponding 1·5 grade.

2:5—ratio 8:2 gives most fusible. This is the most fusible of all lime-magnesia silicates.

3:0—about 12:1 is the most fusible ratio.

Lime-Alumina Silicates.

The tri-silicate is most fusible when Al_2O_3: CaO—1:2. For bi-silicate, best ratio is 1:9, for mono-silicate 1:4, and for sub-silicate 1:2.

Lime-MnO silicates—1 to 2 silicate most fusible proportion is MnO:CaO—4:1; 2·5 grade, ratio—3:2. 3 grade, ratio—2:3. Whence one would expect that the more basic the silicate is the more MnO in proportion to CaO should go in to preserve fusibility. The work of Boudouard (*Jour. Iron and Steel Inst.*, i., 1905) on blast-furnace slags contains a large amount of data fusibilities.

Leaving now the somewhat scientific aspect, and considering the practical application, it will easily be understood why in the case of an acid siliceous gangue a base must be added to form a fusible flux. Since the double silicates are more fusible, we find these very frequently, as, for example, blast-furnace slag, a double silicate of lime and alumina. Cupola slags contain silicates of lime, alumina, ferrous oxide, manganous oxide, etc.

For basic gangues, an acid, silica sand, or siliceous slag may be used for fluxing.

Two main axioms to be remembered in considering slags are:—

(1) There is always a tendency for an acid material to search out and combine with basic, and *vice-versa.*

(2) For every class of combination of a series of acid and basic oxides, there is a certain ratio of one to the other which will produce the most fusible slag.

APPENDICES.

APPENDIX I.

NOMENCLATURE.

It was considered that an index of the more important terms now current in metallurgical literature would prove a valuable addition to this volume. It will be found that, with a few exceptions, the following definitions are those given in the Report[1] of the Nomenclature Committee appointed by the Council of the Iron and Steel Institute.

Ac, Ac 2, Ac 3, etc.—Critical points, points of flexure in the heating curves of iron and steel.

ALLOTRIOMORPHIC. (Ger. *Allotriomorph*, Fr. *Allotriomorphe*—Rosenbusch, 1887.)—A term applied to crystals which have taken their shape from their surroundings.

ALLOTROPY. (Ger. *Allotropie*, Fr. *Allotropie*—Berzelius.)—Is the capacity of an element to exhibit different properties, although its conditions are identical, as regards chemical composition, physical state, and external influences (pressure, temperature, etc.).

"Allotropy is a change of internal energy occurring in an element at a critical temperature unaccompanied by a change of state" (Roberts-Austen).

Professor Howe proposes the following definition: Allotropy is a change in the properties of an element without change of state. It is habitually accompanied by a change of internal energy. It is due in some and perhaps in all cases to a change in the number or in the arrangement of the atoms in the molecule.

ALLOY, METALLIC. (Ger. *Legierung*, Fr. *Alliage métallique.*)—An alloy is a substance possessing the general physical properties of a metal, but consisting of two or more metals or of metals and non-metallic bodies in intimate mixture, solution, or combination with one another, forming, when melted, a homogeneous fluid.

ALPHA IRON. (Ger. *α-Eisen*, Fr. *Fer-alpha*—Osmond.)—A term used by the "Allotropists" to denote the normal condition of pure iron below *A* 2 (750° C.); crystallises in the cubic system.

AMORPHOUS. (Ger. *Amorph*, Fr. *Amorphe.*)—Without structure, in contradistinction to crystalline.

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[1] *Jour. Iron and Steel Inst.*, vol. i., 1902, p. 90.

ANNEAL. (Ger. *Ausglühen*, Fr. *Recuire.*)—This process involves slow and even heating to a selected temperature, then a more or less prolonged period of maintenance at that temperature, followed by a more or less slow and even cooling to atmospheric temperature. Sudden and rapid changes of temperature are opposed to the idea of annealing.

Ar1, Ar2, Ar3, etc.—Critical points. Points of flexure in the cooling curves of iron and steel.

ARBORESCENT. (Ger. *Tannenbaumförmig*, Fr. *Arborescent.*)—Tree-like; a term applied to certain crystallites with the appearance of fir trees, which sometimes occur in drusy cavities in metals or imbedded in solid alloys.

ATOMIC VOLUME. (Ger. *Atomvolumen*, Fr. *Volume atomique.*)—The atomic volume of an element is its atomic weight divided by its specific gravity.

AUSTENITE. (Ger. *Austenit*, Fr. *Austenite*—Osmond.)—According to the Report of the Nomenclature Committee, this is described by Osmond as "a constituent of steel softer and less magnetic than martensite, with which it is often associated. It is produced by quenching small sections of steel containing more than 1·5 per cent. carbon in ice-cold water from a temperature of 1100° C. The structure of such quenched steel is developed by polishing upon parchment moistened with liquorice solution, or nitrate of ammonia, after reheating to 200° C., or by etching with hydrochloric acid in an electric current. The austenite remains white, the martensite becomes brown and appears in a zigzag form. A sewing-needle drawn across the section scratches the austenite more deeply than the martensite."

Such constitutes the official description. The author, however, uses the term austenite in this book in describing the matrix of the material in supersaturated iron-carbon alloys that have with high temperatures become a solid solution of carbide iron containing more carbide than hardenite (0·89 per cent. carbon). It is also used to denote the product obtained by rapidly quenching this solid solution from such temperatures. (See figs. 17 and 18.)

BETA IRON. (Ger. *β-Eisen*, Fr. *Fer-béta*—Osmond.)—According to Osmond, this is an allotropic non-magnetic condition of pure iron, existing at temperatures between *Ar* 2 (750° C.) and *Ar* 3 (860° C.). It is isomorphous with Alpha, crystallising in the cubic system. When Beta iron changes to Alpha iron, heat is evolved and magnetic properties are developed. The term was formerly applied to iron at all temperatures above *Ar* 2.

BLOWHOLES. (Ger. *Blasenhohlräume*, *Blasen*, Fr. *Soufflures.*)—Small cavities, spherical or ellipsoidal, found in ingots, etc., of cast metal. They consist of bubbles of gas which have not been able to escape before the metal became completely solid. Blowholes are of two kinds, (*a*) silvery, (*b*) many-coloured; the former are due to occluded gases given off during solidification, the latter to air entrapped during casting operations.

CARBON. (Ger. *Kohlenstoff*, Fr. *Carbone.*)—This element occurs in the iron carbon alloys in several conditions, and in combination:—

(1) **Graphite.** The free carbon which separates from highly carburised fluid irons during and immediately following the process of solidification (see p. 22).

(2) **Kish.** The free carbon which separates from bulks of molten iron. It is produced by the dissociation of the carbide of supersaturation, which separates during the cooling down of the molten metal to the temperature of solidification.

(3) **Annealing Carbon.** (Ger. *Temperkohle*, Fr. *Carbone de recuit.*)—The apparently amorphous, finely divided carbon, having some graphitic properties, which separates from white cast iron and from certain steels during prolonged annealing, and, according to Ledebur, from high carbon steel, when it is raised to a red heat by rapid hammering.

It is insoluble in dilute acids. Ledebur describes this carbon as temper carbon, the word "temper" having in Germany a different meaning to what it has in England. Annealing carbon is the term that best expresses Ledebur's meaning.

(4) **Temper Carbon.** (See Annealing Carbon.)

(5) **Cementite.** (Ger. *Cementit*, Fr. *Cémentite.*)—This term was first applied by Howe to carbide of iron in the separate state as a constituent of steel. The researches of Abel, Arnold, Müller, Osmond, and others show it to have the formula Fe_3C. The term may be, however, and actually has been, used to embrace all the separate carbides in cast iron, and steel containing manganese, chromium, etc. The free carbides in nearly all commercial metals and steels, as a rule, are not composed of Fe_3C alone, but are admixtures in molecular union with Mn_3C. Cementite may exist in fine granules, thin plates, or in comparatively large masses in steel and pig metal.

According to Osmond, it is the hardest constituent in metal and steel, not colourable by polishing, and etching with dilute nitric acid, iodine solution, hydrochloric acid in alcohol, etc.

Sauveur distinguishes "segregated" and "free" cementite; the former is a constituent of pearlite, while the latter occurs independently. This distinction was noticed by Sorby. As the term "segregated" suggests separation, and as one authority has called free cementite "segregated," it appears advisable to discard the word "segregated" and substitute the term "pearlite-cementite."

(6) **Carbide.** (See Cementite.)

(7) **Hardening Carbon.** (Ger. *Härtungskohlenstoff*, Fr. *Carbone de trempe.*)—The condition of the carbon when it confers hardness to steel, as in steels chilled from above *Ar* 1. It is, like carbide carbon, combined carbon (carbide Fe_3C in solid solution in iron, or, as Arnold suggests, Fe_3C combined with its quota of iron to constitute what he names "subcarbide" ($Fe_{24}C$ approximately).

(8) **Missing Carbon.** (Fr. *Carbone manquant.*)—That part of the carbon in hardened and tempered steels which does not give colour on dissolving the steel in nitric acid 1·20 sp. gr.

CELLULAR. (Ger. *Zellig*, Fr. *Caverneux.*)—Containing irregular spheroidal or ellipsoidal cavities. Applied by Osmond to net-like structure.

CLEAVAGE. (Ger. *Spaltbarkeit*, Fr. *Clivage.*)—As applied to minerals and metals, is the property possessed by crystals of separating along certain planes. These cleavage planes are parallel to one or more of the crystal faces of the system to which the crystal belongs, but have not necessarily any relation to the boundaries of allotriomorphic crystals.

CONCHOIDAL. (Ger. *Muschlig*, Fr. *Conchoïdal.*)—Having the shape of a shell. Applied to the concave and convex fractures of some alloys of zinc-copper, tin-copper, glassy slags, etc.

CONSTITUENTS. (Ger. *Bestandtheile*, *Gefugebestandtheile*, *Gefugebildner*, Fr. *Constituants.*) As applied to metallography, are the structural parts of which alloys and metallic substances are built. Alloys containing only two or more elements may contain three or more constituents.

COOLING CURVE. (Ger. *Abkühlungskurve*, *Kühlungskurve*, Fr. *Courbe de refroidissement.*)—A diagrammatic representation of thermal changes which occur when liquid or solid substances cool from a higher to a lower temperature, and in which time and temperature are co-ordinates. Cooling curves may be represented in several ways: (1) By taking as co-ordinates the temperature T and the time "t" from the commencement of cooling: the curve so obtained will then more or less approximate to a parabolic curve. (2) By taking as co-ordinates the temperature of the metal T and the space of time necessary for cooling down from that temperature through a definite number of degrees: this is expressed by $\frac{dt}{d\mathrm{T}}$. (3) One can choose for co-ordinates the temperature and the difference between the time required for the cooling of the metal under investigation and the time necessary for some other metal (*e.g.* platinum) to cool. These latter may be termed differential cooling curves. (Ger. *Differentialabkühlungskurven.*)

CRITICAL POINTS. (Ger. *Kritischepunkte*, *Haltepunkte*, Fr. *Points critiques.*)—The point or zone at which a physical or chemical change takes place, as when in cooling pure iron and steel from 900° C. an evolution of heat, indicative of a physical change, occurs at the critical points $Ar\,3$ and $Ar\,2$. When the change is not at one fixed point but extends over several degrees, the area of change is called a "zone" or "range."

CRYSTAL, CRYSTALLISED, CRYSTALLINE. A substance having a definite and regular molecular structure is said to be "crystalline." If the structure is shown by the resulting external form of the substance, by its cleavage, by optical means, or by etching processes to be the same in all parallel directions throughout its mass, it is described as a single individual, a crystal. If it varies from part to part of the mass, it is called a "crystalline aggregate," being made up of several individuals. When the individual has developed the proper external form due to its internal structure, it is called an "idiomorphic crystal," but when its external form is the result of its contact with its neighbours, then it is known as an "allotriomorphic crystal." When a body exhibits distinct and well-developed idiomorphic crystals, it is said to be crystallised.

DENDRITIC. (Ger. *Dendritisch*, *Verastelt*, Fr. *Dendritique.*)—Tree-like; a term applied to certain crystallite forms common in many metals and alloys (see Arborescent).

DIFFUSION. (Ger. *Diffusion*, Fr. *Diffusion.*)—The gradual and spontaneous mixing of two substances which are placed in contact.

DUCTILITY. (Ger. *Dehnbarkeit*, Fr. *Ductilité.*)—Ductility is the property of solid bodies, particularly metals, which renders them capable of being permanently extended by drawing, with correlative diminution of their thickness or diameter, but without any actual fracture or separation of parts.

ELASTIC LIMIT. (Ger. *Elasticitätsgrenze*, Fr. *Limite d'élasticité.*)—Is the maximum stress a substance will bear without suffering permanent distortion or set. This is expressed in tons or pounds or kilogrammes per unit area of cross section, usually per sq. in. or per sq. millimetre.

ELASTICITY. (Ger. *Elasticität*, Fr. *Élasticité.*)—The property in virtue of which a body tends to resume its original form or volume when a disturbing force, which has altered this form or volume, ceases to act.

ELASTICITY, MODULUS OF. (Ger. *Elasticitätsmodul*, Fr. *Coefficient d'élasticité.*)—Young's modulus may be defined as the force which, acting in the direction of the length of a bar, when applied to one end of it, the other end fixed, would double the length of the bar, the cross section being of the unit area (say 1 sq. in.). As no substance can thus be doubled in length, the modulus may be defined as 1,000 times the force which would increase the length by the $\frac{1}{1,000}$ part of the whole or 1,000,000 times the force which would increase the length by the $\frac{1}{1,000,000}$ part of the whole. In iron and steel the value of Young's modulus is about 13,000 tons per inch; in other words, a stress of one ton per sq. in. produces an extension which is $\frac{1}{13,000}$ of the original length.

EQUILIBRIUM CURVE. (Ger. *Gleichgewichtskurve*, Fr. *Courbe d'équilibre.*)—This is a curve showing the relation of temperature and composition of a heterogeneous system, in which the phases present are in equilibrium with each other. An *approximation* to such a curve can be obtained by plotting a series of cooling curves, but in order to obtain a true equilibrium curve in this way it would be necessary for the cooling to be infinitely slow. The expression "equilibrium curves" probably dates from some time back, and might therefore be found in the works of Gibbs, van't Hoff, Vander Laar, Ostwald, Le Chatelier, etc. In any case this term is used to denote other curves, *e.g.* temperature-pressure curves in the case of equilibrium between ice, water, and steam.

ETCHING. (Ger. *Aetzen*, Fr. *Attaque chimique.*)—In order to develop the constitutional and crystalline structure of metals and alloys, the polished surfaces are subjected to action by suitable reagents, such as nitric acid, iodine, sulphuric acid, hydrochloric acid, etc. This action is termed etching.

ETCHING FIGURES. (Ger. *Aetzfiguren*, Fr. *Figures de corrosion.*)—According to Baumhauer, figures, generally hollowed-out pits, which are obtained by the suitable etching of crystalline surfaces, of polished surfaces, or of the surfaces of cleft crystals. They have the very closest connection with the orientation of the respective surface of the crystal. On crystallographically equivalent surfaces the figures, both with regard to their form and to their orientation, are uniform, but upon surfaces which differ crystallographically the figures differ. They are an unmistakable means for deciphering the crystalline structure of the body in the case of "crystallised bodies." In amorphous bodies they are not met with. Their size varies (and their form too, in some cases) with the duration of the etching process, and according to the etching medium employed, for which reason it is thought that they cannot in general be identical with the crystal elements which build up the crystal. These etched geometric forms have been divided (Thomas Andrews, *Proc. Roy. Soc.*, 1895, vol. lviii. p. 59; *Jour. Iron and Steel Inst.*, 1895, No. 2, p. 542) into two series, and termed "secondary" and "tertiary crystals," the allotriomorphic crystals having been called "primary." The names refer only to the relative dimensions, and do not suggest sequence of formation.

EUTECTIC. (Ger. *Eutektisch*, Fr. *Eutectique.*)—The term commonly applied to the eutectic alloy, whether in the molten or solidified condition.

EUTECTIC ALLOY. (Ger. *Eutektische legierung*, Fr. *Alliage eutectique.*)—The important points connected with an eutectic alloy are: (1) That it is the most fusible alloy in a given series of alloys or in a certain range of the series. (2) That its composition is constant and independent of the initial composition within certain limits. (3) That its composition is not habitually in simple atomic proportions. (4) That, when solidified, it usually consists of interstratified plates of two or more definite substances, which may be pure metals or definite chemical compounds of different metals or saturated solid solutions. The term was originally defined by Guthrie (*Philos.*, June 1884). See pages 7, 12, 13, etc.

EUTECTIC MIXTURE. (Ger. *Eutektische mischung*, Fr. *Mélange eutectique.*)—An eutectic after solidification and separation into its constituent parts which remain in microjuxtaposition. White iron of eutectic composition constitutes an eutectic mixture. See page 182.

EUTECTIC POINT. (Ger. *Eutektischer punkt*, Fr. *Pointe eutectique.*)—The common point of intersection of two inclined branches, and an approximately horizontal line in the freezing curve (see Points B, figs. 6 and 7, pages 7 and 9). The horizontal line is called the "eutectic line." The temperature corresponding with this line in the freezing point curve is termed the eutectic temperature.

EUTECTIC SOLUTIONS. (Ger. *Eutektische lösungen*, Fr. *Solutions eutectiques*—Suptner.)—Eutectics in the liquid state at or near the point of solidification.

FERRITE. (Ger. *Ferrit*, Fr. *Ferrite.*)—A term first used by Howe for pure iron. It is now commonly used for that condition of iron or steel containing no carbide, or at least not more than traces in solid solution. It covers, therefore, iron which may or may not contain silicon, manganese, nickel, etc., which form solid solutions or isomorphous crystalline mixtures with iron. Ferrite is the softest structure-constituent. The unmistakable characteristic is the occurrence of cuboid etching figures subsequent to treatment with nitric acid or copper ammonium chloride.

FOLIATED. (Ger. *Blättrig*, Fr. *Lamellaire.*)—Composed of thin leaves or layers.

FRACTURE. (Ger. *Bruch*, Fr. *Cassure.*)—The broken surface of a metal or alloy. It may be :—

Conchoidal. Hackly. Rough. Smooth. Splintery.

FREEZING POINT CURVE. (Ger. *Erstarrungspunkts Kurve, Gefrierpunkts Kurve*, Fr. *Courbe de fusibilité.*)—The diagrammatic representation showing the summary of a complete set of cooling curves of a series of alloys consisting of two or more metals or metallic substances, temperature and composition being co-ordinate.

GAMMA IRON. (Ger. *γ-Eisen*, Fr. *Fer-gamma*—Osmond.)—According to Osmond, it is an allotropic non-magnetic condition of iron existing at temperatures above *Ar* 3 (860° C.). It is supposed to crystallise in the cubic system, and its crystalline forms are given as combinations of the cube and octahedron, but more frequently of the octahedron derived from the cube. The evolution of heat at 860° C. (*Ar* 3) is claimed to mark the passage of Gamma iron to Beta iron.

GLASS HARDNESS. (Ger. *Glashärte*, Fr. *Dureté du verre.*)—A loose and unscientific term for the utmost degree of hardness which steel is capable of receiving on quenching above *Ar* 1. As glass is of very varying hardness, the term "flint hardness" is to be preferred.

GLIDING PLANE. (Ger. *Gleitfläche*, Fr. *Plan de clivage.*)—A definite direction in a crystal in which the molecules glide over one another when it is subjected to suitably directed pressure. The subject was investigated by Ewing and Rosenhain (*Proc. Roy. Soc.*, 16th March 1899). A sharp distinction was drawn between deformation by twinning and deformation by translation. (*Phil. Trans.*, vol. cxciii. p. 353; Heyn, *Zeit. Ver. Deutsch. Ing.*, vol. xliv.) If a change of form had occurred due to twin formation, this can be traced by means of etching figures subsequent to polishing the material. This cannot be done, however, in the case of change of form by "slip." The change is then only noticeable if the deformation occurs subsequent to the polishing. It is rendered apparent by the slip-bands. These disappear immediately upon etching, and no further trace is to be seen. The etching figures are not altered in the appearance from the former ones.

GRAIN. (Ger. *Korn*, Fr. *Grain.*)—The grain may or may not be crystalline. It may be rounded or regular-shaped particles, either separate or joined to other grains. Metallurgists commonly use the terms with qualifications to describe the quality of steel such as fine grain, coarse grain, etc. The term really is incorrect, as these grains in steel are actually in the main allotriomorphic crystals.

GRINDING. (Ger. *Schleifen*, Fr. *Adoucir.*)—The process of preparing smooth surfaces by abrasion.

GROUND MASS. (Ger. *Grundmasse*, Fr. *Masse fondamentale.*)—The ground mass of a rock is the semicrystalline or glassy matrix appearing compact to the naked eye in which crystals are imbedded. Similarly in metallography the term may be used for the mass which is in preponderating quantity.

Metallographically, however, this term is generally replaced by the word matrix.

HACKLY. (Ger. *Hackig*, Fr. *Haché.*)—Rough, having fine, short and sharp points on the surface as a hackly fracture, *e.g.* fracture of native metals. Annealed steels give a hackly fracture.

HARDENING. (Ger. *Härten*, Fr. *Trempe.*)—The process of heating steel to above *Ar* 1 and suddenly abstracting the heat as by quenching in water or by any other means (see Quenching).

HARDENITE. (Ger. *Hardenit*, Fr. *Hardenite.*)—This is pearlite that has been heated and quenched so as to give it the maximum degree of hardness. The term is used to denominate the solid solution equal in composition to pearlite, previous to its resolution into the free carbide and ferrite.

HARDNESS. (Ger. *Härte*, Fr. *Dureté.*)—Hardness is understood by Professor T. Turner to be the property whereby a body is enabled to blunt or wear away the edge of a tool used upon it. In this it differs from tenacity, which, though increasing the force necessary to be employed in cutting, does not wear away the edge of the tool.

By hardness is understood the resistance offered by a body to the separation of its particles. The hardness of a mineral is measured by the force required to scratch it with a steel point or pointed fragments of certain standard minerals. The results obtained from one and the same mineral are found to vary slightly with the crystalline face experimented upon, and even with the direction on one and the same face.

Relative hardness may be expressed by reference to the following scale (Mohr):—

1. Talc.
2. Rock Salt.
3. Calcite.
4. Fluor Spar.
5. Apatite.
6. Orthoclase.
7. Quartz.
8. Topaz.
9. Corundum.
10. Diamond.

Behrens uses sharply pointed needles of different hardness to determine relative hardness.

The various methods of determining hardness may be summarised as follows (Martens):—

1. *The hardness of a body is determined by the penetration into it of another body:*—

Method A.—The respective position of both bodies remains unchanged.

(*a*) The pressing-in method. The penetration of the foreign body is effected by means of steady pressure. In this case are measured—

(1) Depth of penetration at even pressure.

(2) Pressure which produces a certain depth of penetration.

(*b*) The driving-in method.—The foreign body is driven in by means of a falling weight. In this case are measured—

(1) The depth of penetration due to an equal force of blow.

(2) The force of the blow which produces a certain depth of penetration.

Method B.—The respective positions of both bodies vary during the operation of testing. (The process of surface scratching.)—(*a*) Determination of the relative hardness by means of scratching with normal substances of various hardness. (Process of determination of mineralogical hardness, according to Mohr and Behrens.)—(*b*) The harder body is pressed against the body to be tested. In this case are measured:—

(1) The pressure which is necessary to plough a way through a certain distance or in a certain time a definite portion of the test body.

(2) The weight of material which is removed from the test body by a definite pressure in a definite time.

(3) The pressure which is necessary to produce on the test body a furrow of a definite width.

(4) The width of the furrow which is produced in the test body by a definite loading of a body used for making the furrow.

2. *The hardness of a body is deduced from the properties of tenacity of the material.*

HEATING CURVE. (Ger. *Erhitzungskurve*, Fr. *Courbe d'échauffement.*)—A diagrammatic representation of thermal changes which occur when solid substances are heated, and in which time and temperature are co-ordinates. (See "Cooling curve" and "Equilibrium curve.")

INTERCRYSTALLINE. (Ger. *Zwischen Krystallen liegend oder verlaufend*, Fr. *Intercristallin.*)—Between crystals applied to the eutectic and other substances in certain alloys surrounding the crystalline grains.

ISOMERIC. (Ger. *Isomer*, Fr. *Isomèrique.*)—All bodies of identical molecular weight were originally termed isomeric, but it is now found convenient (Thorpe) to restrict this term to bodies which not only possess identical molecular weight, but are also of similar chemical type, and possess different physical and chemical properties.

ISOMERISM. According to Professor Howe, is a change in the properties of a compound without change of state or ultimate composition.

It is supposed to be due to change in the number or in the arrangement of the atoms in the molecule. It is to compounds what allotropy is to elements.

ISOMORPHOUS. (Ger. *Isomorph*, Fr. *Isomorphe.*)—A term applied to substances that crystallise in analogous forms. According to Bauerman it is, in the strictly literal sense, only applicable to such substances as are cubic in crystallisation. It is, however, largely used in describing substances which crystallise together to form a homogeneous whole; and even although the two or more constituents do not crystallise in exactly the same form. The term isomorphous mixture is used for such bodies as crystallise together to a homogeneous whole.

JOINT. (Ger. *Fuge*, *Korngrenze*, Fr. *Joint.*)—This has been used to describe the surfaces of junction of crystalline grains.

LAMELLÆ. (Ger. *Plättchen*, *Blättchen*, Fr. *Lamelle.*)—A term used in microscopic petrography for a thin plate. Plates of graphite in grey iron and plates of cementite in pearlite are lamellæ.

LAMELLAR. (Ger. *Blättrig*, Fr. *Lamellaire.*)—Divisible into thin plates.

LAP. (Fr. *Crique.*)—A lap is caused by careless hammering or badly proportioned grooves in rolls, or by careless rolling, or by projections on the ingot. A portion of the iron or steel is folded over on itself; the walls are oxidised and cannot unite. If castings are poured with the metal too sluggish, a similar occurrence is noted, in this case described by the word "cold-lapped."

LIQUATION. (Ger. *Ausseigerung*, Fr. *Liquation.*)—The separation from partially solid metals or alloys of a portion of the mass still fluid. This still fluid portion is generally of the nature of a mother-liquor, and contains in solution considerable quantities of varying impurities, hence the unequal composition of steel ingots and castings due to liquation.

LUSTRE. (Ger. *Glanz*, Fr. *Éclat.*)—A term used in describing the character of the reflections obtained from the fractured surfaces of minerals and rocks.

MACROSCOPIC. (Ger. *Makroskopisch*, Fr. *Macroscopique.*)—A term used in contradistinction to microscopic, to imply that the character in question is visible to the naked eye.

MARTENSITE. (Ger. *Martensit*, Fr. *Martensite*—Osmond.)—According to Osmond, the solid solution of carbon in iron when quenched above the recalescence point which occurs in the neighbourhood of 700° C. (see Hardenite).

MARTENSITIC STRUCTURE. The latticed structure presented by some quenched steels.

MASSIVE. (Ger. *Massig*, Fr. *Massif.*)—A term applied to eruptive rocks in contradistinction to the sedimentary rocks which are stratified. Metallographers have used the term for free cementite as distinguished from that in pearlite. The term does not, however, imply homogeneity.

MATRIX. (Ger. *Grundmasse*, Fr. *Magma.*)—This term appears to embrace the terms mother-substance and eutectic.

MEGASCOPIC. See Macroscopic.

METALLOGRAPHY. (Ger. *Metallographie*, Fr. *Métallographie*—Osmond.)—In the most general sense is a description of the structure of metals and their alloys, but may also be regarded as the science that deals with the composition, structure, and physical properties of metals and alloys, but does not include the art of metallurgy.

METALLURGY. (Ger. *Hüttenkunde*, Fr. *Métallurgie*).—The art of extracting metals from their ores and of adapting them to the various purposes of manufacture.

MIXED CRYSTALS. (Ger. *Mischkrystalle*, Fr. *Cristaux mêlés.*)—A term used for two or more substances which crystallise together into a homogeneous whole. The homogeneous solution of two or more crystallised bodies whilst in the solid state. The term does not refer to a mechanical mixture of different substances, as the name tends to suggest. From the point of view of the phase-doctrine, these form a single phase.

MOTHER-LIQUOR. (Ger. *Mutterlauge*, Fr. *Liqueur-mère.*)—During the process of congelation of any system consisting of several substances in a state of solution, a portion of the solution remains in a fluid state after the separating out of solid crystals. This liquor is termed "mother-liquor." In systems of two constituents with a eutectic point, the composition of this liquor approximates, as congelation proceeds, to that of a eutectic mixture, and quite attains to that composition before the whole mass passes into the solid state.

NATURAL HARDNESS. (Ger. *Naturhärte*, Fr. *Dureté naturelle.*)—The original degree of hardness possessed by steel before quenching about $Ar\,1$.

NON-EUTECTIC CEMENTITE. That part of the cementite which is external to the pearlite in high carbon iron and steel.

ORIENTATION. (Ger. *Orientirung*, Fr. *Orientation.*)—The relative direction of the axes of elasticity in two or more crystals, or the relative position of these axes with regard to a certain surface or line: for instance, the polished surface of a cleavage plane, etc.

OSMOTIC PRESSURE. (Ger. *Osmotischer druck*, Fr. *Pression osmotique.*)—When two liquids are separated by the intervention of a porous diaphragm, a flow of liquid takes place from one side to the other, or sometimes an unequal flow of the two liquids in opposite directions. This phenomenon is termed "osmose," and the pressure exerted by a dissolved substance in its solution is termed its osmotic pressure.

PEARLITE. (Ger. *Perlit*, Fr. *Perlite*, U.S. *Pearlyte.*)—See Carbon.

PEARLY CONSTITUENT. Sorby's name for pearlite.

PHASE. (Ger. *Phase*, Fr. *Phase.*)—In the sense adopted by J. W. Gibbs in his *Physical Chemistry.* It is excellently rendered, and described with apt explanation by Le Chatelier in his memoir, "*La loi de phases,*" *Revue génerale des Sciences*, 10 année, No. 20, 1899, ii., first paragraph; and by Bakhuis Roozeboom in his book, *Die Heterogenen Gleich-Gewichte von Standpunkt der Phasenlehre.* A phase is defined as a mass chemically or physically homogeneous, or as a mass of uniform concentration. The state of a phase is completely determined if the pressure and temperature, together with the chemical potential of its components, be known. The phase rule states that in a system of n components there can exist in equilibrium $n+2$ phase if the system be non-variant; $n+1$ if it be mono-varient, n if it be di-varient, and so on (Stansfield). In physical chemistry, phase is understood to mean the homogeneous particles which occur within a body and are separated by dividing surfaces from the other parts of that body. For example, ice, water, and steam. Examples of phases occurring in steel are ferrite and cementite, while pearlite contains two phases, *i.e.* ferrite, cementite.

PHASE DOCTRINE. (Ger. *Phasenlehre*, Fr. *La doctrine des phases.*)—The doctrine or teaching relating to the phase rule, the expression used by Professor Roozeboom.

PHASE RULE. (Ger. *Phasenregel*, Fr. *Loi des phases.*)—The rule for finding the number of phases that can exist in a system containing a certain number of components, and having a certain number of degrees of freedom. It connects together the number of components, degrees of freedom, and possible phases in equilibrium. (Gibbs.)

PIPE. (Ger. *Lunker*, *Schwindungshohlraum*, Fr. *Retassure.*)—A pipe is a cavity formed in the central upper part of an ingot or casting. It is due to contraction during solidification.

POLISH ATTACK. (Ger. *Reliefpolieren*, Fr. *Polissage en bas-relief*—Osmond.)—When alloys contain two or more constituents of different degrees of hardness, by long-continued friction on a soft polishing surface they are worn away in different degrees, the hardest constituent being least acted upon, the softest the most. The surfaces have the appearance of having been etched.

POLISH ETCHING. (Ger. *Ätzpolieren*, Fr. *Polissage attaque.*)—The process of slightly acting upon polished surfaces of metals by friction on parchment moistened with a solution of nitrate of ammonia, so as to reveal the structure.

POLISHING. (Ger. *Polieren*, Fr. *Polissage*).—The process of preparing a perfectly bright and smooth surface, free from even microscopic scratches.

POLYMORPHISM. (Ger. *Polymorphismus*, Fr. *Polymorphisme.*)—The property possessed by some substances of assuming two or more essentially different crystal forms.

PRISMATIC. (Ger. *Prismatisch säulenförmig*, Fr. *Prismatique.*)—As applied to alloys, a term indicating that the crystals present occur in columnar form, giving lathe-shaped sections.

PSEUDOMORPH. (Ger. *Pseudomorph*, Fr. *Pseudomorphe.*)—The term applied to a mineral possessing a crystalline form other than its own, which it has obtained by the displacement or the alteration of the original mineral.

QUENCHING. (Ger. *Abschrecken*, Fr. *Tremper.*)—Suddenly abstracting heat. The common effect of quenching is to confer hardness, but the term is a wider one than hardening. "Hardening" is to confer relative hardness, usually, but not necessarily, by quenching. Quenching is suddenly abstracting heat, whether the result is hardness or not; *e.g.* manganese steel heated to yellow and immersed in water is quenched, but not hardened.

RECALESCENCE. (Ger. *Recalescenz*, Fr. *Recalescence*—Barrett.)—The term used to express the phenomenon of evolution of internal heat which occurs when iron or steel cools through the critical zones.

RETICULATED. (Ger. *Netzförmig*, *Netzartig*, Fr. *Réticulé.*)—Having the appearance of network; traversed by two sets of parallel lines.

ROKE.—Longitudinal surface-markings occasionally met with in steel bars, rods, and the like.

SATURATED STEEL. (Arnold, 1896.)—Steel consisting of nearly pure iron, containing 0·89 per cent. carbon.

SCLEROMETER. (Ger. *Sklerometer*, Fr. *Scléromètre.*)—An instrument designed to determine the relative hardness of metals.

SCORIÆ. (Ger. *Schlackenartiger körper*, Fr. *Scories.*)—Cinder or slags from metallurgical processes.

SEGREGATION. (Ger. *Ausscheidung*, *Saigerung*, Fr. *Ségrégation.*)—Separation from the main mass, and gathering about centres. The term is used to describe the phenomenon which is observed when masses of metals or alloys are solidified and further cooled.

SHORT, COLD-RED.—Cold-short steel is weak and brittle when cold. Steel is red-short when it is brittle on working at red heat.

SKELETON CRYSTALS. (Ger. *Krystallskelette*, *Gestrickte formen*, Fr. *Cristallite.*)—The incipient forms of crystallisation in which some metals or metallic substances appear in cast metals and alloys.

SLAG INCLUSIONS. (Ger. *Schlackeneinschlüsse*, Fr. *Inclusions de scories.*)—Particles of slag enclosed in a metal.

SLIP BANDS. (Fr. *Stries de clivage*—Ewing and Rosenhain.)—A microscopic appearance in smooth surfaces of metals after straining, caused by slips along the cleavage or gliding planes of the crystalline grains.

SOLID SOLUTION. (Ger. *Feste lösungen*, Fr. *Solutions solides*—van't Hoff.)—A solid solution is a homogeneous mixture of two or more substances in the solid state. In metals no one has yet worked at non-crystalline mixtures, and the solid solution of metals when crystalline are "isomorphous mixtures" or "mixed crystals." (Sir Roberts-Austen.) Professor Howe suggests the following definition: "A solid solution is a solid having the essential properties which characterise liquid solutions as distinct from chemical compounds. These characteristics are twofold: (1) The solution resembles a definite chemical compound in that its components completely lose their identity and become integrated to form a new substance. (2) Solutions differ from definite chemical compounds in that their components are not in definite but in indeterminate proportion, which vary by infinitesimal gradations from specimen to specimen. The variations in composition between definite chemical compounds are *per saltum*, those between solution are *per gradum*. The properties of solutions, both liquid or solid, habitually differ much less from the mean of their components than from the properties of definite chemical compounds."

SOLUTION PLANE. (Ger. *Lösungsfläche*, Fr. *Surface de facile solution.*)—The name proposed by Von Ebner in 1814 for a plane in a crystal along which it is most usually attacked when submitted to chemical action. Such solution planes are commonly observable on acid-etched surfaces of iron.

SORBITE. (Ger. *Sorbit*, Fr. *Sorbite*—Osmond.)—The name given by Osmond to the appearance presented by the solid solution or hardenite during one phase of its translation into laminated pearlite. It might be called "unsegregated pearlite." The microstructure described under this heading is obtained irregularly by cooling sufficiently slow to allow the transformation to proceed sufficiently rapid to produce an imperfect separation of the ferrite and cementite. In practice, these conditions are more or less fulfilled in the cooling in air of small samples, in quenching in cold water towards the end of the recalescence, in quenching in molten lead in certain *doubles tremps*, or in reheating the quenched solid solution or hardenite to a blue colour. On etching the polished steels by the polish etching, or by iodine and dilute acids, is brown in colour.

SPHERULITIC STRUCTURE. (Ger. *Sphärolithische struktur*, Fr. *Structure sphérolitique.*)—Peculiar to vitreous rocks, and in the eutectic of alloys rapidly cooled, and so called because of the small spherular bodies (spherulites) they contain. The latter, viewed under the microscope, are seen to possess a divergent fibrous crystalline structure. This structure is common in rapidly cooled eutectics of lead-tin, antimony-lead, and gold-lead.

SUFFUSION. (Ger. *Ueberschmelzung*, Fr. *Suffusion.*)—A transitory liquid state at temperatures below the normal freezing point.

SULPHIDE AREAS. (Arnold.)—A micro-constituent consisting of sulphide of iron, sulphide of manganese, or a mixture of these. They may be either dove-coloured or a pale brown before etching.

SULPHO FILMS. (Arnold.)—Dark etching films containing sulphur, and probably silicon, enveloping large groups of crystals formed in small steel castings, or in small parts of large castings, and producing great mechanical weakness. These films ball up into minute globules under the influence of efficient annealing.

SUPERSATURATED STEEL. (Arnold, 1896.)—Steel consisting of nearly pure iron containing more than ·89 per cent. carbon. Free cementite is invariably a constituent of such steel.

TEMPER. (Ger. *Kohlungsgrad*, Fr. *Nuance.*)—Used by the steelmaker, it means the mixture suitable for a given purpose—thus, chisel temper, drill temper. It is generally varied by varying the percentage of carbon; hence high, medium, low tempers; sometimes it is designated by numbers, as temper No. 7, suitable for cold chisels, miners' tools, etc. Applied to the steel itself, it indicates the possibilities or potential properties, mainly perhaps in the direction of hardness and resistance to shock. Applied by the steel-user or by the temperer, it means the colour to which the hardened steel has been drawn—straw, brown, blue, etc.; and it is the steel-user's measure of his final modification of the maximum hardness of the particular steel he is treating.

TEMPERING.—The act of partially or wholly undoing what has previously been done by hardening.

TENACITY. (Ger. *Zugfestigkeit*, Fr. *Ténacité.*)—The resistance to rupture presented by a substance whose elastic limit has been exceeded.

TROOSTITE. (Ger. *Troostit*, Fr. *Troostite.*)—This is a name given by Osmond to one of the appearances presented by the solid solution areas during their resolution into pearlite.

TWINNED. (Ger. *Verzwillingt*, *Zwillings bildung*, Fr. *Hémitrope maclé.*)—A crystal is twinned when two portions of the same individual or two different individuals are related to one another according to a definite law.

UNSATURATED STEEL. (Arnold, 1896.)—Steel consisting of nearly pure iron containing less than ·89 per cent. carbon. Free ferrite is invariably a constituent of such steels.

APPENDIX II.

IRONS ON MARKET.

Typical Analyses of Pig Iron, etc.

In compiling the following list of analyses the author has made very liberal use of the figures[1] published in a paper given to the Sheffield Society of Engineers and Metallurgists. It was considered that some such Appendix would serve a useful purpose to students as yet unfamiliar with the irons available for use in works practice.

West Coast Hematites.

	G.C.	CC.	Si.	S.	P.	Mn.	Mn.	Cu.
No. 1	3·750	·300	2·60	·02	·045	trace	0·50	·04
„ 2	3·500	·460	2·40	·03	·045	„	0·50	·04
„ 3	3·250	·540	2·10	·04	·045	„	0·50	·04
„ 4	2·800	1·000	1·65	·10	·045	„	0·50	·04
„ 5	2·400	1·600	1·20	·20	·045	„	0·50	·04
Mottled	1·600	1·950	·90	·25	·045	„	0·20	·04
White	trace	3·250	·65	·30	·045	„	0·10	·04
	From native ores only.						Average actual Mn. and Cu.	
Special	3·75	·300	2·60	·02	·02	0·500		

East Coast Hematites. (“Seaton.”)

	G.C.	CC.	Si.	S.	P.	Mn.	Cu.
No. 1	3·725	·300	2·50	·02	·05	1·00	·05
„ 2	3·525	·450	2·25	·03	·05	1·00	·05
„ 3	3·150	·560	2·00	·04	·05	1·00	·05
„ 4	2·750	1·000	1·50	·10	·05	1·00	·05
„ 5	2·450	1·550	1·00	·20	·05	·75	·05
Mottled	1·500	2·050	·75	·25	·05	·50	·05
White	trace	3·150	·65	·30	·05	·50	·05
Special No. 1	3·525	·300	2·50	·015	·03	1·00	·05
„ 2	3·350	·400	2·25	·020	·03	1·00	·05
3	3·000	·500	2·00	·025	·03	1·00	·05

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[1] Adamson, *Sheffield Society Engineers and Metallurgists*, 1903.

SCOTCH HEMATITES. WELSH HEMATITES.

These are practically of the same composition as the East Coast Hematites.

BESSEMER BASIC. ("CARLTON.")

G.C.	CC.	Si.	S.	P.	Mn.
Traces	2·65	·35 to 1·00	·05	2·850	1·50

	C.	Si.	S.	P.	Mn.
FERRO-MANGANESE,	6·640	·610	·028	·180	80·100
FERRO-SILICON,	1·300	11·000	·040	·060	2·500
Do. (Electro)	·270	28·520	·040	·040	·400
SILICO-SPIEGEL,	1·700	11·000	·040	·049	18·32
Do. (Special)	·690	20·900	·018	·097	55·76
SPIEGEL,	4·500	·900	·030	·070	18·00

Note.—Ferro-Manganese is usually 80·00 Mn.
Ferro-Silicon varies from 8·00 to 16·00 Si.
Silico-Spiegel varies from 10·00 to 14·00 Si and
18·00 to 20·00 Mn.
Spiegel varies from 10·00 to 25·00 Mn.

SCOTCH PIG IRON. ("CARRON.")

	G.C.	CC.	Si.	S.	P.	Mn.
No. 1	3·500	·140	2·800	·035	·880	1·450
„ 2	3·370	·250	2·275	·045	·907	1·450
„ 3 Soft	3·280	·180	2·650	·038	·902	1·400
„ 3 Foundry	3·350	·200	2·150	·055	·907	1·311
„ 3 Close	3·170	·280	1·750	·050	·905	1·420
„ 4	3·160	·290	1·570	·060	·905	1·450

YORKSHIRE IRON. ("CLARENCE.")

	G.C.	CC.	Si.	S.	P.	Mn.
No. 1	3·030	·30	3·170	·03	1·600	·50
„ 3	3·050	·30	2·800	·03	1·570	·60
„ 4 Foundry	2·990	·43	2·240	·06	1·540	·52
„ 4 Forge	2·750	·55	1·850	·10	1·560	·50
Mottled	1·490	1·65	1·270	·18	1·510	·40
White	·100	3·10	·880	·28	1·570	·38

LINCOLNSHIRE IRON. ("REDBOURNE.")

	G.C.	CC.	Si.	S.	P.	Mn.
No. 3 Foundry	3·100	·560	2·751	·038	1·326	1·680
„ 4 „	2·816	·751	2·610	·045	1·318	1·589
Grey Forge	2·525	·895	2·508	·056	1·316	1·456
No. 4 Close	2·459	·945	2·452	·059	1·296	1·344
Mottled	1·480	1·520	1·325	·100	1·296	1·130
White	·675	2·285	·450	·155	1·295	1·100

DERBYSHIRE IRONS. ("RENISHAW.")

	G.C.	CC.	Si.	S.	P.	Mn.
No. 1	3·410	trace	2·939	·036	1·680	·362
„ 2	3·260	1·79	2·146	·034	1·62	·707
„ 3	3·850	·112	2·333	·024	1·581	·572
„ 4 Foundry	3·300	·225	2·099	·053	1·771	·647
Close Forge	2·800	·330	1·819	·079	1·730	·520
Mottled	1·550	1·560	1·200	·200	1·500	·350
White	2·650	·100	·450	·250	1·350	·250
Glazy	3·450	trace	4·500	·070	1·600	·610

NORTHAMPTON AND DISTRICT IRONS. ("HOLWELL.")

	G C.	CC.	Si.	S.	P.	Mn.
No. 1 Foundry	3·350	...	2·612	·022	1·190	·490
„ 2 „	3·650	...	2·473	·036	1·173	·403
„ 3 „	3·850	...	2·379	·041	1·190	·403
„ 4 „	3·350	...	2·333	·047	1·255	·389
„ 4 Forge	2·971	...	2·331	·056	1·088	·484
„ 5 „	1·750	...	1·376	·062	·929	·245
Mottled	1·540	...	1·261	·225	·970	·217
White	·840	...	1·049	·305	·937	·188
Glazy	2·500	...	4·850	·028	1·285	·532

WELSH IRON.

	G.C.	CC.	Si.	S.	P.	Mn.
Grey Forge	3·02	trace	2·56	·05	1·47	·43
Foundry	3·30	„	3·26	trace	1·75	·34

YORKSHIRE COLD BLAST. Ex. Sir J. LOWTHIAN BELL.

	G.C.	CC.	Si.	S.	P.	Mn.
No. 1	3·421	·583	1·708	·073	·630	1·606
„ 2	3·155	·581	1·646	·070	·635	1·472
„ 3	3·361	·393	1·382	·063	·602	1·475
„ 4	3·308	·319	1·381	·081	·602	1·169

STAFFORDSHIRE IRONS (COLD BLAST). ("GLAZEBROOK.")

	G.C.	CC.	Si.	S.	P.	Mn.
No. 1	3·07	...	1·48	·03	·43	·96
„ 2	3·04	...	1·27	·04	·34	·80
„ 3	3·12	...	1·16	·05	·44	·94
„ 4	3·03	...	·83	·04	·31	·27
„ 5	2·81	...	·57	·06	·29	·13

STAFFORDSHIRE IRON (SEMI-COLD BLAST).

	G.C.	CC.	Si.	S.	P.	Mn.
No. 3	3·10	·75	1·50	·03	·25	·50
„ 4	2·92	·81	1·22	·04	·49	·75
„ 5	2·78	·51	·93	·03	·30	·68

Malleable Cast Pig Irons.

West Coast Refined.

	C.	Si.	S.	P.	Mn.
Grey	3·80	1·25	·10	·05	·10
Mottled	3·45	·70–1·00	·10–·25	·05	·10
White	3·20	·60	·30	·05	·10

East Coast Refined. ("S.C.M.")

	C.	Si.	S.	P.	Mn.
Grey	3·80	1·00	·08	·05	·80
Mottled	3·40	·50–·85	·10–·20	·05	·60
White	3·10	·45	·25	·05	·40

Special Malleable Brand "Lorne." (Charcoal Cold Blast.)

	G.C.	CC.	Si.	S.	P.	Mn.
Grey	3·35	·88	·84	·015	·08	·12
White	...	3·35	·25	·055	·112	·09

Foreign Pig Irons.

Swedish Iron.

	G.C.	CC.	Si.	S.	P.	Mn.
Grey	4·080	·027	1·24	·02	·015	·10
White	trace	3·750	·16	·01	·018	·06

American Washed Iron.

G.C.	CC.	Si.	S.	P.	Mn.
Nil.	3·50	Nil.	·015	·01	Nil.

American Charcoal for Malleable Castings.

G.C.	CC.	Si.	S.	P.	Mn.
2·0–4·0	nil–2·0	0·5–1·20	·05	0·20	0·60

American Hematites.

District.	Brand.	G.C.	CC.	Si.	S.	P.	Mn.
Ohio	"Brier Hill"	3·650	·300	1·250	·022	·093	·750
,,	"Girard"	...	...	1·250	·015	·088	·500
				to	to	to	to
				1·750	·040	·100	·800
,,	"Dover"	...	...	1·000		below	
				to			
				2·500	·050	·100	·500
,,	"Seneca"	...	...	1·000	·020	·090	·500
				to	to	to	to
				2·000	·060	·180	·800

Pennsylvania.	Bethlehem Steel Co.	Si.	S.	P.
	Low P. Bessemer.	·750–2·000	·010–·040	·025–·040
	Ordinary ,,	·500–1·500	·020–·050	·750–·900

Pennsylvania.	Carnegie Steel Co.	G.C.	CC.	Si.	S.	P.	Mn.
	Bessemer	3·00	·75	·50	·04	·052	1·20
	Special Bessemer	...	...	1·300	·020	·028	·500

American Basic Irons.

These are very similar to the English Basic.

G.C.	CC.	Si.	S.	P.	Mn.
Traces	2·70	·40 to 1·00	·06	2·800	1·65

American Foundry Iron.

	G.C.	CC.	Si.	S.	P.	Mn.
No. 1 Foundry	3·000	·270	2·750	·031	1·250	·650
,, 2 ,,	2·970	·300	2·500	·021	1·250	·650
,, 3 ,,	2·770	·320	1·750	·026	1·250	·600
,, 4 ,,	2·750	·340	1·400	·032	1·250	·600
,, 1 Soft	3·000	·200	3·250	·022	1·250	·700
,, 2 ,,	3·220	·180	3·000	·025	1·250	·700
Grey Forge	...	·400	1·000	·039	1·250	·400

American Special Foundry Iron. District, Connecticut. Brands "Salisbury" and "Carbonate." Charcoal Cold Blast.

	G.C.	CC.	Si.	S.	P.	Mn.
No. 2	3·900	·080	1·843	·049	·254	·400
,, 3	3·120	·120	1·290	·045	·300	·400
,, 4	2·980	·160	·733	·044	·329	·650
,, 4½	2·320	·900	·676	·035	·225	·120
,, 5	1·850	·900	·368	·042	·290	·160

Example of Grading in the United States.

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