

colour being paler than in the case of the corresponding copper alloys. Until comparatively recently the sovereigns struck in Australia at the Sydney Mint were alloyed with silver instead of copper.

The constitution of the gold-silver alloys has received the attention of many metallurgists, and more particularly Gautier, Roberts-Austen, Rose, Erhards and Schertel, who all agree that the metals are isomorphous and form homogeneous solid solutions throughout the whole series of alloys. The freezing-point curve determined by Roberts-Austen and Rose is shown in fig. 52, and it will be noticed that the lowering of the freezing-point of gold by the addition of silver is very slight until 35 per cent. is reached.

It follows from the constitution of these alloys that they will be uniform in composition, and since 1902 a gold-silver alloy has been used at the Mint for the purpose of assay checks in place of fine gold.

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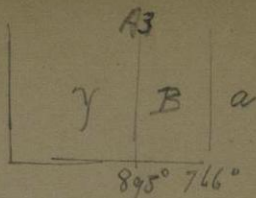
CHAPTER XV.

IRON ALLOYS.

IN attempting to deal with the alloys of iron our attention is naturally directed to steel, and the question arises, Is steel an alloy? Many years ago Matthiessen declared his belief that steel should be considered as an alloy of iron and carbon, and his opinion has been amply confirmed by modern research. But here we are face to face with another difficulty, for the study of steel has received so much attention, and is in itself so vast a subject, that it would be obviously impossible to compress it into a part of a book on alloys. On the other hand, no book professing to deal with the subject of alloys can possibly ignore the alloys of iron. A compromise must therefore be made, and in the following chapter an attempt has been made to deal briefly with the essential facts and to supplement these with a bibliography sufficiently complete to form a reference to the important work dealing with the subject of steel and cast iron.

Iron and Carbon.

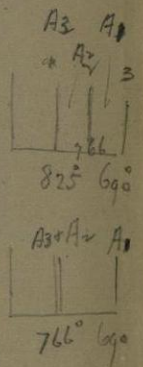
The constitution of the alloys of iron and carbon is somewhat complicated by the fact that iron is capable of existing in at least three allotropic modifications; and it is necessary, before dealing with the alloys, to consider the changes which may take place in the iron itself. Roberts-Austen showed that if a cooling curve is taken of the purest iron obtained by electrodeposition, two remarkable irregularities in the curve, due to an evolution of heat in each case, occur at temperatures of 895° and 766°. He considered that these evolutions of heat were due to allotropic changes in the metal, and this view has been supported by the



fact that there is a profound change in the physical properties of the metal at these temperatures. Osmond first described the three allotropic modifications as Alpha iron, Beta iron, and Gamma iron, and this nomenclature is now universally adopted. Alpha iron (or α -iron) exists at temperatures below 766° , Beta iron (or β -iron) between 766° and 895° , and Gamma iron (or γ -iron) above 895° .

The physical properties which have received the most attention, and which serve to indicate the molecular changes taking place in iron at different temperatures, are, magnetism, dilatation, electrical resistance, and thermoelectric behaviour. These will be referred to later, and it is only necessary to mention here that they fully confirm the existence of three modifications of iron. The crystalline character of the three modifications has also been studied by Osmond, who concludes that they all crystallise in the cubic system, but that while α and β iron both crystallise in cubes and are capable of forming isomorphous mixtures, γ -iron crystallises in octahedra and does not form isomorphous mixtures with β -iron. Osmond observes that if the allotropy of iron were not conclusively proved by other evidence, it would not be revealed by its crystallography.

If, now, a cooling curve is taken of an iron containing, say, 0.2 per cent. of carbon it will be found that the first evolution of heat is very much less than before, and occurs at a much lower temperature, namely, 825° , while a third evolution of heat is noticed at 690° . Further additions of carbon lower the temperature at which the first evolution of heat takes place, until with 0.37 per cent. of carbon the first two evolutions of heat merge into one at 766° , while the third remains constant at 690° . Still further additions of carbon again lower the temperature at which the first evolution of heat occurs; and when 0.9 per cent. of carbon is reached only one evolution of heat is noticed at 690° . These three evolutions of heat have been named by Osmond A_1 , A_2 and A_3 ; A_1 being the change which occurs at 690° and which is also known as the *recalcescence* point; A_2 , the change which occurs between 766° in the case of pure iron and 690° in the case of iron containing 0.9 per cent. of carbon; and A_3 the change which occurs between 895° in pure iron and 766° in iron containing 0.37 per cent. of carbon. The same points are observed on



heating steel as well as during cooling, but they do not occur exactly at the same temperatures; and in order to distinguish the points observed during heating or cooling the letters c (*chauffant*) and r (*refroidissant*) are added; thus the evolutions of heat during cooling are Ar_1 , Ar_2 , and Ar_3 , and the corresponding points during heating are Ac_1 , Ac_2 , and Ac_3 . The influence of carbon upon the molecular changes taking place in steel can best be observed by submitting to a microscopical examination samples of steel which have been heated to various temperatures and suddenly cooled by quenching in water or mercury, in order to fix as far as possible the structure which they possess at the temperature at which they are quenched. Let us consider, for example, a steel containing 0.4 per cent. of carbon. If such a steel is quenched at a temperature above Ar_2 its structure will be found to consist entirely of an acicular constituent, of which Photograph 1, No. 3, represents a typical example, and which is known as **martensite**. The highest powers of the microscope are unable to resolve this material with the needle-like structure into different components, and it is evidently a solid solution of carbon in iron. It is a hard, brittle substance, and is the chief constituent of hardened steels.

If, now, the same steel is quenched from a temperature between Ar_2 and Ar_1 the same constituent will be observed, but in this case it is not the only constituent, but occurs in patches surrounded by a structureless and much softer material which is practically pure iron and is described as **ferrite**. Again, the same steel quenched at a temperature below Ar_1 , or allowed to cool naturally, will be found to possess a different structure. It still contains two constituents, but the martensite has undergone a change. The carbon is no longer dissolved in the iron, but has separated out as carbide of iron, Fe_3C , and has formed with a part of the free iron a constituent possessing the typical structure of a eutectic as shown in photograph 7. This constituent is known as **pearlite**. It is the eutectic of iron and carbide of iron (or **cementite**), and contains 0.85 per cent. of carbon. It is much softer than martensite, and is characteristic of all slowly-cooled steels. Steels containing less than 0.85 per cent. of carbon consist of grains of pearlite embedded in a ground mass of ferrite, and are sometimes described as hypo-eutectic, while those con-

taining more than 0.85 per cent. of carbon consist of massive cementite embedded in a ground mass of pearlite and are known as hyper-eutectic. Hyper-eutectic steels quenched at temperatures above Ar_1 consist of massive cementite embedded in martensite; while in hypo-eutectic steels the quantity of martensite varies and is greater with the higher quenching temperature; from which it will be seen that martensite does not possess a definite composition, but is a solution of variable concentration.

The accompanying diagram (fig. 53), which is due to Mr. Sauveur, shows the composition of a number of steels quenched at different temperatures. The effect of carbon upon iron may be summed up in the following manner. Carbon to the extent of 0.85 per cent. is soluble in γ -iron, and lowers the temperature at which the molecular change from γ to β - and α -iron takes place. It is, however, not soluble in α -iron; and when the molecular change does take place it is accompanied by the separation of carbide of iron in the form of a eutectic.

The complete freezing-point curve of the iron-carbon alloys was plotted by Roozeboom from Roberts-Austen's results, and has been confirmed, with only slight modifications, by Carpenter and Keeling. The curve, which is somewhat complicated, is shown in the accompanying diagram (fig. 54), and in order to make its meaning clear we will follow the changes which occur during the cooling of one or two typical steels. Take first the case of a steel containing 0.2 per cent. of carbon cooling down from a molten condition. The first break in the curve occurs at a point in the line AB when the metal begins to solidify, and a few degrees lower (represented by a point in the line ba) solidification is complete. The mass now consists of a solid solution of carbon in γ -iron (martensite), and no further change occurs until the line GO is reached at about 820° (Ar_3). At this point pure iron in the β -condition separates out, the carbon being concentrated in the remaining martensite. The next point occurs when the line MO is reached at 776° (Ar_2), when the free β -iron changes into α -iron and becomes magnetic. The last change occurs when the line PSK is reached at 690° (Ar_1), at which temperature the martensite breaks down into pearlite.

Although the point Ar_1 has just been described as the last

[To face page 230.]

1.20 per cent.

Carbon, 2.5 per cent.

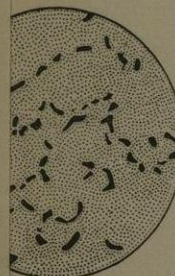


Fig. 13

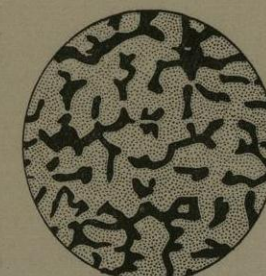


Fig. 15

the γ
martensitic

Martensitic γ
(Cementite .85% softer than Martensitic
 Fe_3C - Carbide of Fe)

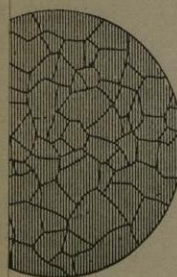


Fig. 14

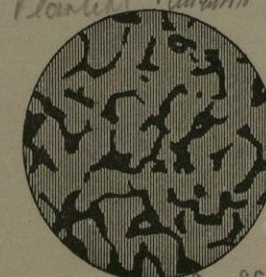
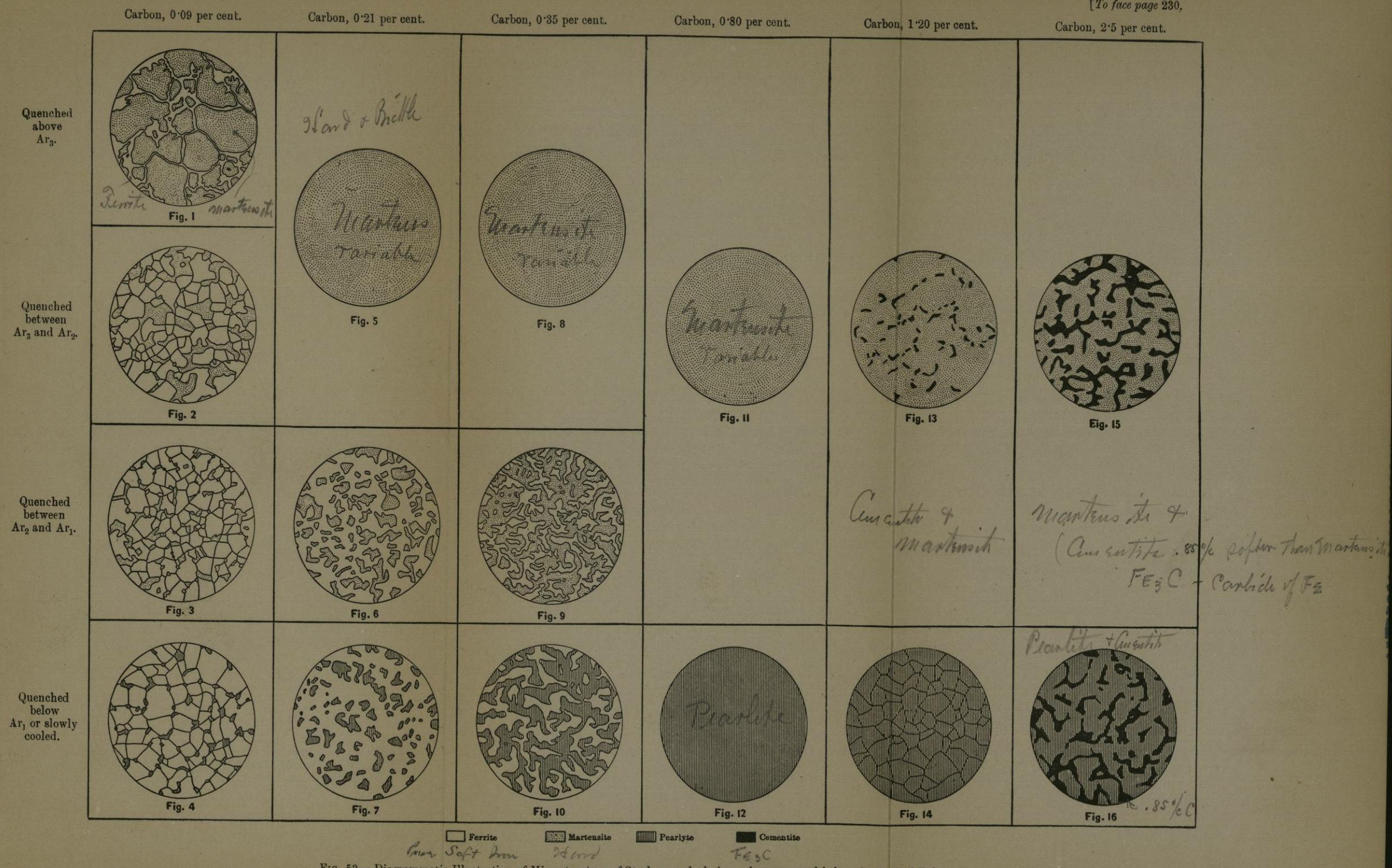


Fig. 16

.85% C



Ferrite
 Martensite
 Pearlite
 Cementite

FIG. 53.—Diagrammatic Illustration of Microstructure of Steel, quenched above, between, and below the Critical Points.

change occurring in a cooling steel, the expression is not strictly accurate, as Roberts-Austen detected, and Carpenter and Keeling

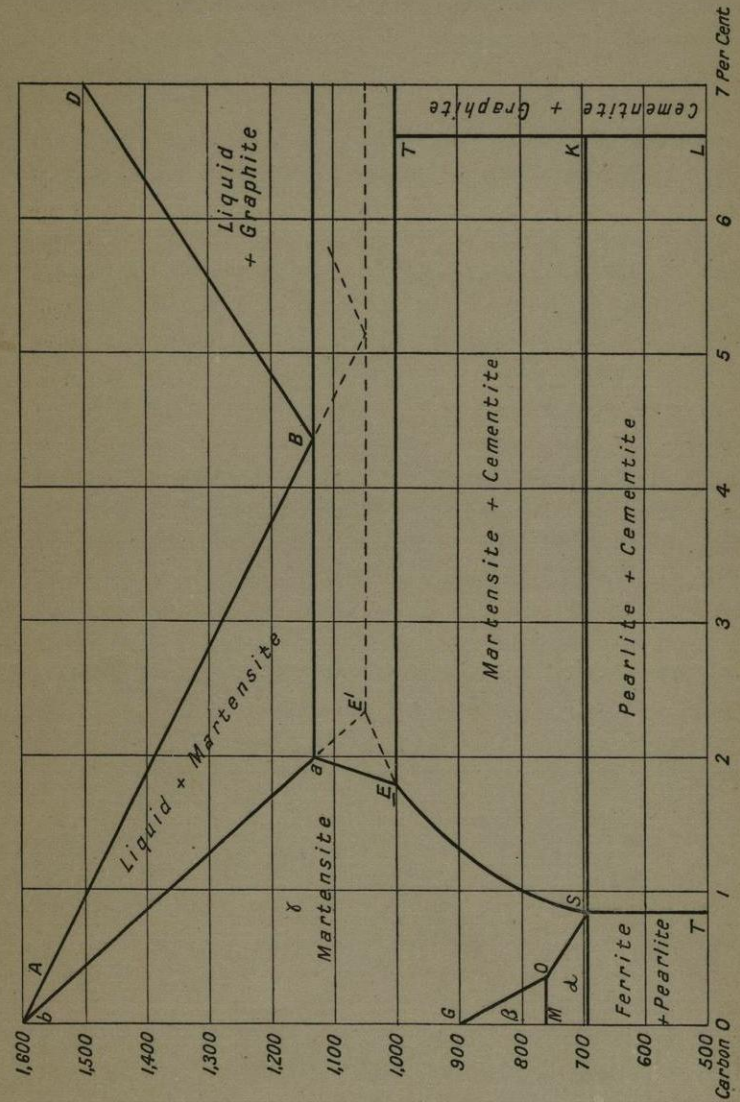


Fig. 54.—Freezing-point Curve of Iron-carbon Alloys.

have confirmed, the existence of a change, shown by an irregularity in the cooling curves of a wide range of alloys, at 600°. This point has been described as Ar₀, but Rosenhain has shown that it

is due to the tube in which the cooling takes place, and is not connected with the steel itself.

The changes occurring in a steel containing 0.5 per cent. of carbon are similar, except that α -iron separates directly from martensite at about 750° without the preliminary separation of β -iron.

The case of a steel containing 1 per cent. of carbon is somewhat different. The solidification of the metal extends over a range of nearly 100°, that is to say, the distance between the points on the lines AB and ba. As before, the solid metal consists of martensite; but when the line SE is reached at a temperature of 850° massive cementite separates out in the martensite. At 690° the martensite breaks down into pearlite, and the result consists of massive cementite embedded in a matrix of pearlite. As a last example, let us consider the case of an alloy containing 3 per cent. of carbon. At 1240° martensite begins to solidify, but as γ -iron is only capable of dissolving about 2 per cent. of carbon to form martensite, it follows that the separation of martensite is accompanied by a concentration of carbon in the mother liquor. This concentration continues until the carbon reaches 4.3 per cent., when the eutectic of martensite and graphite separates. As the temperature falls below 1000° part of the graphite again enters into combination, with the formation of cementite, so that the metal consists of cementite and martensite; and at 690° the martensite breaks down into pearlite, the final result being cementite and pearlite with free carbon or graphite. When more than 4.3 per cent. of carbon is present, graphite is the first constituent to separate out.

The microscopical appearance of the important constituents of steel has already been described; but other constituents, or perhaps it would be more correct to say modifications of these constituents, may be produced by thermal treatment, and they must be briefly described.

Troostite is an intermediate or transitional product which is formed during the transformation of martensite into pearlite, and is found in steels which have been quenched at the critical temperature A_{r1} . It is softer than martensite, and owing to the fact that it can only exist within a very limited range of temperature it is seldom met with. Photograph 42, which

is by Osmond, shows the appearance of troostite under the microscope.

Sorbite is also an intermediate formation between martensite and pearlite, but is more closely related to pearlite. It has been described as "un-segregated pearlite," or pearlite in which the separation of ferrite and cementite is imperfect owing to rapid cooling. Sorbite is found in small samples which have been cooled in air, and in larger samples which have been quenched in water towards the end of the recalescence, or quenched in molten lead. It is also produced by heating martensite to a blue colour. It is hardly possible to define the intermediate formations between martensite and pearlite, as there appears to be a gradual change with no sharply-defined limits through troostite, troosto-sorbite, sorbite, granular pearlite, and lamellar pearlite.

Austenite is found in steels containing more than 1.2 per cent. of carbon which have been quenched from a temperature above 1000° in water cooled to zero, or better, in a freezing mixture. The appearance of austenite is shown in photograph 1, No. 4, the lighter constituent being austenite and the darker martensite. It is softer than martensite, and, owing to the fact that it is only stable at high temperatures, Baron Juptner has suggested that it may be a solution of elementary carbon in iron.

As regards the microscopical methods of detecting the constituents of steel and their distinguishing characteristics, a few words may be useful.

The structure of ordinary steels may be made apparent by etching with nitric acid, but it is difficult with so strong a reagent to regulate the degree of etching. Many years ago Osmond recommended an aqueous extract of liquorice root as an etching reagent used in the following way:—A piece of smooth parchment was moistened with the liquorice extract and a small quantity of precipitated calcium sulphate added. The specimen was then rubbed vigorously upon the moist parchment until the structure was revealed. The calcium sulphate serves the purpose of a polishing powder, and keeps the surface of the steel clean. This is the combined "polish attack," as it is sometimes called. Subsequently Osmond showed that a 2 per cent. solution of ammonium nitrate might be used in place of the liquorice extract, and is more convenient on account of its uniformity. By either

of these methods the various constituents can be distinguished as follows:—

Pearlite by the unequal etching of its constituents.

Sorbite is coloured yellow to dark brown.

Troostite, yellow, brown or blue bands merging into each other.

Martensite shows its characteristic acicular structure.

Ferrite by its crystalline structure.

Cementite and austenite are unaffected.

In order to distinguish martensite from austenite, Osmond connects the sample with the positive pole of a bichromate battery and immerses it in a 10 per cent. solution of ammonium chloride, the negative pole consisting of platinum or iron foil. In this way the martensite is coloured successively yellow, brown and black.

The combined polishing and etching produces very beautiful specimens, and Osmond's photographs, taken some years ago, have never been surpassed, but the method is somewhat tedious where perfect results are not essential, and an etching reagent, consisting of a 5 per cent. solution of picric acid in alcohol, as suggested by Igewski, is now largely used. With this reagent no rubbing is necessary, the specimen merely being immersed in the solution, washed in alcohol, and dried. One of the great advantages of this method is the fact that although extremely rapid there is little risk of obtaining misleading effects by over-etching, as is so often the case with nitric acid. A great many other more or less complex etching agents have been suggested, which it is unnecessary to mention in detail; but an example may be given of a complex reagent which it is claimed by its author, M. Kourbatoff, will colour troostite and troosto-sorbite, leaving other constituents unaffected. This reagent is composed of one part of ethyl alcohol, one part of methyl alcohol, and one part of a 4 per cent. solution of nitric acid in acetic anhydride.

From what has been said of the constituents of steel and their formation, it will be seen that austenite and troostite are very rarely met with, whereas ferrite and pearlite are found in all the classes of steel used for constructional purposes such as bridge work, railway and tram rails, etc. Cementite is found in all high carbon steels, and martensite is characteristic of all steels hardened by quenching, and, as will be seen later, certain steels

which remain hard without quenching. Sorbite is sometimes found in steels which have been quenched after rolling.

So far, only pure iron carbon alloys have been dealt with, but commercial steels invariably contain small quantities of other elements; these have an important influence on the quality of the alloys, and must be considered. The more important of these elements are silicon, sulphur, phosphorus, and manganese.

Silicon forms a solid solution with iron, and appears to go into solution in the form of a silicide FeSi . It is therefore not detected under the microscope. On the other hand, a certain amount of silicon is frequently found in steel in the form of silicate slag. In good steel the quantity of slag is very small, but in inferior steels it is occasionally found in considerable quantities. The ordinary chemical analysis fails to distinguish between silicate and silicide, only the total silicon content being returned, but a microscopical examination reveals the existence of silicates.

Sulphur invariably occurs as manganese sulphide in steel. It is of a pale slate colour, somewhat lighter than manganese silicate. Unlike the silicates, however, it is elongated without being broken during the rolling of the steel, and is found in long threads in rolled steels. Photograph 39 shows both manganese sulphide and iron silicate occurring side by side, and photograph 38 shows a patch of manganese sulphide and manganese silicate occurring together. On treating with dilute acid the manganese sulphide is dissolved out, leaving pits, while the silicate remains unattacked.

Phosphorus forms a solid solution with iron, entering into solution as phosphide of iron, Fe_3P . Phosphide of iron, especially when present in fairly large quantities, frequently segregates, the parts of the steel rich in phosphide being harder and whiter than the rest of the metal. These segregations are apparent during the turning, cutting, or filing of the steel, and are known by the workmen as "ghosts."

Manganese occurs in steel in at least three forms. It combines with all the sulphur present to form manganese sulphide, as already noted. It also occurs, to a certain extent, as manganese silicate, and most probably as manganese silicide. Moreover, it forms with carbide of iron a double carbide which is represented by Carnot and Goutal as $4\text{Fe}_3\text{C}$, Mn_3C , and by Behrens as $\text{Fe}_7\text{Mn}_2\text{C}_3$. Considering the experimental difficulties involved in

the determination of the composition of these carbides, the results agree remarkably well, as is readily seen if the formulæ are brought to the same value in manganese. They then become $\text{Fe}_{24}\text{Mn}_6\text{C}_{10}$, and $\text{Fe}_{21}\text{Mn}_6\text{C}_9$.

In addition to the elements already mentioned several others, such as arsenic, copper, nitrogen, oxygen, and hydrogen, are nearly always found in small quantities in steel. Their influence (in the quantities in which they are usually found in steel) is either less important, as in the case of arsenic and copper, or very imperfectly understood, as in the case of nitrogen and hydrogen, and it is impossible to do more than mention them here.

From the foregoing description of the constituents to be found in an ordinary sample of steel it follows that the microscopical examination should be conducted in three stages. First, the specimen should receive as perfect a polish as possible and be carefully examined in order to determine the quantity and nature of the slag present. Then it should be lightly etched in order to reveal the quantity and condition of the carbide, that is to say, whether it occurs as pearlite, sorbite, etc. Finally, it should be deeply etched to show up its crystalline structure.

Although the series of iron-carbon alloys possess a very wide range of properties, it has been found that they may in many cases be improved by the addition of another element. The resulting alloys are largely used at the present time, and constitute the class of alloys frequently referred to as "special steels." The most important of these alloys are the nickel steels, manganese steels, chrome steels, and tungsten steels, while a number of others, including vanadium, molybdenum, silicon, and aluminium, are also used industrially. More recently quaternary alloys containing two of these elements have attracted considerable attention. The principal characteristics of the more important of these alloys will be briefly considered. It may here be pointed out, however, that in all the steels now used for the purposes of construction the result of adding a third component is the production of a stronger and harder alloy than the simple iron-carbon steel, but without any corresponding increase in brittleness. That is to say, a triple alloy containing 0.3 per cent. of carbon can be obtained as strong as an ordinary steel containing 0.7 per cent., or more,

of carbon, but without the brittleness of the simple iron-carbon steel.

Nickel Steels.

Nickel alloys with iron in all proportions and some of the alloys possess remarkable properties. As regards the effect of nickel upon the molecular changes which occur during the cooling of steel, Osmond has shown that in low carbon steels the changes Ar_3 , Ar_2 , and Ar_1 are successively lowered. With 4 per cent. of nickel, Ar_3 and Ar_2 unite at about 640° , and with 8 per cent. of nickel only one change takes place at about 510° .

In 1889 Hopkinson showed that a nickel steel containing 25 per cent. of nickel was non-magnetic at the ordinary temperature, but when cooled to 0° it became slightly magnetic and at -50° was strongly magnetic. Moreover, on again reaching the ordinary temperature it remained magnetic, and did not lose this property until raised to a temperature of 580° .

Since the communication of these results by Hopkinson the magnetic properties of the alloys have been carefully studied, and the figures obtained by Osmond, showing the temperatures at which magnetism appears during cooling and disappears during heating, are plotted in the form of a curve (fig. 55). It will be seen that the alloys may be divided into two groups, the reversible and the irreversible. Dumas has re-determined the temperatures of transformation with special reference to the alloys lying between the two groups, containing 20 to 30 per cent. of nickel; but the results are somewhat irregular.

Another equally interesting property of the nickel-iron alloys is that of expansion or dilatation. Guillaume has determined the variation of dilatation of the series of alloys, and he finds that the addition of nickel causes a decrease in the dilatation until 35 to 36 per cent. of nickel is reached, after which there is a rapid increase. In some cases the alloys containing about 36 per cent. of nickel show a slight contraction with rise of temperature. It is thus possible to obtain alloys possessing any desired coefficient of expansion from that of iron or nickel down to zero, and this valuable property of the alloys has been made use of in several industries. Formerly platinum was the only metal with a coefficient of expansion sufficiently near that of glass to enable

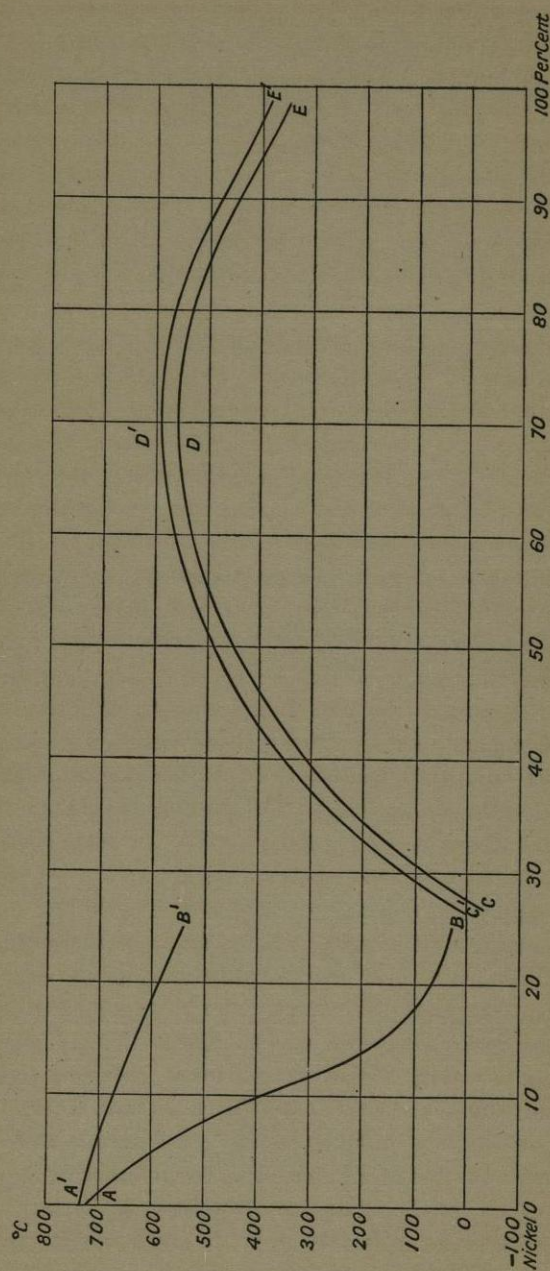


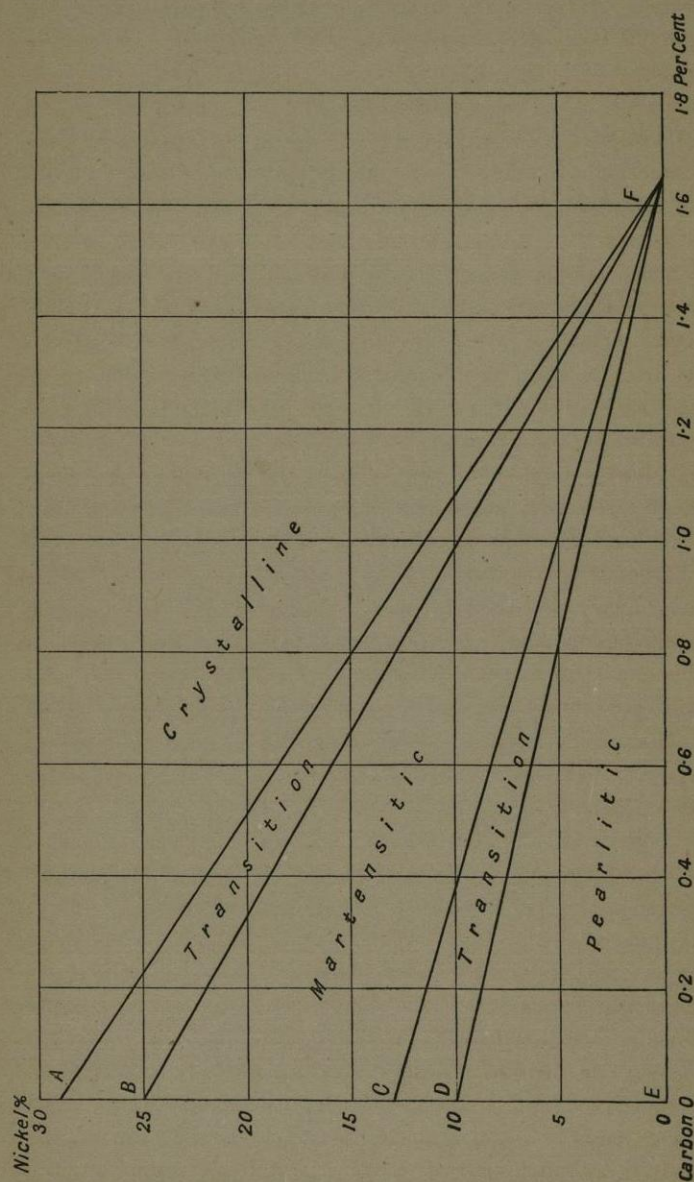
FIG. 55. — Magnetic Transformations of Nickel Steels.

it to be used in the manufacture of incandescent electric lamps without risk of fracture at the base of the lamp where the wire was fused into the glass. Platinum, however, has now been entirely replaced for this purpose by an alloy of nickel and iron containing 46 per cent. of nickel and about 0.15 per cent. of carbon, which Guillaume has named *platinite*. An alloy possessing no coefficient of expansion with rise of temperature is obviously of the greatest importance in the manufacture of watches, clocks, and scientific instruments, as well as standard measures of length, measuring tapes, etc. For this purpose Guillaume has introduced an alloy containing 36 per cent. of nickel and about 0.2 per cent. of carbon under the name of *invar*.¹ Every batch of the alloy is tested, and it is sold in three grades — extra superior, superior, and ordinary with guaranteed maximum coefficients of expansion of .0000008, .0000015, and .0000025 per one degree respectively. The average figure is, however, well within these limits, and a recent test showed a slight contraction equal to -0.00000005 per one degree. In addition to this valuable property invar is much less readily corroded and oxidised than ordinary steel.

Alloys possessing these remarkable properties might be expected to reveal interesting structures when examined microscopically, and such is found to be the case. The alloys may be divided into three groups according to their structure. Those containing less than 8 per cent. of nickel have the same structure as ordinary carbon steels; those containing from 8 to 25 per cent. possess a martensitic structure characteristic of quenched carbon steels; and those containing more than 25 per cent. exhibit a simple crystalline structure characteristic of pure metals and homogeneous solid solutions. These limits are not absolutely defined, as there is no sudden change between the groups, and the change takes place with somewhat lower percentages of nickel if the quantity of carbon is increased. Thus with an alloy containing 0.8 per cent. of carbon the first change occurs when 5 per cent. of nickel is passed; and the second change takes place when 15 per cent. of nickel is reached. Guillet represents the influence of carbon on the structures of the nickel-iron alloys in the form of the diagram here reproduced (fig. 56). The alloys lying within the

¹ Patented 1897, No. 11,695.

triangle DEF have a pearlitic structure, those within the triangle BCF are martensitic, and those above the line AF are crystalline



solid solutions. The triangles ABF and CDF represent transition

FIG. 56.—Constitution of Nickel Steels.

stages between the pearlitic and martensitic, and the martensitic and crystalline respectively.

Knowing the structure of the alloys the mechanical properties might be fairly accurately predicted. Determinations of the mechanical properties have been made by a number of workers, including Hadfield and Dundas, whose work must be referred to for detailed figures. It is only necessary to say here that with the addition of nickel to steel the tensile strength and elastic limit increases regularly with increasing additions during the pearlitic stage. When the martensitic stage makes its appearance the tensile strength and elastic limit rise rapidly, reaching a maximum about the middle of the martensitic stage, and then decrease rapidly until the crystalline stage is reached, when the variations are small and regular. The rapid rise in the tensile strength in the martensitic steels is accompanied by a corresponding fall in the elongation and contraction.

The pearlitic steels are stronger than the corresponding carbon steels, though the increase is not very great. They are very little harder, but their resistance to shock is considerable.

The martensitic steels are very much stronger and harder than ordinary steels of the same carbon content. They show a high elastic limit, and their resistance to shock is moderate.

The crystalline steels possess the usual properties of pure metals and homogeneous solutions with similar structures. They are not particularly hard, and have no great degree of strength. They are, however, extremely ductile, and withstand shock remarkably well.

As regards the influence of heat treatment, it may be mentioned that the pearlitic steels quenched from a temperature above their transformation point are converted into martensitic steels just as in the case of carbon steels. The quenched alloys have, therefore, a higher tensile strength, but are brittle. The martensitic steels containing low percentages of nickel are also hardened by quenching, owing to the fact that the quenched alloys consist entirely of martensite; whereas in the slowly-cooled alloys a certain amount of free α -iron separates out between the martensite. The steels containing higher percentages of nickel are unaffected by quenching, and those bordering on the third or crystalline group of alloys are slightly softened. By cooling in liquid air some of

the crystalline steels can be transformed into those with martensitic structures.

Considering the structure of the alloys together with the information obtained from their cooling curves, it will be seen that nickel lowers the points of transformation of steel. When more than 8 per cent. of nickel is present the change Ar_1 does not take place until the alloy is cooled below the normal atmospheric temperature, with the result that these steels possess the martensitic structure and mechanical properties characteristic of steels hardened by quenching. Nickel steels, therefore, containing from 8 to 25 per cent. of nickel may be classed as self-hardening steels.

Nickel steel possesses a high electrical resistance, and an alloy containing 25 per cent. of nickel and about 0.8 per cent. of carbon, possessing a resistance about ten times that of iron, is used in the manufacture of resistance coils.

The following table gives the composition of a number of nickel-iron alloys and the purposes for which they are employed.

IRON-NICKEL ALLOYS.

Composition.		Applications.
C.	Ni.	
0.05 to 0.15	2 to 3	Weldless steel tubes.
0.2 to 0.4	2 to 3	Gun steel.
0.3 to 0.5	1 to 3	Cranks, crank shafts, etc.
0.2	3 to 3.5	Boiler plates.
0.5	3.5	Tyre steel.
0.2 to 0.4	5 to 6	Connecting rods, axles, etc.
0.25	30 to 32	Motor valves.
0.7 to 0.9	25	Ferro-nickel resistance wire.
0.2	36	Invar (Guillaume's non-expansile alloy).
0.15	46	Guillaume's platinite.

Manganese Steels.

Manganese, like nickel, lowers the temperatures at which the molecular changes take place in steel. Osmond has shown that when 3 per cent. of manganese is reached the alloy possesses only one critical temperature, Ar_{321} , at about 400° ; and with 7 per cent. of manganese this change does not take place above the ordinary temperature. The microstructure of the alloys is also

similar to those of nickel. In the case of low carbon steels those containing less than 5 per cent. of manganese have a pearlitic structure; those containing from 5 to 12 per cent. are martensitic, and beyond 12 per cent. the structure is crystalline. With a higher percentage of carbon smaller quantities of manganese suffice to produce the same structure; thus with 0.8 per cent. of carbon a change in structure occurs when more than 3 per cent. of manganese is reached, but in the high-carbon alloys Guillet is of opinion that the constituent is troostite and not martensite. It is also worthy of note that in the pearlitic steels the pearlite, which contains a double carbide of iron and manganese, is much more broken up and granular than that found in ordinary carbon steels, and has some resemblance to sorbite.

The influence of heat treatment upon manganese steels is very much the same as in the case of the nickel steels.

A similar diagram to that employed in the case of the nickel alloys may be used to indicate the structure of the manganese alloys (fig. 57). The increase in tensile strength and elastic limit due to the introduction of manganese into steel is small during the pearlitic stage, but rises when the martensitic stage is reached. These steels are extremely hard and brittle, and are of no practical use. When the crystalline stage is reached, however, the alloys lose their brittle character, but retain a very considerable degree of strength and hardness. These steels are represented by the well-known Hadfield manganese steel, which contains about 13 per cent. of manganese and 1 per cent. of carbon.

Chromium Steels.

The influence of chromium on steel is somewhat different to that of nickel and manganese. It appears to raise slightly the point Ar_1 ; but according to Osmond the point of magnetic transformation is only slightly affected.

As regards the constitution of the chromium steels, those containing less than 7 per cent. of chromium are pearlitic, and those containing from 7 to about 15 per cent. are martensitic. With more than 15 per cent. a double carbide makes its appearance in the form of small particles, which are perfectly white and very hard. As in the case of nickel and manganese steels these changes

occur with smaller percentages of the metal when the carbon

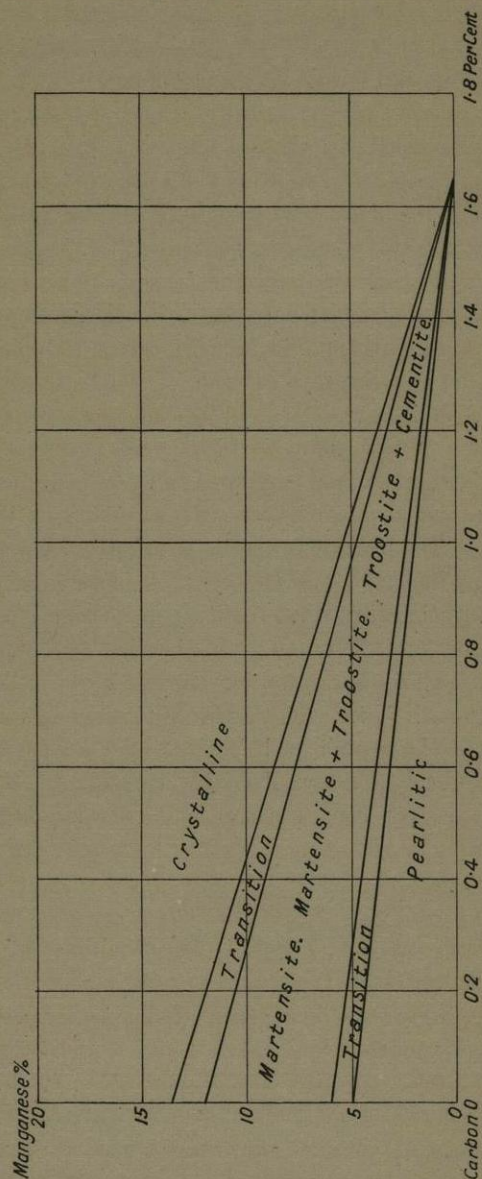


FIG. 57.—Constitution of Manganese Steels.

content is higher and the martensite tends to alter into troostite. In the alloy containing 0.8 per cent. of carbon the structure

ceases to be pearlitic with 3 per cent. of chromium. The pearlitic steels are stronger and harder than the corresponding carbon steels, but somewhat more brittle. Those possessing a martensitic structure are extremely hard and give high tensile tests, but are not as brittle as might be expected until the chromium present is sufficient to produce the double carbide. When an appreciable quantity of this constituent is present the alloys give low tensile tests and good elongations, as in the case of the crystalline alloys of nickel and manganese; but, unlike these alloys, they are very brittle on account of the presence of the double carbide.

As regards heat treatment, the pearlitic steels are converted into the hard martensitic variety by quenching, and the martensitic and carbide steels are slightly softened by the same treatment. Only the pearlitic steels are of any industrial value. They are largely used as tool-steels, and also for armour plates and armour-piercing projectiles. The steel used in the manufacture of projectiles contains about 1 per cent. of carbon and 2 to 3 per cent. of chromium. Chromium is also occasionally added to steel intended for springs and tyres, and is frequently a constituent of high-class file-steels.

Tungsten Steels.

The constitution of the tungsten steels is less complex than those previously considered. With less than 10 per cent. of tungsten the alloys of low carbon content are pearlitic, but when more than this quantity is present a double carbide of iron and tungsten makes its appearance. In the high-carbon steels this double carbide appears when 5 per cent. of tungsten is present; but in neither case does an intermediate martensitic structure occur, as in the chromium steels. The addition of tungsten increases the hardness and tensile strength of steel and, to a less extent, the elastic limit, without, however, any noticeable increase in brittleness. With the formation of the double carbide the alloy becomes very brittle and hard, with a high tensile strength and low elastic limit and elongation. It is therefore the pearlitic steels approaching the double carbide alloys that are of industrial value.

The effect of quenching on these alloys is similar to that produced in carbon steels, but much more marked; and by simply cooling in air they attain sufficient hardness to enable them to

be used as tool-steels. These steels are represented by the well-known Mushet self-hardening steels. The composition of a number of Mushet steels is shown in the table:—

Steel.	C.	Si.	Mn.	W.
Mushet steel	1.99	0.09	0.19	7.81
” ”	2.30	1.05	2.57	6.12
” ”	2.00	1.60	1.72	8.22
Crescent ”	2.06	0.05	2.66	6.73
Imperial ”	1.60	0.16	2.11	6.38

Tungsten steels are occasionally used in the manufacture of springs, the alloys employed for this purpose containing about 0.5 per cent. of carbon and 0.6 per cent. of tungsten; they are also used in the manufacture of permanent magnets, the steel in this case containing either 0.6 to 0.7 per cent. of carbon and 4 to 6 per cent. of tungsten, or 1.0 to 1.2 per cent. of carbon and 7 to 8 per cent. of tungsten.

Molybdenum Steels.

The effect of molybdenum on steel is very similar to that of tungsten, but much more strongly marked. That is to say, a smaller percentage of molybdenum is necessary to produce the same result. Thus in carbon steels containing 0.8 per cent. of carbon the double carbide of iron and molybdenum is formed when more than 1 per cent. of molybdenum is present. One part of molybdenum, therefore, is equivalent to about 4.5 parts of tungsten.

The pearlitic steels have a high tensile strength and elastic limit, which increases with the percentage of molybdenum; while the elongation and brittleness show a slight falling-off.

Molybdenum steels have been used as tool-steels, but usually in conjunction with tungsten, and sometimes with chromium and tungsten. The principal use of molybdenum steel, however, is for the manufacture of permanent magnets, for which purpose they are superior to tungsten steels. The usual composition of these steels is about 1.0 to 1.5 per cent. of carbon and 3 to 4 per cent. of molybdenum.

Silicon Steels.

The constitution of the silicon steels differs from those previously considered, inasmuch as silicon forms neither a double carbide nor a solid solution in all proportions with iron. It combines with iron to form a silicide corresponding to the formula $FeSi$, which, within certain limits, forms a solid solution with iron. It follows that the constitution of the silicon steels is independent of the carbon present. With less than 5 per cent. of silicon the alloys possess the same structure as ordinary steels; but beyond 5 per cent. the iron containing silicide in solution appears to be incapable of dissolving the same quantity of carbon, and a part of the carbon is thrown out in the graphitic condition. When the silicon exceeds 7 per cent. the whole of the carbon is found as graphite.

Silicon steels are harder than ordinary carbon steels, and possess a higher tensile strength and elastic limit; but their resistance to shock is not great when more than 2 per cent. of silicon is present. Those containing free graphite are useless.

Quenching hardens the pearlitic steels, and the effect is much greater than in the case of carbon steels.

The principal application of silicon steel is in the manufacture of springs, the percentage of silicon for this purpose varying from 0.8 to 2.0, with carbon from 0.7 to 0.4 respectively. In addition to these true silicon steels there are steels containing somewhat higher percentages of silicon than ordinarily met with in carbon steels. In the manufacture of these steels silicon in the form of ferrosilicon is added to the metal in the ladle before teeming, and answers the double purpose of eliminating oxygen and adding silicon. The destruction of oxide gives a fluid metal which yields castings free from slag and blowholes; while the excess of silicon renders the steels stronger, harder, and tougher. Steels of this description, such as the well-known Sandberg silicon rail-steel, give an increased life of more than 100 per cent. in actual use.

Vanadium Steels.

Vanadium appears to exert a stronger influence on the properties of steel than any other metal. With less than 0.7 per cent. of vanadium the alloys are pearlitic, but with more than this amount a double carbide is formed.

The tensile strength, elastic limit, and hardness, rise rapidly with the addition of vanadium, while the elongation only decreases slightly, and there is no increase in brittleness. With the appearance of the double carbide, however, the brittleness rapidly increases, although the elongation and reduction of area increase and the tensile strength and elastic limit decrease.

The pearlitic steels are hardened by quenching in the same way as carbon steels, but to a greater degree.

Only those steels containing less than 0.7 per cent. of vanadium—that is to say, those consisting of pearlite—are of any industrial value, and the addition of vanadium up to this amount possesses the unique property of greatly increasing the tensile strength and elastic limit of the steel without any corresponding decrease in the elongation or increase in brittleness. Unfortunately, the high price of vanadium is a serious drawback to its use except for special steels.

Quaternary Steels.

In addition to the ternary steels just described a large number of quaternary, or even more complex, steels are in use at the present time. It is impossible to describe these complex steels, but it may be remarked that their constitution is in every way comparable with the ternary alloys, and not more complicated. By adding two or more metals, however, it is often possible to obtain a steel combining the useful properties conferred by each of the added metals singly.

The more important of the quaternary steels are the nickel-chromium, chromium-tungsten, and manganese-silicon, while the nickel-vanadium, chrome-vanadium, and nickel-tungsten have been described and appear to possess properties which should ensure for them a successful future. Among the more complex steels may be mentioned the chrome-tungsten-molybdenum steels, which, in the form of tools, may be used at a speed which maintains them at a red heat without suffering any serious deterioration.

As regards the applications of the quaternary steels mentioned above, the nickel-chrome steels are used for armour plates and armour-piercing projectiles as well as for the shafts and gearing

of motors. The composition of the steels employed for these purposes is as follows:—

	C.	Ni.	Cr.
Armour plates . . .	0.2 to 0.5	2.0 to 2.5	0.2 to 0.8
Projectiles . . .	0.8	2	2
Shafts, gearing, etc. . .	0.2 to 0.5	2.5	0.25 to 0.5

Chrome-tungsten steels are used entirely as high-speed tool-steel. The following table shows the composition of a number of steels used for high-speed work. In these steels manganese is always low, and silicon usually about 0.2 per cent. Carbon varies from 0.2 to 0.8 per cent.

COMPOSITION OF CHROME-TUNGSTEN TOOL-STEELS.

Number.	C.	W.	Cr.	Mo.
1	0.71	12.0	3.0	...
2	0.43	15.5	4.5	...
3	0.45	13.0	1.6	...
4	0.45	9.5	2.1	...
5	0.60	13.5	8.0	...
6	0.20	7.0	2.1	...
7	0.60	9.9	2.8	...
8	0.80	18.3	2.9	...
9	0.72	13.5	5.2	...
10	0.50	12.0	3.0	1.0
11	0.50	5.0	3.0	4.0

The structural constituents of quaternary steels are the same as those found in ternary steels, and the same relations between structure and mechanical properties hold good. With small additions of other metals the alloys are pearlitic, while with larger additions the structure may consist of martensite, pearlite and carbide, pearlite and graphite, or sorbite and carbide, and with still larger additions, martensite and carbide, martensite and graphite, ferrite and graphite, γ -iron, γ -iron and carbide, or γ -iron and graphite.

The presence of graphite indicates silicon in fairly high percentages.

Martensite indicates nickel, manganese, or chromium. γ -iron indicates a high percentage of nickel or manganese, or both together.

In conclusion, we cannot do better than quote the words of Guillet in summing up the alloys of industrial value. After pointing out that the steels containing graphite are useless and those containing martensite are too hard to be machined, he adds:—"The steels containing carbide are devoid of interest if they also contain γ -iron. It is only when they are pearlitic or sorbitic that they can be of commercial utility, and even in this case they can offer but few special outlets for employment, the most interesting of which are for tool-steels and for ball-bearings. There remain, therefore, but two structures—Pearlitic steels, and steels containing γ -iron. The latter can only be obtained by the use of high percentages of nickel, or of manganese, or both, in order to avoid the production of steels easily transformed by quenching, annealing, cooling, etc. These percentages should be higher than is usually believed to be necessary, and the cost of production is proportionately increased. Further, it is necessary to remember that their elastic limits are lower and that they are difficult to machine. This renders their applications exceedingly limited.

"Thus, the following conclusion is arrived at:—Putting aside steels containing pearlite and carbide, or sorbite and carbide, which are of great interest as tool-steels, and in certain special instances for mechanical constructions, and steels containing γ -iron, of which use can only be made in exceptional circumstances, the only structure which should be sought for general purposes is pearlite. This being so, the statement may be further made that steels possessing this structure and its accompanying mechanical properties should not, as a rule, contain high percentages of carbon."

Cast Iron.

Cast iron, or pig-iron, as it comes from the blast furnace is classed or graded according to its fracture. In other words, it is classed according to the condition of the carbon, as the nature of the fracture depends upon whether the carbon exists as graphite or combined carbon. The method of grading and the number of grades vary in different localities, but the iron with the most open grain and grey fracture in which the carbon occurs almost entirely as graphite, is always known as No. 1; and "white" iron, in which the carbon is entirely in the combined form, is the

last of the series. The following analyses, due to Ridsdale, show the composition of a series of Cleveland pig-irons:—

	No. 1.	No. 2.	No. 3.	Forge.	Mottled.	White.
Carbon, graphitic	3.20	3.16	3.16	2.72	1.84	...
„ combined	trace	0.20	0.48	0.58	1.25	3.05
Silicon	3.50	2.90	2.59	1.93	1.01	0.67
Sulphur	0.05	0.06	0.08	0.10	0.32	0.40
Phosphorus	1.67	1.69	1.57	1.55	1.57	1.60
Manganese	0.68	0.62	0.60	0.75	0.62	0.42

From these figures it will be seen that carbon and silicon are the important elements, and, to a less degree, phosphorus. Moreover, it will be observed that there is a relation between the amount of silicon and the condition of the carbon; as the silicon decreases, more and more of the carbon is found in the combined condition. The constitution of cast iron is, in fact, similar to that of steel in many respects, and we have already seen that silicon combines with iron to form a silicide corresponding to the formula Fe_2Si , which is more soluble in iron than carbon, and throws the carbon out of solution in the form of graphite. The condition of the carbon in cast iron depends, to a certain extent, on the rate of cooling; rapid cooling tending to produce a hard white iron and slow cooling a soft grey iron. It is true that a very soft iron cannot be converted into a white iron or a white iron into a grey by cooling slowly or rapidly; but with the stronger "forge" irons lying between the grey and white, the rate of cooling is a matter of importance. With such an iron a small casting which had cooled rapidly might be found to consist wholly or partly of white iron; while a large casting of the same metal would consist of grey iron. Now, white iron is too hard to be machined; so that the small casting, if it requires any finishing, is unsatisfactory, and a greyer or softer iron must be used. Hence it follows that the percentage of silicon in a cast iron should be regulated according to the size of the casting; the smaller the casting the higher the percentage of silicon.

Sulphur occurs in cast iron as manganese sulphide, where there is sufficient of this metal; but in some white iron, where the

sulphur is high, it is found in the form of sulphide of iron surrounding the sulphide of manganese.

Phosphorus combines with iron to form a phosphide Fe_3P , which is soluble in iron to the extent of 1.7 per cent. Beyond this quantity free phosphide separates out and forms a eutectic which melts at about 910° . Phosphorus, however, forms another eutectic with the carbide, which Stead has described as the phospho-carbide eutectic. This eutectic has a much finer structure than the iron and phosphide eutectic, and frequently forms fringes, as shown in photograph 7. Owing to the low melting-point of the phosphide, eutectic iron high in phosphorus is extremely fluid and gives fine castings, but the metal is brittle. The constituents of grey cast iron, therefore, are graphite, ferrite containing phosphide and silicide in solution, phosphide of iron, sulphide of manganese, and carbide in the form of a phospho-carbide eutectic. In white iron the constituents are manganese sulphide, iron sulphide, carbide, and phosphide.

Stead has shown that where massive carbide and phosphide occur together, the only satisfactory way of distinguishing between them is by heat-tinting the specimen, when the carbide will be found to oxidise more readily than the phosphide.

As regards the composition of cast iron for various purposes, sulphur should never exceed 0.09 per cent. and phosphorus should not exceed 0.7 per cent. if strength is required. Manganese should not exceed 0.7 per cent. except for chilled castings. Silicon varies according to whether a hard, medium, or soft iron is required, but average figures may be taken as 1.4 per cent. for hard iron, 1.8 per cent. for medium iron, and 2.5 per cent. for soft iron. These figures are, however, only approximate, and allowance must be made for the size of the casting.

Alloys Employed in the Manufacture of Steel.

Within the last few years there has been a great demand for alloys of iron to be used in steel manufacture, both as deoxidisers and as a means of introducing a new constituent. These alloys are made either in the blast furnace or the electric furnace, and sometimes by means of Goldschmidt's aluminium reduction process. The alloys produced in the electric furnace are purer and contain higher percentages of the metals (other than iron)

than those made in the blast furnace. The first of the "ferro" alloys to be used in steel manufacture was ferro-manganese, which was introduced in the early days of the Bessemer process, as it was found to greatly improve the quality of the steel.

Ferro-manganese is made in the blast furnace. It consists essentially of iron and manganese, the latter varying from 40 to nearly 90 per cent., and about 6 per cent. of carbon. The following analyses show the composition of a number of samples of commercial ferro-manganese:—

	1.	2.	3.	4.	5.	6.	7.
Manganese	87.92	84.33	80.62	70.55	61.81	50.60	41.45
Carbon	6.31	6.95	7.00	6.68	6.28	6.12	5.62
Silicon	0.53	0.54	0.30	0.49	0.63	0.14	0.10
Phosphorus	0.15	0.15	0.16	0.20	0.16	0.11	0.09

Manganese behaves partly as a deoxidiser. Its existence in steel in the form of sulphide, silicate, and carbide has already been discussed.

Spiegeleisen is a ferro-manganese containing a lower percentage of manganese than ordinary ferro-manganese. It varies from about 10 to 30 per cent. of manganese.

Silicon spiegel is an alloy of iron and manganese, in which these metals occur as silicides. The alloy is made both in the blast furnace and the electric furnace, some of those made in the electric furnace being practically pure silicide of manganese. The silicon in these alloys is a powerful deoxidising agent. The following analyses show the composition of several commercial silico-spiegels produced in the blast furnace and in the electric furnace:—

SILICON SPIEGEL MADE IN BLAST FURNACE.

	1.	2.	3.	4.	5.	6.
Manganese	20.87	20.39	17.50	18.90	20.32	20.50
Silicon	14.23	13.31	12.52	11.80	10.33	9.45
Carbon	1.39	1.51	1.05	1.89	1.26	1.45
Phosphorus	0.10	0.01	0.06	0.08	0.07	0.07

SILICON SPIEGEL MADE IN ELECTRIC FURNACE.

	1.	2.	3.	4.	5.
Manganese	74.20	73.50	55.00	51.00	38.00
Silicon	24.70	24.25	25.00	21.00	21.00
Carbon	0.30	0.65
Phosphorus	0.02	0.05

Ferro-silicon is used both as a deoxidiser and for introducing silicon into steel. It is made both in the blast furnace and the electric furnace.

FERRO-SILICON MADE IN BLAST FURNACE.

	1.	2.	3.	4.	5.	6.	7.
Silicon	17.00	13.45	12.42	11.50	10.37	9.25	8.10
Manganese	1.50	1.71	1.17	1.35	1.86	1.86	2.20
Carbon	0.90	1.21	1.40	1.50	1.51	1.55	1.75
Phosphorus	0.07	0.06	0.05	0.06	0.06	0.05	0.05

FERRO-SILICON MADE IN THE ELECTRIC FURNACE.

	1.	2.	3.	4.
Silicon	32.70	48.70	75.80	94.80
Manganese	0.31	0.13	0.11	0.08
Carbon	0.27	0.09	0.00	0.00
Phosphorus	0.05	0.04	0.02	0.01
Aluminium	0.13	0.17	0.08	0.10

Ferro-chrome is the form in which chromium is introduced into steel. It also is made both in the blast furnace and the electric furnace. The blast furnace alloys contain from about 12 to 40 per cent. of chromium, 1.5 to 2.5 per cent. of manganese, and 5 to 7 per cent. of carbon; while those made in the electric furnace contain about 6.5 per cent. of chromium and 5 to 10 per cent. of carbon. Refined alloys are also made containing as much as 70 per cent. of chromium and only 0.5 to 1.5 per cent. of carbon.

Ferro-tungsten is employed in the manufacture of tungsten-steels. It is made by melting together Swedish iron, charcoal, and tungsten powder, obtained by heating tungstic oxide with charcoal. Three grades of ferro-tungsten are manufactured commercially, the first containing about 65 per cent. of tungsten and 1.5 per cent. of carbon, being intended for open hearth steel; while the second, containing 80 per cent. of tungsten and 1.5 per cent. of carbon, and the third, containing nearly 90 per cent. of tungsten and only about 0.4 per cent. of carbon, are intended for the manufacture of high-class crucible steels.

Ferro-molybdenum, used in the manufacture of molybdenum steels, is made in the same way as ferro-tungsten, which it resembles. It is supplied in various grades containing from 50 to 85 per cent. of molybdenum and 0.4 to 2 or more per cent. of carbon.

Ferro-vanadium is now a commercial alloy, and is made by reducing vanadic acid in presence of iron and charcoal in an electric furnace. The alloy contains from 40 to 50 per cent. of vanadium and about 1 per cent. of carbon.

Ferro-titanium has been suggested as a deoxidiser, and its efficiency for the purpose appears to be undoubted. At present, it is used more particularly as a deoxidiser for cast iron; but it may also be used for steel, and it has recently been suggested as an agent for removing nitrogen from iron and steel. Our knowledge of the part played by nitrogen in iron and steel is very limited, but there is little doubt that it exerts a prejudicial influence on the quality of the metal. An alloy which will remove both oxygen and nitrogen at the same time should have a future before it. Commercial ferro-titanium contains about 50 per cent. of titanium and 3 per cent. of carbon; but a special quality is also supplied containing only 0.5 per cent. of carbon.

Besides these alloys a number of others are used either as deoxidisers, or for introducing another metal, or for both purposes. Among these may be mentioned **ferro-uranium** and **ferro-boron**, used in the manufacture of uranium and boron steels. Such steels are, however, extremely rare. **Ferro-phosphorus**, containing 15 to 20 per cent. of phosphorus, is used as an addition to cast iron, where fluidity is of more importance than strength. Among the complex deoxidisers we have **ferro-aluminium silicide**,

containing 45 per cent. silicon and 10 per cent. of aluminium; ferro-calcium silicide, containing 70 per cent. of silicon and 15 per cent. of calcium; and ferro-sodium, containing 25 per cent. of sodium. Lastly, for the manufacture of quaternary steels we have such alloys as nickel-chrome, nickel-tungsten, chrome-molybdenum, and nickel-molybdenum.

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CHAPTER XVI.

MISCELLANEOUS ALLOYS.

Amalgams.

THE word *amalgam* is used to describe the alloys of mercury with other metals. Owing to their low melting-points they were the first alloys to be investigated, but recently they have attracted little attention.

Mercury alloys with a number of metals, the union being in many cases accompanied by the evolution of considerable heat, but very few of the amalgams have been put to any use, and the applications of those that are used industrially are strictly limited.

The principal amalgams are those of tin, copper, cadmium, bismuth, sodium, silver, gold, and palladium.

Tin-amalgams are made by adding mercury to molten tin. The amalgam of equal parts of mercury and tin is a brittle solid; but with more mercury a plastic mass is obtained which becomes hard in the course of a few days. This and similar alloys containing cadmium, silver, or gold, are used by dentists for stopping teeth. The amalgams are used in a plastic condition, and harden with little or no expansion.

Copper-amalgams.—Copper does not alloy readily with mercury under ordinary conditions. By mixing mercury with precipitated copper in presence of mercuric nitrate solution, however, the mercury unites with the copper to form an amalgam.

Copper-amalgam is plastic when newly made, but becomes hard in a day or two. It may be softened again by immersing it in boiling water or by simply pounding it; and it is capable of