Steel 8400 1100 1000 + CEMENTITE MESELT FORM OF THE CARBONJRON EQUILIBRIUM IV BRICKID PEARLITE PAFERRITE FORMENTITE FORAPHITE b. Isa) adt Figs 68. Reberts-Ar dary and other lines which are not transformation lines - - References Beliefis, 111, p. 293; "Leafer an Facier an Point de Vue de in Bosttine des Pha

integrally with a backing, which is in the ductile pearlite state. Thus the cutting edge of a cold-chisel is hard and brittle because it is in the austenite state thanks to its sudden cooling, i. e., hardening; and this brittle edge is prevented from breaking by its integral union with the shank of the chisel, the temperature of which has been so manipulated as to leave the metal in the pearlite state, malleable and relatively stressless. So with the hardened point of a projectile, integrally united with its unhardened body; the hardened face of the armor-plate integrally united with a back of low-carbon steel, which, even in the austenite state, is relatively malleable.

objects are, more accurately speaking, intermediate between the austenite and the pearlite state, as has been pointed out in § 149, p. 179, i.e., they never consist solely of pure unaltered austenite. Even in objects which are used in the suddenly cooled or hardened state without subsequent drawing of the temper, the austenite is more or less altered, because no cooling, however rapid, can completely prevent its alteration towards the condition of pearlite. In the more common cases such as springs and most cutting tools, in which the suddenly cooled object is afterwards slightly tempered by slight reheating, the change from the austenite towards the pearlite state goes still further. Nevertheless, for our present

purpose we may regard all these objects as of the austenite series in the broad sense that we owe their properties chiefly to their

austenite.

of the Iron-carbon Compounds. — The inflections which we have studied in Chapter II in our cooling curves are due to the liberation of heat, or in other words to the change of energy in passing from the molten to the solid state. But as was pointed out in § 12, p. 19, every change, chemical or physical, within the metal after it has solidified will probably be accompanied by the evolution (or more rarely by the absorption) of heat, and these will in like manner cause inflections in the cooling curves, which thus will record automatically not only the progress and method of solidification, but also all changes of constitution which take place in cooling from the freezing-point downwards. And this brings us by an easy stage to Roberts-Austen's diagram (Fig. 68) which shows us simultaneously the freezing-point curves and the trans-

formation curves of the iron-carbon compounds, as well as the constitution corresponding at different temperatures to these different percentages of carbon.

Regarded in a broad way, this diagram really consists of two sets of the familiar underscored V curves, of the family which as we have seen, habitually represents the freezing of a eutectiferous alloy.

The first or upper set, ABC, aBc, indeed represents the freezing of just such a eutectiferous series, for that is what the iron-carbon compounds really are. The eutectic contains about 4.30 per cent of carbon, and its two constituents are (1) the solid solution of carbon in iron, austenite, and (2) graphite. The austenite should normally be saturated with carbon, in short a saturated solid solution, like those in other eutectics. About 2.00 per cent of carbon should saturate it.

Eae is clearly a fragment of the saturation-point or critical curve, showing the supposed percentage of carbon which at each temperature suffices to saturate the austenite.

The second or lower set, GHSER, PSP', represents a parallel transformation within the solid metal, closely comparable with the freezing of a eutectiferous alloy. That is to say, just as the freezing of a series of eutectiferous alloys yields a series of conglomerates, each consisting of the eutectic plus an excess-substance; so this transformation within the solid metal in cooling causes the solid solution, austenite, to break up into a conglomerate consisting of a quasi-eutectic or "eutectoid" plus an excess-substance. And as in the freezing of a eutectiferous alloy this transformation from molten solution to solid conglomerate takes place along this underscored V set of lines, so this present transformation within the solid austenite, the solid solution, takes place along this underscored V set of lines.

The eutectoid or quasi-eutectic is pearlite, and its constituents are ferrite, Fe, and cementite, Fe<sub>3</sub>C.

The Terms Ar<sub>1</sub>, Ac<sub>1</sub>, etc. — These are explained in § 192,

p. 215.

The present diagram, like similar ones for other series of alloys, represents the freezing-points as distinguished from the melting-points, and the transformation-points in cooling as distinguished from heating. The corresponding lines for rising temperature and for melting should theoretically coincide with these;

actually owing to lag there are considerable discrepancies. (See § 164.)

In general the meaning and indeed the position of the lines to the right of the 1.50 per cent carbon ordinate are by no means well established. In particular, since the first edition of this book was written grave doubts have been thrown upon the then accepted interpretation of the line BC, which may represent the formation of cementite.

163. Position of the Steel Cast-Iron Boundary as Re-LATED TO THE SATURATION-POINT OF SOLID AUSTENITE. — Just as it is in general desirable that the boundaries of countries should be natural ones, such as mountain ranges or bodies of water, so it is desirable that our different classifications of iron and steel should as far as practicable be based on such natural divisions, instead of being purely arbitrary. In this work the dividing line between cast iron and steel has been arbitrarily drawn at 2.00 per cent of carbon, in rough accordance with commercial usage. But this arbitrarily chosen line has the advantage of being very near to the great natural division between the normally non-eutectiferous range and the normally eutectiferous range. So soon as the position of this natural boundary has been determined with reasonable accuracy, it may be well to adopt it as the dividing line between steel and cast iron. Steel would comprise the normally non-eutectiferous and cast iron the normally eutectiferous carboniron compounds.

While this plan is attractive in case of pure iron-carbon compounds, it may not be practicable to apply it to impure irons, for the reason that the boundary of the eutectiferous range may shift widely with variations in the proportions of the impurities. Should this be the case, then instead of such a precise basis of demarcation we may have to use the vaguer one adopted in § 142, p. 170, according to which the distinction between those steels which approach cast iron in nature and those cast irons which approach the nature of steel is that steel must be forgeable in at least some one range of temperature, while the cast iron is not.

164. GENERAL DIVISION; CONSTITUTION; LAG. — This diagram is divided by these freezing-point and transformation-point lines into nine important regions. To each of these, according to our present theories, a certain constitution normally corresponds. As the metal cools from one of these regions into another,

its constitution ought theoretically to change from the theoretical constitution of the region it is leaving to that of the region which it is entering. But owing to what we may call lag or molecular inertia, these transformations which should occur on crossing such a boundary may be suppressed partly, and perhaps even completely. In other words, these transformations, especially those which occur within the solid metal, require a certain length of time; and they are opposed by the cold; so that if the cooling across a given boundary is rapid, the transformation due at that boundary may be incomplete there, and if the temperature falls quickly to the cold, this transformation may be permanently arrested, and thus remain permanently incomplete.

This lag is a matter of very great importance, and to it we are in large part indebted for our power of giving to a given piece of steel or cast iron a great variety of different properties by different methods of heat-treatment. These methods act chiefly by inducing certain desirable degrees of lag, or by stimulating some reaction which has already lagged, and thus reviving it under favorable conditions. We shall in due time see that this is true of the hardening, tempering and annealing of steel, the chilling and annealing of cast iron, and the manufacture of malleable iron castings.

One effect of this tendency to lag is to cause transformations represented by these different lines of Fig. 68 to take place in cooling at temperatures considerably below what may be called the theoretical temperatures, and in particular below the temperatures at which they occur during rise of temperature. There is also a certain amount of lag during rise of temperature, but this is generally much less marked.

Hence the observed position of the transformation lines in cooling may actually be much lower than that observed during rise of temperature.

Certain foreign elements, such as nickel and manganese, appear to act through lowering the temperatures at which these transformations occur, and a large part of the important influence of these foreign elements has been referred to their thus lowering these temperatures.

These nine regions will now be enumerated, and at the same time their theoretical constitution and the transformations which should theoretically occur in cooling through them will be given. Equations will be given representing these transformations, and these equations will be grouped together in Table 8, p. 203.

165. REGION I, ABCF, MOLTEN SOLUTION OF CARBON IN IRON. — This has for its lower boundary the upper freezing-point curve ABC, and it represents simply molten steel and molten cast iron, each of which is a molten solution of carbon in iron. The boundary between them is imaginary. It will simplify our ideas if we assume that when solid iron containing graphite melts, the graphite in melting loses completely its graphitic nature, and becomes simply carbon dissolved in iron, exactly as if before fusion it had existed in solution or combination, instead of as graphite.

166. REGION II, AaB, Selective Freezing Occurs, MOLTEN CARBURETTED IRON AND SOLID AUSTENITE. The metal in this region consists of (1) solid austenite, a solid iron-carbon solution, the excess-substance, together with (2) the mother-metal of molten carbon-iron solution.

The theoretical reactions on cooling through this region are as follows:

- A. For all compositions at the left of the 2.00 per cent carbon ordinate (line ea), selective freezing:
  - (1) molten solution = solid austenite.
- B. For compositions between 2.00 and 4.30 per cent of carbon, in cooling through this region, down to but not including the transit across the lower boundary, *aB*, selective freezing:
- (2) molten solution = solid 2.00 per cent austenite + molten eutectic.
- (By 2.00 per cent austenite is meant austenite containing 2.00 per cent of carbon dissolved in it.)
- On crossing the lower boundary aB, freezing of the eutectic:
- (3) molten eutectic = solid eutectic = 2.00 per cent austenite + graphite.

Taking both the passage down to the lower boundary and the crossing of that boundary, the sum of reactions (2) and (3) may be written thus:

(4) molten solution = 2.00 per cent austenite + graphite.

This transformation from molten solution into graphite appears to be relatively slow, unless stimulated by the presence of silicon. Hence if the metal is free or nearly free from silicon and

is cooled at any usual rate, the resultant austenite may contain much more than 2 per cent of carbon. Instead of reaction (4) we then have:

(5) molten solution = supersaturated austenite + graphite, or

(5) molten solution = (2 +) per cent austenite + graphite. It is probably to this suppression of the formation of graphite, this substitution of reaction (5) for reaction (4), that we are indebted for the existence of white cast iron.

167. REGION III, CBc, Selective Freezing Occurs, MOLTEN CARBURETTED IRON AND GRAPHITE.—The mass in this region probably consists of (1) solid graphite, the excess-substance, together with (2) the still molten mother-metal of iron-carbon solution.

The theoretical reactions in this region are as follows:

In cooling through this region, down to but not including the transit across its lower boundary Bc, selective freezing:

(6) molten solution = molten eutectic + graphite.

On crossing the lower boundary Bc, freezing of the eutectic:

(3) molten eutectic = solid eutectic = 2.00 per cent austenite + graphite.

Taking both the passage down to the lower boundary and the crossing of that boundary, the sum of reactions (6) and (3) may be written thus:

(4) molten solution = 2.00 per cent austenite + graphite.

The remarks as to the lagging of reaction (4) made in case of region II apply here also, so that reaction (5) is probably substituted for the theoretical reaction (4) in most cases.

168. Region IV, AaESHK'G, AUSTENITE, solid iron-carbon solution, resulting from reaction (1). Theoretically no transformation should occur in cooling through this region.

169. REGION V, GHSP, Selective Transformation Occurs, AUSTENITE AND FERRITE. — Ferrite as the excess-substance, and austenite the still untransformed solid mother-metal. Above the line Ar<sub>2</sub> the ferrite is beta, below it is alpha. (See § 191, p. 214.)

To explain, just as in selective freezing the excess-substance progressively freezes out, and the remaining molten mother-metal correspondingly approaches the eutectic ratio, so in cooling through this region, iron which may be regarded as the excess-substance,

progressively separates\* in the free state, i. e., as ferrite, within the solid red-hot austenite, which consequently becomes enriched in carbon, and approaches the "hardenite" or quasi-eutectic or eutectoid ratio of 0.90 per cent of carbon, reaching it when the temperature in falling reaches the eutectoid transformation-temperature PSP'. The reaction may be written

(7) austenite = hardenite + ferrite, or

(7) austenite = 0.9 per cent austenite + ferrite.

And just as, when the temperature falls past the eutectic freezing-point, this eutectic in turn breaks up into its constituents; so here when the temperature falls past the eutectoid transformation-temperature, the remaining untransformed solid mother-metal is now transformed into ferrite and cementite, interstratified as pearlite. The reaction may be written

(8) hardenite = pearlite = ferrite + cementite, or

(8) 0.9 per cent austenite = pearlite = ferrite + cementite. The sum of these transformations (7) and (8), the progressive transformation in region V plus the transformation of the eutectoid on leaving this region, may be written thus:

(9) austenite = ferrite + cementite.

The whole of the cementite is interstratified with ferrite as pearlite in the ratio of 1:6, and the remainder of the ferrite in excess of this ratio is the excess-substance, the "structurally free ferrite" of Sauveur.

170. REGION VI, PSWO, PEARLITE AND FERRITE resulting from reaction (9).—Of these ferrite is the excess-substance, and pearlite the eutectoid, or quasi-eutectic. Theoretically no reaction occurs in cooling through this region.

171. REGION VII, aERc, 2 PER CENT AUSTENITE AND GRAPHITE resulting from reaction (4).

Our theories as to this region still lack proof: they must therefore be accepted very cautiously.

<sup>\*</sup> When it is said that ferrite "separates" within the solid austenite, it is not meant that this ferrite removes itself bodily away from the mother austenite; the little particles of ferrite as it were remain in the womb which conceives them, for the simple reason that the degree of plasticity of this red-hot austenite, while sufficient to enable the ferrite made free by reaction (7) to unite into particles large enough to be detected by the microscope, is yet far too slight to permit those microscopic particles to remove themselves out of the mother-mass.

Part of the austenite and part of the graphite are associated as the eutectic, which as already pointed out is a mixture of graphite with saturated austenite, and contains 4.30 per cent of total carbon.

At the left of the eutectic ordinate the mass is a conglomerate of the eutectic plus the excess-substance, austenite; at the right of this ordinate it is a conglomerate of the eutectic plus the excess-substance, graphite.

As already explained, owing to the lag of reactions (1) to (4) the austenite may contain more than 2 per cent of carbon, i. e., may be supersaturated, especially if there is but little silicon present, an element which appears to stimulate reaction (4), or at least to stimulate the passage of carbon into the state of graphite.

Theoretically no reaction occurs in cooling through this region.

172. REGION VIII, ESP'R Selective Transformation Occurs, AUSTENITE AND CEMENTITE. — GRAPHITE also is habitually present through lag, though theoretically absent. Cementite is the excess-substance, and austenite the still untransformed solid mother-metal. This region thus mates region V; region VIII is hyper-eutectoid, region V is hypo-eutectoid.

Our theories as to this region still lack proof: they must therefore be accepted very cautiously.

An extremely important reaction occurs theoretically on entering this region, *i. e.*, on cooling past the line *ER*. The graphite existing in region VII should, on crossing this line, react with part of the iron of the austenite which accompanies it to form cementite, thus:

(10)  $Gr + 3Fe = Fe_3C$ , or

(10) graphite + austenite = cementite.

The sheets of graphite which exist in region VII are naturally those with which we are familiar in gray pig iron, coarse, thick, and at a considerable distance apart. Now it is relatively easy for the graphite to react with the molecules of iron in the layer of austenite with which it is in immediate contact. But these molecules are by no means enough to convert the whole of that graphite into cementite by reaction (10). The rest of the graphite cannot undergo that reaction unless it can, through molecular migration or otherwise, actually reach the molecules of iron in other layers

of austenite with which it is not initially in contact. Hence it is not surprising that reaction (10) should lag, and should indeed habitually be extremely far from complete; in short that most of the graphite which we have reason to believe exists in region VII is habitually found in the cold cast iron, passing undecomposed through regions VII, VIII, and IX. Hence the existence of gray cast iron.

Because the austenite of the eutectic as it comes into existence at the end of the freezing, *i. e.*, on cooling past line *aBc*, should theoretically be saturated with carbon, and because reaction (10) should remove iron from that austenite, the austenite should thereby become supersaturated with carbon. To meet this condition, we may suppose that this supersaturation will, if equilibrium is reached, cure itself by a further combination of part of the carbon and part of the iron of the austenite to form more cementite.

Returning now to the selective transformation which occurs on cooling through this region down to but not across line SP', it of course consists in the progressive formation of more and more cementite within the solid red-hot austenite, by the union of part of its iron and part of its carbon. The reaction may be written:

(II) 2 per cent austenite = hardenite + cementite, or

(II) 2 per cent austenite = 0.9 per cent austenite + cementite. As cementite contains 6.67 per cent of carbon, or much more than the austenite itself, this formation of cementite progressively impoverishes the austenite in carbon until it eventually reaches the hardenite or eutectoid composition of 0.90 per cent of carbon, simultaneously reaching the eutectoid transformation temperature. On cooling past this point, the remaining austenite, now called hardenite, in turn transforms into pearlite. The reaction may be written:

(8) hardenite = pearlite = ferrite + cementite, or

(8) 0.90 per cent austenite = pearlite = ferrite + cementite.

The sum of these transformations may as in case of region

V be written thus:

(12) 2.00 per cent austenite = ferrite + cementite
Or, taking reactions (10), (11), and (8) collectively, the end reaction for the total journey through this region, including both upper and lower boundary, may be written: