

tain important aspects of the subject, and as furnishing a hypothesis susceptible of ready test, and thus likely to serve as a stepping-stone to more thorough knowledge of the subject.

To simplify the discussion it is supposed to be confined to non-eutectiferous alloys, *i. e.*, to those in which no eutectic should be present if equilibrium was reached, or in other words to those in which one of the two metals present is theoretically capable of dissolving the whole of the other.

If equilibrium is not reached, such an alloy may contain a eutectic, which would be absorbed and would thus disappear if diffusion should later perfect itself. (§ 96, p. 113.)

84. DIFFUSION TENDS TO LESSEN THIS SEGREGATION. — This heterogeneous structure of the alloy which we have just been considering, with its three sets of layers, (1) unsaturated and (2) saturated bismuth-bearing tin, and (3) the eutectic, clearly is very far from being a condition of equilibrium. Looking no farther than the initial heterogeneousness of the unsaturated layers, this itself is not of equilibrium, for from the later deposited and richer part of these unsaturated layers, part of their bismuth tends to diffuse into the earlier ones which are poorer in bismuth. So too part of the bismuth of the saturated layers tends to diffuse out into the unsaturated ones, so that these which were initially saturated thus tend to become unsaturated. Then into these layers thus become unsaturated, part of the bismuth of the eutectic tends to pass through diffusion. This tendency, therefore, in so far as it is obeyed, will diminish the quantity of eutectic, by causing a regrouping of its constituent metals, somewhat as grouping 3 changed to grouping 4, and this in turn to grouping 1, in § 73, p. 80. If this transfer of bismuth from the eutectic into layers (2) so far impoverishes the eutectic in bismuth that its tin now is theoretically sufficient to dissolve the whole of that bismuth if it could get at it, then, as we saw in § 71, p. 78, it will tend so to dissolve that bismuth through regrouping. And if that tendency is obeyed fully, our conglomerate eutectic will disappear and be replaced by a solid solution of bismuth in tin. Finally this solution may, through further diffusion, eventually become quite uniform in composition throughout, both the microscopic and the macroscopic segregation being thus effaced; and this might eventually happen even if the ingot was initially much segregated, and even if it was several feet thick.

85. DIFFUSION LESSENS BOTH MICROSCOPIC AND MACROSCOPIC SEGREGATION. — This leveling tendency of diffusion evidently applies to both the microscopic and the macroscopic segregation. It tends to undo both of them, and to reduce the alloy (1) to a homogeneous solid solution if (as is assumed in the present discussion), the proportion between the total quantity of the two metals present in the whole mass is such that one is theoretically sufficient to dissolve when solid the whole of the other; and (2) to a eutectic plus a saturated homogeneous solid solution, if this proportion is such that neither can dissolve the whole of the other.

86. HOW COMPLETE IS DIFFUSION? — Under the conditions usual in manufacture, this tendency clearly is not completely fulfilled. Diffusion does not so perfect itself as regards the macroscopic segregation of large steel ingots, even if their cooling is so slow as to extend over many hours; for these ingots are habitually much segregated, so much so that for certain special purposes, for instance gun-forgings, the segregated axial part of the ingot is cut out and thrown away.

How far diffusion perfects itself as regards microscopic segregation, remains to be investigated. Certainly the gradual shading off of tint shown in Figs. 32 and 36 suggests strongly that much of this initial microscopic heterogeneousness persists in spite of diffusion. But these indications must be received with extreme caution. Even the experienced microscopist must exercise the greatest care in interpreting such appearances; for while this shading off may indeed be due to corresponding heterogeneousness of the alloy, yet it also may be due to the manner of preparing the metallic surface for microscopic examination.

But apart from such indications, we may reasonably hold that the slower the cooling is from the melting-point downwards, the greater should be the opportunity for diffusion, and the less should be the residual segregation.

The reader should here distinguish sharply between this equalizing action of diffusion, which ought to be favored by long exposure to a temperature only slightly below the eutectic freezing-point, and the liquation effect which may be brought about by holding an alloy at a temperature between the upper and lower freezing-points. In this latter range of temperature the alloy as a whole is in part solid, and in part molten; and the molten part

tends to draw together, to coalesce, and under favorable conditions even to liquate and sweat out from the mass of the alloy.

87. FREEZING DIFFERENTIATES, DIFFUSION EQUALIZES. — Let us at once recognize that we have here two agencies, freezing and diffusion, with diametrically opposite tendencies. Freezing is a process of differentiation, tending to split up the alloy into the three sets of components of Fig. 34, p. 85, with which we are now so familiar; diffusion is a process of equalization, tending to efface the heterogeneousness which freezing induces.

Having just seen that the rate of cooling from the freezing-range downwards should be expected to influence the degree of residual segregation, we may now pass on to enquire what influence the rate of cooling through the freezing-range itself ought to have on residual segregation. But at once we must discriminate between two different things going on simultaneously in this range, the differentiation taking place at any given instant in the very particles which are freezing at that instant; and the equalizing action of diffusion in the layers which have frozen prior to this instant. If we hasten the freezing of a given layer, we necessarily hasten also the cooling of the previously frozen layers, and we thereby lessen the opportunity which diffusion has to equalize the composition of those layers.

Let us for the present disregard this latter influence of the rate of cooling through the freezing-range, and confine our attention to the influence of rapid cooling on the differentiation which freezing itself causes.

Then later let us go on to consider other features of this problem, and let us enter our results as we reach them in Table 2, p. 112.

88. RAPID FREEZING SHOULD LESSEN SEGREGATION. — Just as rapid cooling from the freezing-point downwards should restrain the equalizing action of diffusion, so rapid cooling through the freezing-range appears to restrain the differentiation which freezing tends to cause. Thus in Fig. 35, p. 86, we find that the differentiation which the ingot as a whole shows, does not include the outer layers of the ingot. The progressive enrichment of the successive layers in carbon from without inwards does not begin until we have passed a considerable distance inwards from the outer crust.

We may reasonably refer this to a restraint put upon the dif-

ferentiation by the suddenness of the freezing. This suddenness has checked in the outer layers the impoverishment to which differentiation normally leads, with the result that these layers are richer in carbon than they normally would be, if differentiation and impoverishment took their full and natural course.

[The matter between these brackets is to explain the foregoing more fully to any to whom it is not clear.

Let us refresh our memory as to what occurs or tends to occur in freezing. When the first layer freezes, the differentiating tendency causes it to be purer, *i. e.*, to contain less carbon, than the molten metal from which it freezes, so that the freezing of the first layer gives us two bodies, this frozen layer poorer in carbon and the residual mother-metal richer in carbon. The next layer to freeze, however, while again poorer in carbon than the mother-metal which it in turn leaves, should be richer in carbon than the first frozen layer, simply because the mother-metal out of which the second layer freezes is itself richer in carbon than the mother-metal out of which the first layer froze. And so on, each layer at the instant of its birth should be richer in carbon than the layer which froze just before it; and this is a result of differentiation.

Thus this differentiation itself, this very impoverishment of the early frozen layers, leads to the enrichment in carbon of the later frozen ones. This enrichment will be continuous and progressive if differentiation takes place normally, so that after the whole ingot has solidified we should, on analyzing it, find a progressive increase in the percentage of carbon from the first frozen outer layers to the last frozen inner ones.

If some means was discovered by which differentiation could be wholly prevented, then this impoverishment of the early freezing layers would thereby be wholly prevented, and the mass, when frozen throughout, would be uniform in composition. If differentiation was partly restrained, for instance in the first freezing layers, then the impoverishment of these layers would be somewhat restrained, which means that they would be left richer in carbon than they would have been had differentiation and impoverishment had full play without this restraint; or in short they would be abnormally rich in carbon. They would thus be more nearly saturated than they would have been if this impoverishment had had full play, *i. e.*, if they had been impoverished to the normal degree. And if in the outer and first freezing layers impoverishment was

thus prevented, so that they were abnormally rich in carbon, while in the layers freezing somewhat later differentiation and impoverishment were not thus restrained but took place to their full natural extent, then the outer layers might actually be richer in carbon than those inside them.

Now this is exactly what seems to have taken place in the ingot shown in Fig. 35, in its lower part, which is naturally the part to freeze most rapidly, because it is exposed not only to the sides of the cold mould but also to its cold bottom, whereas the upper part of the ingot is not covered with a cold top but is exposed to the air. Moreover, the hotter metal would naturally rise to the top, and thus tend to delay freezing there. Looking at the lower five of the horizontal rows of numbers, we see that in them the outermost layer is richer in carbon than the layer next inside it. Here, then, the progressive enrichment of the successively frozen layers, instead of beginning at the very skin, begins only when a considerable depth within or beneath the skin is reached; the impoverishment of the outer layers then seems to have been interfered with; evidently it has not taken place to its normal extent. Our natural inference is that it is the rapid freezing of this, the fastest freezing part of the shell, which has restrained its impoverishment, *i. e.*, has given it this abnormal richness.]

To say that the skin is abnormally rich in carbon is only another way of saying that the iron here, while of course not saturated with carbon, is more near to saturation than it would have been had differentiation and impoverishment taken place to their normal extent. That this is the true explanation we hold the more confidently from the fact that we have good reason to believe that sudden cooling may go farther and actually leave the frozen metal not simply abnormally near to saturation, but actually supersaturated.

Thus cast iron when molten contains a large quantity of carbon dissolved in it, of which during slow freezing it expels a large part in the form of graphite. But if frozen rapidly it retains dissolved a very large part of this carbon which it would have expelled if the freezing had been slow. This excess is so great as to indicate that the suddenly frozen cast iron is greatly supersaturated with carbon.

We have something similar in the hardening of steel, which of course consists of iron plus carbon. When the steel is above a

certain critical temperature, its iron is in the *Gamma* state, and in this *Gamma* iron the carbon readily dissolves, forming a solid solution. On cooling below a certain critical range the *Gamma* iron changes to *Alpha*, in which the carbon is apparently wholly insoluble, or at most only very slightly soluble. The normal condition of things is that, when the iron thus changes from *Gamma* to *Alpha* the carbon passes out of solution because insoluble, and unites with part of the iron to form the definite carbide Fe_3C , called cementite; so that the steel when cold normally consists of a conglomerate of (1) *Alpha* iron free from carbon, and (2) this cementite; and this is what we find in slowly cooled, *i. e.*, "annealed" steel. But if the steel is cooled suddenly from above this critical range, this transformation is in a measure prevented, so that the conglomerate consists in part of this cementite, and in part of iron containing carbon actually dissolved, although normally insoluble in the iron at this temperature. It is retained in solution because the passage through the zone of temperature below the critical range, the zone in which the freedom of molecular motion is great enough to permit the carbon to slip out of solution, has been too rapid to permit this tendency to assert itself completely. This will be explained more fully in Chapter VIII.

In each case it is not only that sudden cooling restrains a change which normally tends to occur on cooling past a given temperature, but further that the metal appears to remain absolutely supersaturated with carbon.

Nor is this confined to alloys of iron. Wm. Campbell found that certain copper-tin alloys which were eutectiferous when cooled under normal conditions, were not when cooled very suddenly by quenching in water.* And it is probable that further investigation will show that there are many alloys of which much the same is true.

What here occurs is substantially this. The dissolved substance which, under normal conditions of slow freezing, would be found separated as a distinct entity, such as the graphite of cast iron, the eutectic of a eutectiferous alloy, — this dissolved substance is not thus found if the freezing is sudden. It is true

* "Microscopical Examination of the Alloys of Copper and Tin," *Proc. Institution Mechanical Engineers*, Dec. 20, 1901.

that, in certain cases, our failure to find in the suddenly cooled alloy this separated entity, which we do find when the cooling has been slow, may be due to a minuteness of structure so extreme that the microscope as yet fails to resolve it. By this I mean that, whereas in slow cooling the eutectic or other separated body has time to group itself into particles large enough to be seen by means of the microscope, in sudden cooling this opportunity is so much abridged that the individual particles, while actually present, are so small as to escape detection. In other words, this sudden cooling may actually prevent the formation of a eutectic, *etc.*, by inducing supersaturation or at least abnormally high concentration; or it may merely conceal the eutectic by giving it a structure so fine that it cannot be detected.

In the case of cast iron and steel we are confident that the action of the sudden cooling is not confined to such mere concealment, because it induces profound changes in the physical and chemical properties of the alloy, far too great to be referred to such mere comminution of structure.

It is possible that rapidity of cooling may also lower the temperature *abc*. In the somewhat parallel case of the transformations in solid iron, Osmond early found that hastening the cooling lowered the temperature at which they occur.*

89. IN PARTICULAR, RAPID FREEZING SHOULD RESTRAIN MACROSCOPIC SEGREGATION. — Besides the foregoing general reason, there is a special reason why macroscopic or axial segregation should be restrained by sudden freezing. In §§ 81 and 82, pp. 94 and 97, and in Fig. 42, we saw that as the excess or solvent metal, the bismuth-bearing tin, freezes out, by the selection in freezing part of its bismuth fails to freeze; it is thus liberated, and it then tends to diffuse out into the open sea, thus gradually enriching that sea in bismuth. We further saw that the bismuth-content of each molten landlocked basin would be approximately that of the open sea at the time when landlocking took place. This was on the assumption that the progress of freezing was so slow that this liberated bismuth diffused itself out uniformly or nearly so, throughout that open sea. But the bismuth-content of each basin, more strictly speaking, should follow the bismuth-content of the littoral region of that sea, rather than the average

* "Transformations du Fer et du Carbone," 1888, p. 36.

of the whole sea, since it is this littoral part of the sea which is landlocked.

Now, if freezing is rapid, *i. e.*, if the position of the shore and littoral layers shifts centripetally rapidly, there will be so little time for the seaward diffusion of this liberated bismuth that the littoral layer, including that part of it landlocked in each basin, will be materially richer in bismuth than the average of the open sea. Thus more of the bismuth will be locked up in these landlocked basins, and there will consequently be less to migrate out centripetally to form finally the macroscopic or axial segregation, than if the freezing were slow. Thus in short, rapidity of freezing should in particular restrain axial segregation.

90. THE TWO FEATURES OF RAPID COOLING THROUGH THE FREEZING-RANGE, TAKEN JOINTLY. — We have now seen with regard to rapid cooling through the freezing-range that (1) in that it lessens the opportunity for diffusion in the already frozen layers, it leads towards greater residual segregation, and (2) in that it hastens the freezing itself, it leads towards less residual segregation, *i. e.*, it tends to lessen segregation.

Thus rapid cooling through this range has two opposite effects. Which of these is the greater may not easily be foretold. We may however note one consideration for our guidance. To take an extreme case in order to illustrate the principle to which I now refer, let us assume that the cooling through this range is extremely slow, occupying say a year. If that is not long enough for your imagination, select a longer period that will satisfy you. Let us further suppose that the rate of freezing is uniform throughout this period. At the end of eleven months or 92 per cent of the total time, some 92 per cent of the whole mass will have frozen; there then remains a month in which to equalize the composition of this mass by diffusion. Let us assume that this month is long enough practically to perfect this equalization.

At the end of 11.5 months some 96 per cent of the whole will have frozen, and there remain still two weeks to distribute through the previous frozen layers the excess of any element contained in the four per cent which has been deposited in these two weeks just ended. Let us assume that this is time enough practically to perfect this distribution.

Proceeding in this way we see that, if we only make the passage through the freezing-range slow enough, the extra op-

portunity for diffusion in the frozen layers will more than compensate for the extra opportunity for differentiation in freezing which the slowness of the freezing itself offers.

From such considerations our natural inference is as follows:

As between (1) extremely slow and (2) moderately slow cooling through the freezing-range, the extremely slow cooling ought to lead to greater homogeneousness through better opportunity for diffusion.

As between (1) extremely rapid and (2) moderately rapid cooling through this same range, the former may be expected to lead to greater homogeneousness through impeding the differentiating action of the freezing itself.

91. TAKING THE TWO PERIODS JOINTLY, WHAT PROCEDURE IN FREEZING-PLUS-COOLING SHOULD YIELD THE LEAST RESIDUAL SEGREGATION?—Now let us take these two successive processes, (1) cooling through the freezing-range, and (2) cooling from that range to the cold, and let us for convenience call these jointly "freezing-plus-cooling," a term hardly suited for general adoption but perhaps convenient for this present discussion.

Two sets of conditions suggest themselves, (1) that we are free to change artificially the rate of cooling at the end of the freezing period, so that we may if we so elect cool slowly through the freezing-range and quickly below it, or *vice versa*; or if we so elect quickly through both ranges, or slowly through both. This then is an artificially variable rate of cooling.

The other set of conditions is that we are not thus free; that if for instance we remove heat rapidly, and hence cool rapidly, through the freezing-range, we must allow the external conditions which have induced this rapid removal of heat, this rapid cooling, to continue undisturbed till the mass is cold, so that the cooling below the freezing-range also would be relatively rapid.

It is true that, even if we thus leave the external conditions of cooling undisturbed throughout the whole freezing-plus-cooling, *i. e.*, even if we do not vary the rate of removal of heat artificially, the fall of temperature will vary from inherent and natural, as distinguished from artificial, causes.

Two sources of such natural variation in the rate at which the temperature will fall deserve notice. They are as follows:

(1) The removal of heat will slacken progressively both during freezing and during the cooling from the freezing-point

downwards, simply because the temperature is continuously approaching that of the cooling medium, with the inevitable consequence that the flow of heat from the mass we are cooling to that medium must slacken as the temperature difference between the two decreases.

(2) The actual fall of temperature will be retarded during the freezing proper, by the liberation of the latent heat of solidification. Again, during this freezing the fall of temperature of the containing walls of the crucible, furnace, or whatever contains our freezing mass, will on this account outrun the fall of temperature of the freezing mass itself; therefore, as soon as freezing has ended and this liberation of heat has ceased, the fall of temperature of the mass just frozen will accelerate spontaneously. A like retardation and subsequent acceleration will occur whenever the mass in cooling passes a temperature or range of temperature in which occurs some exothermic transformation, such as the recalescence of steel.

But these variations or perturbations of the fall of temperature are natural; they are very slight compared with the artificial variations which we may introduce, for instance by allowing the mass experimented on to freeze extremely slowly in a furnace, the temperature of which is purposely held only a very few degrees below the freezing-range of that mass, and then, so soon as that mass has frozen, but before it has cooled many degrees below its freezing-point, while it is still say red-hot, plunging it into iced brine or some other freezing-mixture.

Let this suffice to explain the distinction between a natural and an artificially variable rate of cooling-plus-freezing.

Let us consider these two sets of conditions consecutively.

92. CASE I, THE RATE OF COOLING IS ARTIFICIALLY VARIABLE.—In this case, what rate of freezing-plus-cooling should be expected to lead to the least residual segregation? For given length of time available for the whole, it seems probable that it should be (1) rapid passage through the freezing-range, in order to restrain the initial segregation, followed by (2) slow cooling below that range. It is true that the quick passage through the freezing-range lessens the opportunity for equalization by diffusion in that range; but on the whole it seems probable that this loss may be compensated for by correspondingly retarding the cooling below the freezing-range or even by holding the alloy at