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著者	IWASE Keizo, HOMMA Masao
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Abnormal Steel and its Structure*

Keizô IWASÉ and Masao HOMMA

The Research Institute for Iron, Steel and Other Metals

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I. The nature of the abnormal steel**.

(a) Introduction. Some carburized steels show strange structures in the hyper-eutectoid zones as shown in Photos. 1 and 2. The steel which shows such a structure is called in general as an abnormal steel. As to the nature of abnormal steel there exist many important papers(1)-(17), according to which the following three different theories have been proposed as to the cause of the occurence of the abnormality.

(a) Pure iron theory(2)-(5).
(b) Oxygen theory(6)-(9).
(c) Fine grain theory(10)-(11).


×400×1/2
Photo. 1. Abnormal structure, (etched with picrate and Nital)


×250×1/2
Photo. 2. Abnormal structure; cooling rate 7°C per min.; Ar_1 point at 704°C.

When electrolytic iron or carbonyl iron is carburized, an abnormal structure is always obtained and this fact is the base of the pure iron theory. On the other hand the oxygen theory is based upon the following facts, namely, (i) The normal steel becomes abnormal when it is oxydized in the molten state or carburized in the solid state with materials containing oxygen(12),(13). (ii) The steel insufficiently deoxydized in the course of refining in the molten state also shows the abnormal structure(7),(8). These facts seem to suggest that the cause of the abnormality lies in iron oxide or the like contained in the steel.

The fine grain theory stands on the fact that steel becomes abnormal when it is very fine grained. It is well known that steel becomes very fine grained when it is deoxydized with aluminium and it is claimed that the use of aluminium for the deoxydation of steel causes its structure to become abnormal(11),(14),(15).

Apparently the first and the second theories contradict with each other because steel contaminated with oxygen is called in general impure or dirty steel, and the third theory seems to make the solution of the phenomena even more difficult because aluminium is a strong deoxydizer. This interesting but complicated phenomenon has also been investigated by the present writers with the anticipation that all the facts observed by the numerous authorities might be satisfactorily explained by a physico-chemical consideration, and hence some experiments have been made to test this aspect.

(b) Experiments and conclusion: A few percent of cobalt or nickel was added to molten normal steel (basic open hearth steel)

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** K. Iwasé, M. Homma., J. Inst. Metal, Jap., 4 (1940), 351.

and after uniform melting of the mixture, a not inconsiderable quantity of iron oxide was added, and after thorough stirring, the molten mass was cast in a mould. A piece of the casting was then carburized with charcoal powder containing barium carbonate and then observed under the microscope. The structure was always normal. In this experiment iron oxide could be observed in the solidified mass before carburization but this iron oxide was found to be reduced on carburization, while other non-metallic inclusions such as SiO_2 and the like remained unchanged. As cobalt and nickel are nobler than iron, they will remain in their metallic state in the above melting process and will go into the solid solution of iron when solidified, which makes the steel normal, the non-metallic inclusions causing no abnormality. The influence of cobalt or nickel upon the normality of the structure of the steel may be seen in Fig. 4 in the next section.

In the next step similar experiments were made in which Al or Si was added instead of Co or Ni, and a marked abnormal structure was obtained in each case. As Al and Si are more basic than the iron, and as a sufficient quantity of iron oxide to oxydize all of these basic metals was introduced in the above experiments, these basic metals were changed into their oxides leaving the iron pure in this meaning. When these steels are solidified, Al and Si do not remain in the metallic state and the solid solution of iron is pure in this meaning, in spite of the large content of the non-metallic inclusions. Such steels should naturally show abnormal structures according to the pure iron theory. The influence of Al and Si upon the normality of the structure of the steel may be seen in Figs. 3 and 4 in the next section. The above explanation may also be supported by the following considerations.

Steel sufficiently deoxydized with Si contains the metal combined with iron as a solid solution because traces of the oxygen in the molten iron can only be removed by using a deoxydizer in such quantity as would inevitably combines with iron as solid solution as shown in Fig. 1. When more than 0.05% of Si is contained in the solid solution of iron, the steel becomes normal as will be seen in Fig. 4 in the next section. As ordinary steel contains 0.2 percent or more of Si, it may naturally be normal. Hence the abnormality of insufficiently deoxydized steel may be attributed to the absence of metallic silicon in the solidified mass.

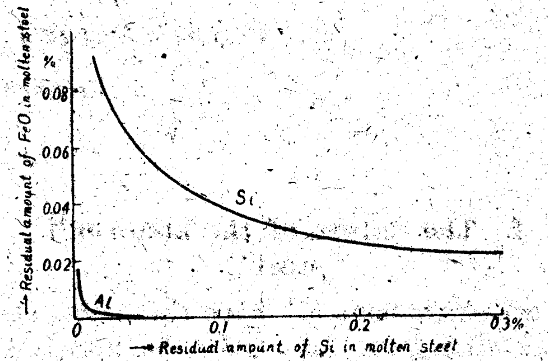

Fig. 1.

As Al is a strong deoxydizer as compared to Si, the steel killed with Al scarcely contains any of the latter in its metallic state as shown in Fig. 2 and hence it is abnormal irrespectively of its grain size.

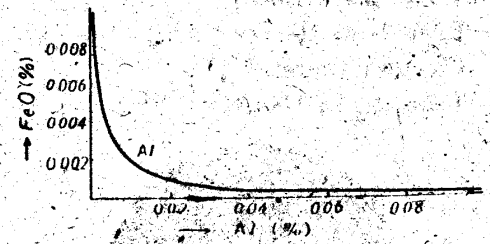

Fig. 2.

When normal steel is carburized with materials cotaining oxygen, the materials act as reducing agents for the iron and will carburize the latter, but act as an oxydiser for metals more basic than iron such as Al, Si contained in the ferrous solid solution, and the above metals are removed from the solution leaving the iron pure, and hence the carburized steel may be abnormal. As has already been said, iron alloyed with a few percent of Co or Ni is normal even when it is carburized with materials containing oxygen.

Thus the pure iron theory and the oxygen theory seem to the present writers to be identical as regards the structure of abnormal steel. As to the fine grain theory, the relation between the austenitic grain size and the abnormality will be explained in the next section, in which it will be shown that this theory is to be considered of secondary significance.

II. The influence of the alloying element upon the abnormality of steel*.

In another series of experiments by the present writers, the influence of the alloying element upon the abnormality of steel was investigated, the results of which will be summarized briefly as follows.

As in the course of the previous experiments it was found that the melting of the specimen in porcelain crucibles induces the reduction of the silica when the carbon content of the steel is high and the silicon thus formed combines with iron. Hence in the following experiments all the specimens were carburized in the solid state to such depth as the carbon content at the center of the specimen became neary 1%.

The ferro-alloys were prepared from electrolytic iron with various alloying elements numbering about fifteen, melting the two together and then casting in a mould. The casting was then carburized in the ordinary way and then cooled in a furnace. The austenitic grain size and the structure were next observed under the microscope. Fig. 3 represents as an example the result in the case of Si. In the figure the abscissa represents the percentage of Si in the steel and the ordinate the grain size in ASTM scale. N means normal, A abnormal, while I before A and N indicates that the strtucture is slightly modified from their respective forms. The curve drawn in it separates the normal field from the abnormal. As it can be seen from the figure, Si acts as a strong normalising element so that more than even 0.05% of it normalises the steel when the grain size number is less than 5 or 6.

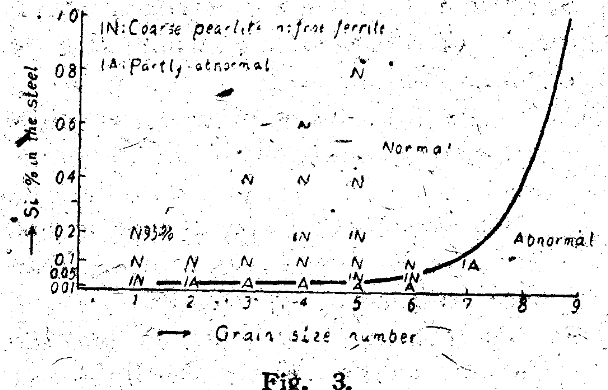

Fig. 3.

Fig. 4 represents a similar relation with regard to other alloying elements. As to the intensity of the normalizing power of the elements, the following classification may be made tentatively.

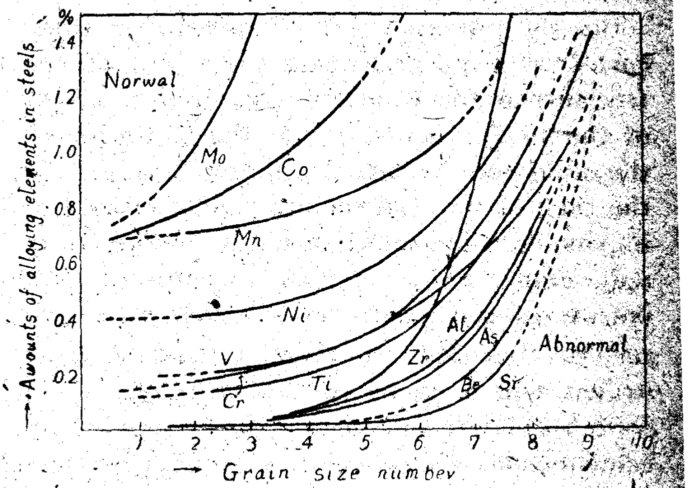

Fig. 4.

(i) Strong normalizers: Si, Be, As, Al, Zr.
(ii) Medium normalizers: Cr, Ti, V.
(iii) Weak normalizers: Ni, Mn, Co, Mo.
(iv) Non-normalizers; W, Cu. (up to about 5% -abn.)

As will be seen from the figure, when the grain is so fine as to be No. 9 or 10, the normal structure is seldom obtained even by alloying one percent or more of the strong normalizing element. The abnormal structures were somewhat modified in some of these alloy steels but the essential features were not altered. It was also observed that when the grain was so fine, no pearlite was formed.

The influence of the co-existence of two alloying elements upon the structure and grain size were also studied by the present writers, but no further description will be made here.

III. Some experiments to find the clue to the mechanism of the formation of the abnormal structure**.

As to the mechanism of the formation of the abnormal structure, various explanations have heen proposed by many investigators, some of whom consider that the cementite

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* M. Homma, J. Inst. Metal Jap., 8 (1944), 106, 206, 315; 9 (1945), No. 4, 3.

** K. Iwase, M. Homma, T. Mochida, J. Inst. Met. Japan, 8 (1944), 587.

formed as a constituent of the pearlite migrates toward the primary cementite through the ferrite by the difference of solubilities of the primary and the pearlitic (finer) cementites, leaving pearlitic ferrite unchanged, or in other words, the pearlitic cementite deposits upon the primary cementite.

But the present writers consider that when cooled at a moderate rate the width of the free ferrite found in the abnormal structure of the steel, is so wide that the migration of the cementite through this ferrite layer during the time of the said cooling would seem to be impossible. The mechanism is considered in a different way by the present writers, and the outline of the experiments which gave the results that led to their conclusion was drawn, will be given in the following.

(a) The hyper-eutectoid steel prepared by cementation of electrolytic iron was quenched from its austenitic state to obtain the martensite, and was then tempered at 710 718°C for about 60 minutes. By this heat-treatment the structure shown in Photo. 3 was obtained, in which the cementite particles near the primary cementite have migrated through the ground mass of ferrite and there appeared a free ferrite area around the primary cementite. However the sorbitic part gradually merges into the ferritic and there is no sharp boundary between them. The same steel was next cooled from its austenitic state to room temperature at a cooling rate of 7° C per minute through the Ar_1 range, during which the horizontal arrest on the cooling curve was found at about 704° C. The structure of the specimen thus obtained was abnormal as shown in Photo. 2, in which a sharp boundary can be seen between the free ferrite and the pearlite. The above fact shows that the abnormal structure is easily obtainable by cooling the steel from its austenitic state through the Ar_1 range and not by a long annealing of pearlite or the like once formed from the austenite.

×250×1/2

Photo. 3. The same steel as that of Photo. 2, quenched and tempered at 715~718°C for 60 min.

(b) In other series of experiments, the same specimen was cooled from its austenitic state through the Ar_1 range at slightly different cooling rates. In each case the structure obtained was the more abnormal the slower the rate. In the next place, in order to quench the specimen after it had begun the reaction corresponding to the horizontal arrest, the cooling curves of specimens of the same kind were again taken with a moderate cooling rate. Then the first specimen was quenched after the beginning of the said arrest, the second at the middle part and the last at nearly the end of the arrest. The abnormality (broadness of the free ferrite) of the structure was nearly the same in all cases and the sum of the areas of the pearlite and of the martensite was also nearly the same in every case, the martensite predominating in the first specimen and the pearlite in the last one. In every case there were sharp boundaries between the free ferrite and the pearlite. The same specimen was next quenched, at the PSK temperature and in this case no free ferrite was found in the specimen, though the cooling rate was same as before. These facts may indicate that the horizontal arrest on the cooling curve corresponds to the formation of the pearlite—Ar_1 change and that the broad ferrite around the primary cementite is formed directly from the austenite, supercooled below the PSK temperature, prior to the formation of the pearlite.

Before explaining the mechanism of the formation of the abnormal structure, it may be convenient to review the characteristic features(16) of this structure, which may be put down as follows:-

(i) The width of the primary cementite is large as compared to that in normal steel(17).

(ii) Between the primary cementite and the pearlite there exists a broad clearance occupied by free ferrite.

(iii) There is a sharp boundary between the free ferrite and the pearlite.

(iv) In the ferrite zone few particles of the cementite can be seen.

IV. Phase changes in the formation of the abnormal structure[*].

It is assumed by the present writers that the formation of the pearlite requires more supercooling below the PSK line (or more strictly below the SR line in Fig. 5) than normal steel. This assumption may be considered as natural because the pearlite is absent around the primary cementite in the abnormal structure (the cause of which may be the nature of the steel that forms the nucleus).

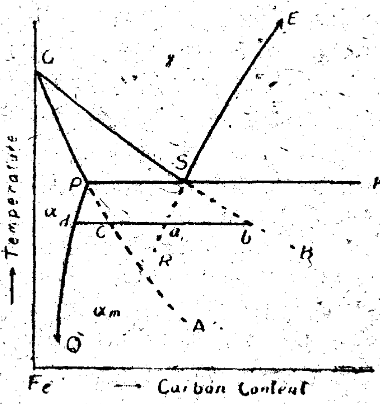

Fig. 5.

The phase changes taking place in the formation of the abnormal structure are considered as follows.

When a hyper-eutectoid abnormal steel is cooled from its austenitic state, it separates out the cementite primarily along the curve ES, passes the point S and further continues its separation along the curve SR, becoming more and more supercooled from the curve GS as the temperature lowers. Therefore the meta-stable ferrite on the curve PA may finally separate out from the austenite on SR, which in turn induces the formation of the pearlite in the case of normal steel, because the austenite leaves the curve SR and becomes supersaturated with the cementite when it separates out the ferrite. But in the case of abnormal steel, the formation of pearlite does not take place and the separation of the ferrite is continued, becoming the more supersaturated as the ferrite is separated. The separation of the ferrite must naturally take place along the primary cementite because the carbon concentration in the austenite is the least at that point. As the ferrite continues to separate out from the austenite it will become more favourable for the formation of pearlite, and will finally realise resulting in the abnormal structure. In the above explanation the separation of cementite from the meta-stable ferrite on curve PA has been neglected for simplicity. This separation of cementite from the meta-stable ferrite is closely related to the broadening of the free ferrite in the abnormal structure as will be shown in the next paragraph.

For the sake of simplicity it may be assumed that the temperature is held constant at the instant at which the austenite, reaching the point *a* along the curve SR, separates out the ferrite. Then this ferrite is represented by the point *b* and by further separation of ferrite *c*, as the time goes on, the remaining austenite becomes more supercooled from SR and the less from SB. If the separation of cementite from the austenite takes place, it may induce the formation of pearlite and all of the austenite will vanish, the width of the free ferrite in this case being not so broad, that is, the abnormality will be less significant. In another case, however, the separation of cementite from the austenite will not take place and only the ferrite will continue to separate out and, before the austenite reaches the point *b*, it may happen that the cementite separates out from the ferrite at *c* as it is supersaturated with carbon. Then at the contact surface between the austenite and the ferrite, which is becoming poorer in carbon than *c*, a reaction may again take place to form the ferrite at *c*. By this reaction the quantity of the ferrite phase increases at the expense of the austenite phase, which may be regarded as a sort of Ar_3 transformation. This may be more easily understood when the reaction takes place after the austenite has reached the point *b*. In this case the ferrite *c* and the austenite *b* are in equilibrium with each other, and the separation of cementite from the ferrite will disturb the said equilibrium, as a result of which a change must take place to regain the equilibrium. This change occurs between the two phases at their contact points in such manner that a part of the austenite at *b* is consumed while the composition of the ferrite returns to the point *c*, the quantity of the ferrite phase increasing as a whole, (if the ferrite reaches the point *d* by

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[*] K. Iwasé, M. Homma and T. Mochida, loc. cit.

the separation of cementite, then the reaction proceeds in such a way that *d* and *b* reacts to form *c*). A similar reaction has been explained in the case of the decarburization of steel in the preceding paper and has been named by the present writers the lateral Ar_3 transformation.

By this lateral Ar_3 transformation the equilibrium is regained and further separation of the cementite from the ferrite will again disturb the equilibrium for which the same transformation will be followed and in such a manner the quantity of the austenite will decrease and that of the free ferrite increase as time goes on, until finally all of the austenite will be converted into ferrite. If, in the course of the above reaction, a separation of cementite from the austenite takes place, it may also induce separation of ferrite, which is no other than the formation of pearlite. Thus the structures shown in Photos. 1 and 2 will be formed. The broadness of the primary cementite is caused by the separation of the cementite from the meta-stable ferrite when the formation of the nucleus in the matrix of the ferrite is difficult.

The above explanation can interprete satisfactorily the observed phenomena already mentioned, that is,

(1) that the free ferrite seems to be formed between the temperatures of PSK and Ar_3.

(2) that slow cooling favours the formation of the abnormal structure.

(3) the sharp boundary between the ferrite and the pearlite (by the co-existence of the ferrite and the austenite at the instant at which the ferrite is formed.).

The fineness of the austenite grain may naturally favour the progress of the lateral Ar_3 transformation above mentioned because the contact area of the ferrite and austenite is large as compared to that of a coarse grained specimen.

In some abnormal structures the primary cementite and the pearlite lie side by side in one part and are separated by free ferrite in another, and in some cases a few cementite needles bridge the pearlite and the primary cementite through the free ferrite. This may be attributed to the character of the steel for the formation of the nucleus in the austenite and the ferrite grains.

In the present study the cause of the occurrence of the soft spot formed when the abnormal steel is quenched has not been touched, but as this is related to the hardenability of steel and is closely related to the purity and to the austenitic grain size of the steel, no further explanation will be needed.

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