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Research on the Relation between Cast Iron and Oxygen. II

On the Mechanism of the Formation of White Cast Iron in the Presence of Carbide Forming Elements*

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Synopsis

Carbide forming elements were similar to oxygen for the formation of white cast iron, although the amount required is greatly different from element to element. Hence, an analogous explanation was found to be applicable to the cases of carbide forming metals. This fact is collaborated by the experiments of reducing oxygen contents in cast iron melts containing carbide forming metals.

I. Introduction

A cast iron melt turns into white cast iron on solidification in the following three cases: 1. When the melt is supercooled. Physically, this may occur when the cooling rate is abnormally high, or chemically, when the oxygen content in the melt is reduced, as proven in our hereafter study; 2. When the percentage of oxygen and sulphur content in the melt is increased; 3. When carbide forming metal elements, such as chromium, manganese, tungsten and molybdenum are progressively added to the melt. We have reported⁽¹⁾ detail the study on the case 2. In the present paper, the study on the mechanism of white cast iron formation in the case 3 is reported.

Carbide forming metal elements (hereinunder referred to as M) tend to stabilize Fe_3C molecules and are prone to build up double carbides, or replace some iron atoms in Fe_3C molecules with their own atoms, and thus interfere with the crystallization of graphite, causing crystallization of ledeburite in its stead, which makes for the formation of white cast iron. This theory has won general conviction thus far, but no research to question the validity of the theory has been reported. Matono,⁽²⁾ who explain the white case iron forming tendency of oxygen by the absorption of oxygen atoms by graphite, touched on the mechanism of white cast iron formation under participation of M, to the following effect. When the percentage of M in solution increases, Fe_3C becomes more and more stabilized, resulting in the approach of the eutectic temperature for Fe_3C to that of graphites and, accordingly, resulting in the reduction of the difference of temperature necessary for causing supercooling. This will in turn result in white

* The 687th report of the Research Institute for Iron, Steel and Other Metals. Published in the Journal of the Japan Institute of Metals, 16 (1952), 169.

(1) K. Iwase and M. Homma, Sci. Rep. RITU, 4 (1952), 392.

(2) T. Matono, J. Iron and Steel Inst. Japan, 27 (1941), 832.

cast iron formation at a slight supercooling. At the same time, chromium and similar metal atoms are absorbed at the active periphery of the graphite crystals, similarly as oxygen atoms are absorbed, hampering the growth of graphite crystals. Thus the cast iron becomes white. We will hereunder make clear the similarity and difference of M and oxygen in their activity in the formation of white cast iron, with regard to the similarity of M to oxygen in their behavior toward cast iron.

II. Similarity of behavior of carbide forming elements to oxygen

It is widely known that chromium, manganese and other carbide forming metal elements interfere with graphitization at annealing treatment of white cast iron, and tend to whiten the cast iron at solidification of cast iron melt. As reported already,⁽¹⁾ oxygen in the melt, has a strong effect on the formation of white cast iron in case of small percentage, and in solid⁽³⁾ it has a tendency to hamper the growth of graphite in white cast iron. For example, an addition of chromium to a grey cast iron rod, 1 inch in diameter, composed of coarse flake graphite and ferrite, will cause a structural change as shown in Table 1.⁽⁴⁾ This change is quite

Table 1

Cr%	Structure
0	Coarse Graphite and Ferrite
0.30	Less Ferrite and finer Graphite and Pearlite
0.60	Fine Graphite and Pearlite
1.00	Fine Graphite and Pearlite and small Carbide
3.00	Graphite disappears
5.00	Much massive Carbide

analogous to that caused by the increase of oxygen content, as pointed out in our previous report,⁽¹⁾ namely: Coarse flake graphite structure → Fine flake graphite structure → Eutectic graphite structure → Inverse chilled structure → White cast iron. It must be pointed out, in this connection, that whereas inverse chilled structure enters into the chain of change induced by oxygen as described above, mottled structure takes its place in the M reaction chain. Sulphur in itself also does not cause inverse chilled structure to appear, unless oxygen is coexistent. We will further touch on this point in the subsequent chapter. The inverse chilled structure appears as a result of segregation of oxygen in a very small amount at the periphery and core of the specimen, but in the presence of sulphur and M, the minute difference of solid solution caused by the segregation is not sufficient to show the effect. When manganese is progressively added to an alloy which is rich in oxygen content and is accordingly very prone to show inverse chilled structure, as shown in Table 2, under extra-furnace cooling at the rate of about 9° per min. between 1,400~900°C, the inverse chilled structure gradually disappears.

(3) H. Sawamura, *Suiyokai-Shi*, **6** (1929); R. Heine, *Foundry*, **77** (1949), 84; 239; Kinoshita, *J. Iron and Steel Inst. Japan*, **37** (1951), 13.

(4) *Symposium on Cast Iron*, Chicago and Philadelphia, (1933), 36.

That is, the addition of 0.2 per cent of manganese will cause appearance of inverse chilled structure partly at the periphery, mottled structure appearing at the core; with 0.3 per cent of manganese, the inverse chilled structure disappears altogether, mottled structure prevailing all over; and when the manganese content is raised to 0.5 per cent, the cast iron becomes entirely white. In this experiment, the addition of manganese caused a corresponding decrease of oxygen content with consequent decline in the tendency of inverse chilled structure formation, the white cast iron forming effect of manganese being strengthened at the same time, which caused the appearance of mottled structure — the structure only one step removed from all-out white cast iron structure.⁽⁵⁾

Table 2

Composition, % Specimen	C	Si	Mn	P	S
Alloy	4.21	0.21	0.035	0.121	0.042

In industrial practice, graphite is, in general, finer in oxygen rich electric furnace cast iron than in cupola cast iron, which is due to the white cast iron forming effect of oxygen. This principle makes it possible to increase the tensile strength of a cast iron by adding an appropriate amount of oxygen to it.⁽⁶⁾ To obtain some high-class cast iron, it is usual to lower carbon content and to increase manganese content, with the end of hampering the growth of graphite crystals and keeping down their size.

Though there is considerable difference in quantitative efficiency, oxygen, sulphur, chromium, manganese, molybdenum and tungsten, all have white cast iron forming tendency, and it is of some interest that the above elements, without exception, belong to the 6th column in Periodic Table. This fact justifies us in presuming a common behavior of all these elements toward carbon in a cast iron melt, for example, a common tendency to combine with iron and carbon atoms into clusters, as described in the previous report.⁽¹⁾ The tendency for white cast iron formation is also strongest in oxygen, and weakens in the order of sulphur, chromium, manganese, molybdenum and tungsten in the same order as they are placed in Periodic Table. Matono estimated the power of white cast iron formation of sulphur and chromium as 1/10 and 1/100 of oxygen, respectively. Tanaka⁽⁷⁾ said that, with 1 per cent of chromium and 4 per cent of each of manganese and tungsten, there is a critical temperature around the melting point of 1,200°C, and white cast iron is formed by solidification below the critical temperature and above the critical temperature grey cast iron is formed. It may be assumed that this phenomenon is caused by the decrease of oxygen in solution with the rise in

(5) A. Boyles, *T. Amer. Inst. Min. Metall.*, **125** (1937), 141; **135** (1939), 376.

W. Williams, *J. Iron and Steel Inst.*, **164** (1950), 407.

(6) Oberhoffer, *Stahl und Eisen*, **47** (1927), 521; T. Sato, *J. Iron and Steel Inst. Japan*, **35** (1949), No. 11, p. 5.

(7) S. Tanaka, *J. Iron and Steel Inst. Japan*, **25** (1939), 630.

temperature, resulting in the weakness of white cast iron forming tendency of the M elements concerned. In the present research, it was ascertained that in a cast iron with ordinary oxygen content containing 3.1~3.3 per cent of carbon, 1.3 per cent of silicon and 0.1~0.2 per cent of manganese, the effect of sulphur appeared as 0.04 per \gtrsim S 0.02 per of sulphur against grey cast iron \lessgtr white cast iron. The mutual behaviors of oxygen, sulphur and M should be examined with specimens in which the quantitative relations among these elements are clearly known. In comparing the efficiency of these elements in their wt per cent, beside the inherent difference in their white cast iron forming effect due to the difference in atomic weight, it may be imagined that M atoms enter in some plural number against each atom of carbon and oxygen in one cluster, but such suppositions must be verified by further researches. At any rate, this fact may be taken to be one of the factors determining the efficiency of forming white cast iron. There is a difference,⁽⁸⁾ anyhow, among the carbide forming elements, in their tendency in changing cast iron structure. The orders, arranged from the weakest to the strongest, are as follows: tungsten, molybdenum, vanadium, chromium in prevention of decomposing white cast iron structure (graphitizing tendency); tungsten, molybdenum, manganese, chromium, vanadium in the tendency to deepen the chilled structure; tungsten, molybdenum, chromium, vanadium in the tendency to produce white cast iron at solidification; tungsten, manganese, molybdenum in preventing decomposition of pearlite.

III. White cast iron formation by carbide forming elements

In the previous report,⁽¹⁾ we have considered the existence of Fe-C-O-Fe clusters, in explaining the mechanism of white cast iron formation under the influence of oxygen, and if we may assume the existence of similar clusters of Fe-C-M in the present case, the same reasoning may be applicable. The reason for postulating the existence of Fe-C-M clusters, their nature and their activity will be given below.

(1) When, in Fe-C alloys, the content of strongly carbide forming metal elements, such as chromium and tungsten, is large, the existence of double carbides, such as $(\text{FeCr})_4\text{C}$, $(\text{FeCr})_7\text{C}$, $\text{Fe}_3\text{W}_3\text{C}$, $\text{Fe}_4\text{W}_2\text{C}$ in the solid state has been ascertained. When such double carbides are contained in the solid, we may be justified in assuming the existence of clusters in the form of Fe-C-Cr, Fe-C-W etc., in considering the quasi-crystalline structure of the melt just above the solidification point. In the case of very dilute solution of such elements, there may be no such clusters, but when the M content rises high enough to cause white cast iron formation, we may well presume the existence of such clusters in the melt. Manganese is weaker in its white cast iron forming efficiency than chromium and tungsten, but, as double carbides such as $3\text{Fe}_3\text{C}\cdot\text{Mn}_3\text{C}$, $2\text{Fe}_3\text{C}\cdot\text{Mn}_3\text{C}$

(8) H. Tanimura, Lecture at the 6th Sectional Meeting of the Japan Inst. of Metals, (1951, Spring).

and $(\text{FeMn})_3\text{C}^{(9)}$ are found in the solid state, there is no doubt that Fe-Mn-C clusters are formed in the melt, provided that the content of manganese is sufficient to produce white cast iron. It must not be imagined, however, that the combination is in the state of molecules, but only that clusters are formed of iron, carbon and M atoms in a special arrangement and in comparatively strong bonding. These atoms in clusters are thought to be chemically less active and physically in more stabilized state than the atoms of free state.

(2) In the melt in which the strongly carbide forming element M is of considerable concentration, it may be assumed that there exist aggregation and segregation of M and carbon above the average concentration. This is similar to the case in which Fe-C-O-Fe clusters were postulated.⁽¹⁾ According to the study by Saito,⁽¹⁰⁾ when nitrogen gas is absorbed in Fe-Cr and Fe-Mn alloys, there occur aggregation and segregation of nitrogen, chromium and manganese atoms, due to the stronger affinity of nitrogen toward chromium and manganese atoms than toward iron atoms. It may analogously be assumed that when carbon is in solution in stead of nitrogen, M and carbon will aggregate and segregate locally in a larger concentration than the average. This fact seems to confirm the existence of clusters of the special combination of Fe-M-C in the melt.

(3) In studying the behavior of manganese toward carbon from the effect of manganese upon the activity coefficient of carbon, Smith⁽¹¹⁾ ascertained that, in γ -iron at 1,000°C, the increase in manganese content lowered the activity coefficient of carbon, while, the increase in silicon content raised it. This fact also caused the decrease of activity coefficient of manganese in the presence of carbon, and indicated the decrease of carbon and manganese atoms in free state and the existence of specially bonded state of their atoms, though, not to the extent of forming molecule due to the affinity between them. The above behavior of atoms in γ -iron can be considered to be applicable to the quasi-crystalline structure of melt. Silicon can be taken to stand in the relation contrary to manganese against carbon, and such clusters as Fe-Si-C cannot be imagined as existing. From the other standpoint, W. Owen⁽¹²⁾ ascertained that silicon does not dissolve into solid carbides to the extent of 1~3 per cent, from the result of powdered X-ray analysis of Fe-Si-C alloy.

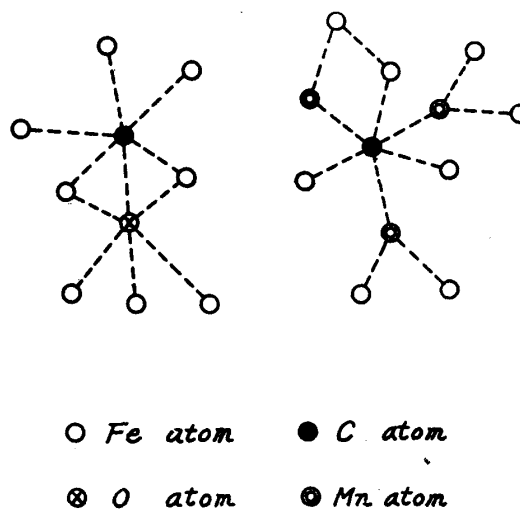


Fig. 1. Fe-C-O-Fe and Fe-C-M Cluster

(9) R. Brick, *Structure and Properties of Alloys*, II Ed. 322.

(10) K. Saito, *J. Japan Inst. Metals*, **B-14** (1950), No. 4, 1.

(11) Smith, *J. Amer. Chem. Soc.*, **70** (1948), 2724.

(12) W. Owen, *J. Iron and Steel Inst.*, **167** (1951), 117.

(4) In comparing the structures of Fe-M-C clusters and Fe-C-O-Fe clusters, under the consideration that M atoms produce molecules of carbides as $(\text{FeCr})_4\text{C}$ and act metallic atoms in the way similar to iron against carbon, it will be more appropriate to assume that more than one atom of M enter in the adjacent combination in one cluster of Fe-C-M, whereas in Fe-C-O-Fe clusters, one of each of oxygen and carbon atoms is assumed. The clusters in comparison may be visualized as in Fig. 1.

(5) The clusters Fe-M-C crystallize into austenite, as do the Fe-C-O-Fe clusters, when they are small in quantity within the limit of content sufficient for white cast iron formation, and M may be assumed to occupy some points of austenite lattice. When the content of M is in great excess, a strong tendency for carbide formation arises, the crystallization of graphite at eutectic point C' is further interfered, crystallization of carbide containing M directly out of the melt may occur and the tendency to form white cast iron is greatly raised. Thus, the tendency for white cast iron formation due to the overabundant manganese atoms in cast iron melt may be ascribed to the existence of Fe-M-C clusters. Depending on the presence or absence of manganese, the melt will solidify into white or grey cast iron as in the case of oxygen. By the way, carbon atoms in such melts exist both in free state and in such combinations as Fe_3C (Fe-C groups) and Fe-Mn-C clusters, and manganese atoms in free state and in Fe-Mn-C clusters.

The degree of white cast iron formation by manganese is determined by the carbon content corresponding to the difference between the point E and E' in the equilibrium diagram and by the amount of Fe-C-M clusters. That is, when the carbon content corresponding to E-E' is comparable to the amount of carbon in Fe-C-M clusters, the amount of M may be taken as the theoretical amount sufficient for the formation of white cast iron. When the amount of M in the melt is lower than this theoretical value, the tendency for white cast iron formation will be lowered, while an excess thereover will strengthen the effect. It will be unnecessary to repeat that the cooling rate has an effect on the process, by reason of the proneness to supercooling; that is, a greater cooling rate will result in white cast iron formation at a lower percentage of manganese.

The above conclusion has been deduced from the comparative stability of the clusters, but the clusters themselves change their behavior with their quantity and other conditions. This fact may be well conceivable when we consider the facile mutability in the cast iron structure by the change in the casting condition.

IV. Experimental proof of the similarity of oxygen and carbide forming elements in changing cast iron structure

As it is beyond dispute that an increase in the content of M will give rise to the tendency of white cast iron formation, we will hereunder give an experimental result that shows the behavior of manganese acting in similarity of oxygen when the decrease of oxygen content is brought about. Oxygen was extracted from the three specimens of chemical composition shown in Table 3, by addition of some

suitable deoxidizing slag. The specimens at first were of coarse flake graphite structure containing the normal amount of oxygen. As the oxygen content was lowered, the structure changed through the following series.

Table 3. Chemical Composition of Specimens.

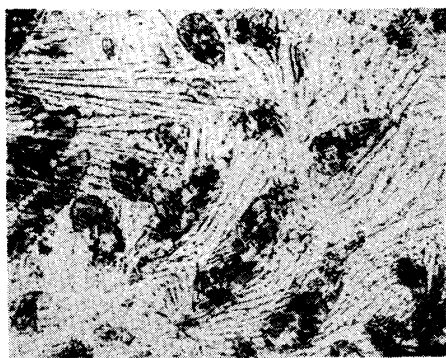
Nos. of Specimen	C	Si	Mn	P	S
1	3.49	1.98	0.003	0.005	0.012
2	3.60	2.03	0.005	0.005	0.008
3	3.68	2.09	0.15	0.010	0.010

Specimen 1; Coarse flake graphite structure (1) → finer flake graphite structure (2) → eutectic graphite structure (3) → superheated (Piwowarsky) structure (4) → supercooled white cast iron structure W_s (5)

Specimen 2; (1) above → (2) above → (3) above → (4) above → (5) above.

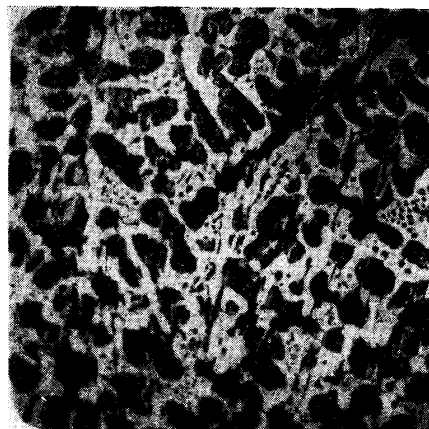
Specimen 3; (1) above → (2) above → (3) above

Of Specimens 1 and 2, white cast iron W_s , different substantially from Oxygen rich white cast iron, W_0 , was produced upon deoxidation while Specimen 3 was stopped at eutectic graphite structure, no further change supervening. The three specimens were deoxidized to the same extent and the chemical composition was the same for the three in respect to carbon, silicon, phosphorous and sulphur, manganese being the only variable, — small in percentage in Sp. 1 (0.003%) and Sp. 2 (0.005%) but large in Sp. 3 (0.15%).



×200

Photo. 1. Structure of White Cast Iron W_s ($\ll O_2$).



×100

Photo. 2. Structure of White Cast Iron W_0 ($\gg O_2$)

The above experiment showed that, at least in the presence of slag with such a degree of deoxidizing power, manganese in excess of a certain amount did not cause the formation of W_s , notwithstanding the decrease in oxygen content. That is to say, in the process of structural change induced by decrease of oxygen, manganese in an excess of a certain amount counteracted the effect of deoxidation, namely, an appropriate amount of manganese behaved in a similar way as oxygen. The process change into supercooled white cast iron structure W_s from coarse graphite structure by deoxidation was due to the fact that, with decrease of

oxygen, the melt becomes gradually supercooled, resulting in solidification at the eutectic point C instead of C', accompanying minimization of graphite crystals. This may be understood also by the supercooled needle-form structure, W_s , of ledeburite as shown in Photo. 1. On the other hand, the ledeburite in white cast iron structure, W_0 , formed by increase of oxygen content was observed as an aggregation of granular austenite, as shown in Photo. 2.

The existence of manganese decreases the supercooling effect in spite of deoxidation, as if the oxygen has not been removed, and by the experiment in which 0.15 per cent of manganese was present, the effect of supercooling was not allowed to go beyond the stage of eutectic graphite structure. Seeing that white cast iron formation is promoted by the increase of oxygen or manganese independently, the case of increase both in oxygen and manganese has been disregarded and only the experimental proof of the behavior of manganese in the case of diminished oxygen content was given. In other words, manganese will act in place of the extracted oxygen, showing results as if no deoxidation has taken place, and, in this respect, manganese behaves in a way quite similar to oxygen in the process of structural change. It must, however, be pointed out that such actions of oxygen and manganese are limited to the case of solidification of cast iron melt, being quite different in solid steel and cast iron.

Many experiments have been reported on the various behavior of cast iron of the same chemical composition under different external conditions, such as inclusion of non-metallic substances or gas, but the above described case will be of interest in that the behavior is affected by the difference in the amount of one chemical component, manganese, under the same extent of deoxidation. The content of nitrogen was constant in all specimens at 0.008~0.009 per cent, and there has been no experimental condition under which hydrogen content was changed.

Conclusion

The carbide forming metallic elements are very similar to oxygen in that they give rise to a tendency of white cast iron formation and in their behavior in the mechanism of structural change of cast iron, though in a wide variation in quantity. The above study approached this problem from various stand-points. As the effect of oxygen in the mechanism of forming white iron can be deduced from the presence of Fe-C-O-Fe clusters and their quantity in relation with the amount of carbon corresponding to E-E', the existence of Fe-C-M clusters in the melt and their effect in the mechanism of white cast iron formation can be demonstrated in the same way. The similarity of behavior of manganese and oxygen toward structural change at the solidification point has been verified by the experiment on deoxidation of cast iron melt.

Our thanks are due to Prof. Keizo Iwase for his valuable instructions. Also we must mention with appreciation that a part of the present experiment was made possible by the assistance granted us in the shape of Scientific Research Fund by the Education Ministry.