Research on the Relation between Cast Iron and Oxygen. I : The Mechanism of the Formation of White Cast Iron under the Influence of Oxygen

著者	IWASE Keizo, HOMMA Masao
journal or publication title	Science reports of the Research Institutes, Tohoku University. Ser. A, Physics, chemistry and metallurgy
volume	4
page range	392-402
year	1952
URL	http://hdl.handle.net/10097/26520

Research on the Relation between Cast Iron and Oxygen. I
The Mechanism of the Formation of White Cast Iron under the Influence of Oxygen*

Keizo IWASE and Masao HOMMA

The Research Institute for Iron, Steel and Other Metals

(Received June 8, 1952)

Synopsis

It has been known that oxygen in the melt gives rise to the tendency of forming white cast iron, but the mechanism of such a phenomenon is yet unknown.

We have herein clarified this mechanism on the basis of the atomic arrangement of the melt of cast iron and the double diagram. In molten cast iron, oxygen atoms behave partly as free atoms and partly as Fe–C–O–Fe clusters, and the latter prevents the melt from solidifying at the eutectic point C′ (austenite-graphite) by unbalancing the lever relation of E′C′F′, with the result that the eutectic point drops from C′ to C of austenite-Fe_3C, inducing the formation of white cast iron. Theoretically, the oxygen content effective for white cast iron formation was estimated to be about 0.01 per cent, an amount equivalent to the carbon percentage corresponding to E–E′.

I. Introduction

It is a well-known fact that the presence of oxygen in melt gives rise to the tendency of forming white cast iron, and, accordingly, any evidence may be thought unnecessary. The mechanism of the phenomenon, however, is not yet convined of. A few studies on the problem have been carried out: for example, the theory that gas tends to stabilize Fe_3C was propounded,(1) but the question why and how the gas stabilizes Fe_3C molecules still remains untouched. According to another theory, oxygen is adsorbed by graphite, or covers the surface of graphite, preventing it from growing, which causes the formation of white case iron.(2) Aside from such theories that assign the cause of white cast iron formation to the presence of oxygen, the graphite nucleus theory states that the presence of graphite nuclei in melt makes for the formation of grey cast iron, which, in reverse, will indicate that the absence of graphite nucleus in melt produces white cast iron.(3) On the other hand, the atomic structure of steel in molten state is becoming more and more clarified. Hence, we investigated the mechanism of the formation of white cast iron, basing on the atomic structure of molten cast iron and the double diagram. We are now in the course of pursuing

---

* The 686th report of the Research Institute for Iron, Steel and Other Metals. Published in the Journal of the Japan Institute of Metals, 16 (1952), 111.

(1) H. Sawamura, The Journal of the Iron and Steel Institute of Japan, 14 (1928), 741.
Baba and Fukuoka, Suiyokai-shi, 8 (1935), 729.

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

(3) H. Tanimura, J. Iron and Steel Inst. Japan, 36 (1950), 6.
M. Hamazumi, *Cast Iron* (1936), 56.

the phenomenon of "heredity" in cast iron, which is as yet unclarified, and it is our belief that the elucidation of the behavior of oxygen in molten iron will lead to the analysis of the heredity.

II. Method of obtaining white cast iron

From the Fe-C double diagram given in Fig. 1, the manner how a given melt of iron becomes grey or white will be explained as follows. Grey cast iron is formed when the melt solidifies at the eutectic point C′ for Fe-G, and then changes according to the diagram for Fe-G. White cast iron is produced when the melt does not solidify at C′ but at C, the eutectic point for Fe-Fe_3C, and then changes according to the diagram for Fe-Fe_3C.

There are three kinds of methods of obtaining white cast iron.

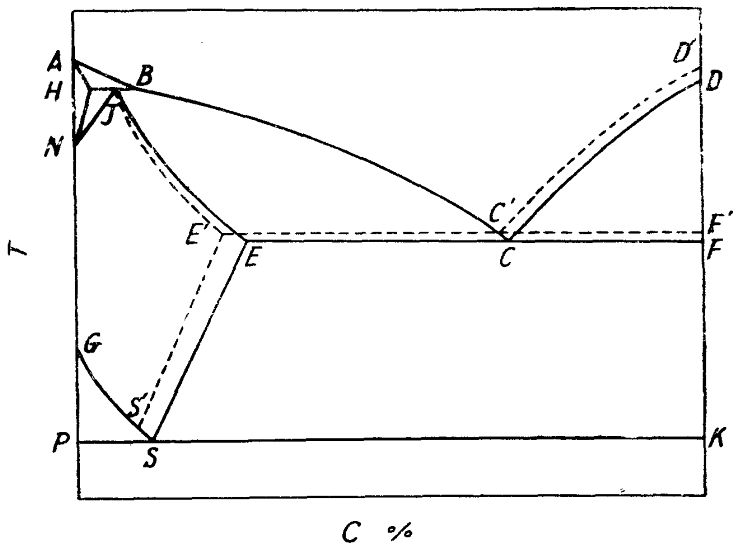

Fig. 1. Double Diagram of Fe-C

1. Supercooling

Supercooling, for example, casting in chilled moulds, or, according to our study,(4) casting under abnormal scarcity of oxygen, which produces supercooling, will produce white cast iron. The melt will not solidify at C′ but drop to C to solidify into Austenite-Fe_3C structure.

2. Increasing oxygen content

As shown in the subsequent papers,(5) by changing the composition and treating time of the slag to increase the oxygen content of the melt, the resulting solid passes the underlisted phases to emerge as white cast iron in the final stage. Taking the usual form of grey cast iron, a piece of cast iron containing coarse flake graphite, which is also the kind of cast iron containing the commonest percentage of oxygen, a gradual increase of oxygen content results in the next series of structural change.

Coarse flake graphite structure → Rose graphite structure → Eutectic graphite structure → Inversed chill structure → white cast iron W_0.

The whitening process by increasing sulphur content may be looked upon as a method coming under this heading.

---

(4) Will be seen in this Report.

(5) Ditto

3. Increasing content of carbide forming metallic elements

Increasing content of carbide forming metallic elements in melt will tend to produce white cast iron. Matono(2) has given the list of such elements in order of their efficacy in the forming of white cast iron as Cr, Mo, W and Mn, but according to Tanimura,(6) the order is V, Cr, Mo, Mn and W. This tendency of white cast iron formation may be considered in relation to the degree of suppressing the decomposition of white cast iron, i.e., the depth of chill and the stability of pearlite.

The above three methods are usual methods of producing white cast iron, and the purpose of the present report is to clarify the mechanism of obtaining white cast iron under the second case, in which oxygen plays an important role.

III. Structure of molten cast iron and double diagram

We will proceed by a brief description of the quasi-crystalline structure of the molten iron just above the point of solidification, and of the double diagram with stress on the location of E and E′.

1. Atomic structure of molten cast iron

In general, when a small amount of solute (in the present case carbon and oxygen atoms) is dissolved in a solvent (iron), that is, in molten steel, when a small quantity of carbon and oxygen atoms is dissolved in molten iron, these atoms may be regarded as being all in a free state and their activity coefficient as 1. But the more carbon atoms, the less carbon atoms in free state become and the activity coefficient becomes less than 1. That is, the atoms in free state decrease as the atoms in fixed state increase. The melt contains free carbon atoms that stand in bonding with iron atoms only through repulsion and attraction and fixed atoms that are in regular arrangement, though not as molecules such as Fe_3C. When oxygen atoms are present in the solution, they are similarly either in a free state neighboring only with iron atoms or in a fixed state in regular arrangement with iron and carbon atoms. When the dissolved oxygen atoms are very high in concentration, regular atomic arrangements, such as FeO, may also be present. When silicon atoms are present, they may be imagined as present in free state, in fixed arrangements as Fe_3Si, FeSi and in a fixed arrangement consisting of iron, silicon and oxygen atoms.

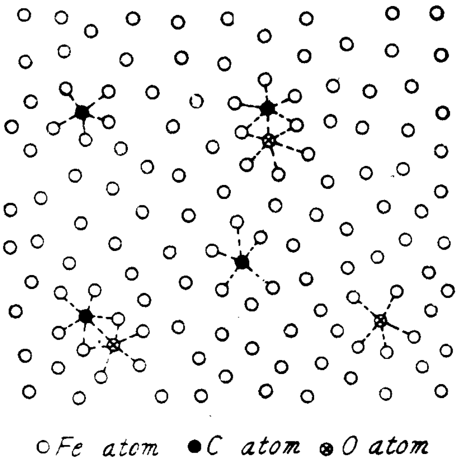

Fig. 2. Atomic Construction of Liquid Fe–C Alloy

Now, let us consider the model of molten cast iron composed of iron, carbon and oxygen as follows.

---

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

A two-dimensional qualitative sketch of cast iron made of iron, carbon and oxygen at just above the melting point, as given in Fig. 2, shows that the iron atoms are not without any order in arrangement, though not so regularly arranged as in crystals. Carbon and oxygen atoms do not enter compounds to form Fe_3C or FeO. In dilute solution of carbon and oxygen, the atoms are bonded to the neighboring iron atoms at a distance due to the mutual repulsion and attraction, the iron atoms are exchanged and the distance between the atoms also undergoes changes. Thus, in this state, we may assume that the activity coefficients of carbon and oxygen atoms are both 1, and that the atoms are free. But, when the carbon content rises, as in a cast iron melt, the activity coefficient of crrbon diminishes, and that of oxygen atom shows a gradual decline, which has been plotted by Chipman⁽⁷⁾ in a curve shown in Fig. 3. At the concentration of 3~4 per cent of carbon, the activity coefficient falls approximatel to 0.1. Under an arrangement of carbon and oxygen atoms in this state, these atoms come into special combinations with the neighboring iron atoms. These combinations do not constitute compound molecules (The term "combination" used hereinunder also does not mean molecules). In this state, it may be assumed that carbon and oxygen atoms are chemically in closer combination than in the state in which each atom is in independent relation only with iron atoms. Chipman considered such combinations in molten steel and called them "complexes" and Rosenqvist⁽⁸⁾ called them "clusters" in expounding the change in activity of sulphur. Hereinunder, the special arrangement of Fe-C-O-Fe will be called clusters, for convenience sake, in proceeding with our exposition.

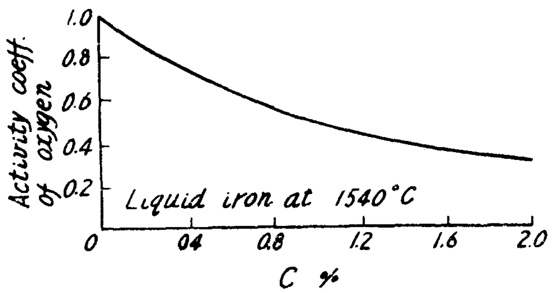

Fig. 3. Activity Coefficient for Oxygen

In alloys with high content of oxygen, as in cast iron, oxygen atoms are for the most part in the form of Fe-C-O-Fe clusters, though a part remains free. If the activity coefficient of oxygen is denoted by f_0 and the amount of oxygen in solution by X, f_0X can be taken as the number of free oxygen atoms and $(1-f_0)X$ as that of oxygen atoms combined in clusters. In molten steel, f_0 is nearly 1, while in molten cast iron it is very small. This indicates that the oxygen dissolved in molten steel is mainly in free state and by using deoxidizing agents, such as silicon, manganese etc., the free oxygen can be eliminated. In cast iron, however, only a small part of the dissolved oxygen is in free state, and deoxydizers can be effective only against this small percentage. This explains why the relatively large amount of oxygen remains in melt after the use of deoxydizers and causes the phenomenon called "heredity" in cast iron, a phenomenon that occasions little problem in steel. These points will be taken up in one of our subsequent reports.

Some metallurgists in the past have maintained that with the increase of carbon

---

(7) J. Chipman, Metals Progress, **56** (1949), 211.

(8) T. Rosenqvist, J. Metals, **188** (1950), 1389.

in iron, which has a deoxydizing effect, the oxygen content is kept down, but this is untenable, since within the scope of dilute solutions manageable thermodynamically, the oxygen content certainly diminishes as the carbon content increases, but this will not be applicable to a more concentrated solution. Furthermore, the fact that Fe–C–O–Fe clusters are formed in molten cast iron is demonstrated by the study (9) which showed that, when some gas is absorbed by a binary alloy, atoms of the metal which is more strongly combined with the absorbed gas atoms aggregate and are localized in a quantity above the average concentration of the metal in the alloy. In the study on nitrogen absorption by Fe–Cr, Fe–Mn and Fe–Ni alloys, chromium, manganese and, in the last alloy, iron atoms are located around nitrogen atoms in a density surpassing the average concentration of these metals. When oxygen gas is absorbed by cast iron, it may be assumed that carbon atoms gather about oxygen atoms and are localized above the average concentration. This means the same thing as the presence of Fe–C–O–Fe clusters in cast iron.

The above fact may also be described as follows: when oxygen is progressively added to the melt of Fe–C alloy, while the oxygen content is still low, they exist in perferctly free state among the iron and carbon atoms, but with the gradual increase of oxygen atoms, an attractive force between oxygen and carbon atoms, which have the stronger affinity with oxygen atoms than the iron atoms, begins to operate, so that the oxygen atoms will lose their free activity under a bonding. Thus a cluster may be assumed to originate. When the oxygen content is further increased, the combination goes beyond the stage of a cluster, and CO molecules burst out and decarbonize the melt. At approximately the same time, Fe–O clusters are also formed, and with further increase of oxygen in solution, FeO molecules will begin to crystallise.

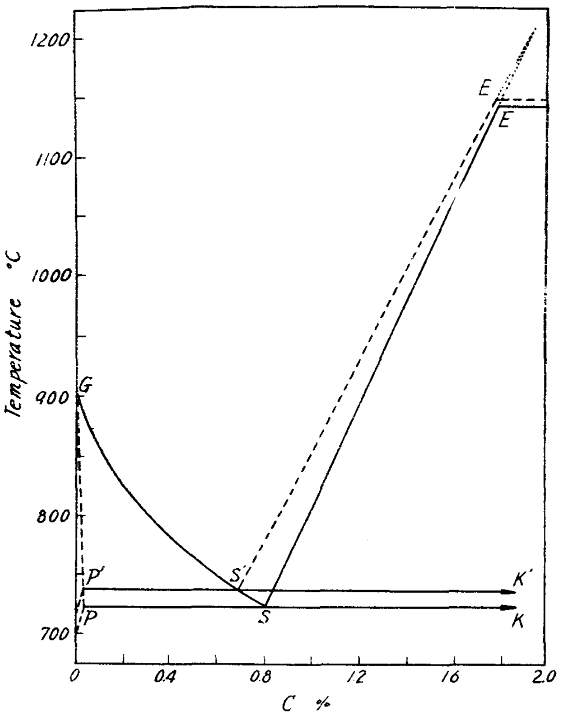

Fig. 4. Fe–Fe_3C and Fe–G Equilibrium Diagram

2. On the Fe–C double diagram

Two kinds of Fe–C diagrams, one based on the single diagram theory of Sauver and Hatfield among others,(10) and the other based on the double diagram theory of Ruer, Merica, Schwartz and others,(10) have been proposed, but we will not touch on the comparative merits of the two. In discussion of the mechanism of white cast iron formation, the necessary factor is the position of E and E′ on the double diagram, as mentioned already.

---

(9) S. Saito, J. Japan Inst. Metals, B-14 (1950), No. 4, 1; 5.

(10) Epstein, *The Alloys of Iron and Carbon*, Vol. 1.

The lines ES and E′S′ have been traced by Piwoarsky, Ruer, Gutowsky, Charpy and others, but we take the values measured by C. Wells(11) in 1938 to be the most reliable, which is shown in Fig. 4. The quantity of carbon at E and E′ cannot be measured directly, but from the position of E and E′ in the figure, the difference of carbon content at E and E′ is about 0.0075 per cent, which corresponds to an equivalent of 0.010 wt per cent of oxygen. As described below, this difference has an important meaning in the influence of oxygen in the formation of white cast iron, and this apparent smallness of the difference in carbon content is the reason why an infinitesimal amount of oxygen so greatly affects the structure of cast iron. The equation, $0.0075\%\,C = 0.010\%\,O$, was adopted on the assumption that in the Fe–C–O–Fe clusters, carbon and oxygen atoms are in the raito of 1:1, as shown below.

IV. Mechanism of white cast iron formation under the influence of oxygen

As stated above, in the molten state of cast iron, carbon atoms exist in the following three states. (1). Free atoms in relation only with iron atoms; (2). Fixed carbon atoms as components of special atom combinations such as Fe_3C (but not in molecules), which will be called Fe–C groups hereunder· (3). Carbon atoms in Fe–C–O–Fe clusters.

1. When oxygen content is low

As very few, if any, Fe–C–O–Fe clusters are present, there is nothing to hamper the crystallization of carbon at the solidification point. (The behavior of Fe–C groups in crystallization at the solidification point can be taken as quite similar in dilute as well as in highly concentrated O_2 solution, as treated in the next paragraph). Consequently, the melt solidifies at the first solidification point C′, the eutectic point for Fe–G, and results in grey cast iron. (In this case, other factors such as supercooling and the presence of carbide forming metal elements affecting the resultant structure will be out of consideration).

2. When oxygen content is very high

This is the case in which the Fe–C–O–Fe clusters are in abundance. (As mentioned below, there is a limit in the amount of about 0.01 wt. per cent of oxygen contained in cast iron, though the content may be sufficient to produce white cast iron). To assure better understanding of the subsequent statements, we will touch upon the nature of these clusters. First, since oxygen and carbon atoms forming these clusters are not free and chemically inactive, they are naturally in firmer combination than other atoms, such as free carbon and oxygen atoms or those in Fe–O and Fe–C groups. Consequently, they offer greater resistance to free crystallization at the solidifying point, in comparison with other oxygen and, especially, carbon atoms. Secondly, carbon atoms in these clusters show difficulty in crystalizing into graphite, as compared with the ease with which other carbon atoms crystalize into graphite. Considering the quasi-crystalline structure of

---

(11) C. Wells. A. S. T. M., **26** (1938), 289.

face-centered cubic lattice with interstitial oxygen and carbon atoms of these clusters, they seem to be more easily crystalized into the nearer-related austenite crystals than into graphite and Fe_3C. Thirdly, as stated below, the amount of carbon behaving as clusters can be considered to be corresponding to that at E–E′. When the melt containing such clusters is cooled down to the upper solidifying point C′, free carbon atoms and a part of carbon atoms in Fe–C groups will tend to crystallize as austenites with carbon contents corresponding to the point E′. Other carbon atoms, except those in Fe–C–O–Fe clusters, tend to crystallize in the form of graphite, similarly to the case of Par. 1. The Fe–C–O–Fe clusters, however, are more resistant to crystallization into graphite than into austenite, and have tendency to crystallize into austenite rather than into graphite, in comparison with other carbon atoms. Hence, if the melt is to crystallize according to the lever relation E′C′F′, there will be a surplus of austenite against the amount of carbon corresponding to the point E′ and, consequently, the solidification cannot take place at the point C′ but at the lower point C. In this case, austenite containing carbon corresponding to E′ crystallizes out of carbon atoms not forming cluster and that containing carbon between E–E′ crystallizes out of the clusters and austenite is produced according to the lever relation ECF, the remainder crystalizing into Fe_3C.

In the above, the number of clusters was taken to correspond to the amount for E–E′, without giving the reason. The reason is that the percentage of carbon atoms corresponding to E–E′ in Well's double diagram is about 0.0075 wt. per cent, which is equivalent to 0.010 wt, per cent of oxygen (as each atom of carbon and oxygen enters a cluster), which is in harmony with the percentage of oxygen content appropriate for white cast iron formation. For cases stated hereunder, in which white cast iron formation occurs under oxygen content not corresponding to E–E′ and under the effect of cooling rate, the mechanism may be deemed as follows: when the amount of clusters surpasses that corresponding to E–E′, austenite is produced from the clusters in excess of the quantity E–E′, and the remainder of austenite necessary for the solidification in the lever relation ECF is crystallized out of carbon atoms present in other forms, which makes the carbon content in austenite lower than the point E. In the case in which the number of clusters is lower than that corresponding to the carbon content at E–E′ and in which white cast iron is formed, the clusters crystallize into austenite with less carbon content than E–E′ equivalent, and the remainder of austenite necessary for the solidification in the lever relation ECF is crystallized out of carbon atoms in other forms, corresponding to the carbon content over the point E′. This is based on the assumption that it is natural for carbon atoms not in clusters to crystallize into austenite in quantity in excess of or lower than that corresponding to E′, when the lower eutectic point C is reached, due to the more or less quantity of clusters, though, in principle, free carbon atoms and carbon atoms in Fe–C groups crystallize into austenite corresponding to E′ according to the principle of equilibrium. The essential difference in the eutectic points C′ and C lies in the fact that solidification and crystallization at C′ does not occur and freely passes when any condition exists to hamper crystallization there, and solidification is brought about when the lower eutectic point C is reached, that is, austenite and Fe_3C are crystallized out.

V. Relation of position of E and E′ and percentage of oxygen sufficient for white cast iron formation

1. Theoretical percentage of oxygen sufficient for the formation of white cast iron

If oxygen content is markedly smaller than the oxygen equivalent to carbon corresponding to E–E′, that is, if the clusters in melt are small in number, oxygen will not interfere with the solidification under the lever relation E′C′F′. Consequently, the larger the difference of E–E′ on the double diagram, the more cluster, or oxygen content, is necessary for the formation of white cast iron. If the difference E–E′ is small, white cast iron will be formed at lower number of clusters or lower oxygen content. This fact results in the determination of the oxygen content sufficient for the formation of white cast iron by the difference E–E′. In other words, the oxygen percentage equivalent to 0.0075 wt. per cent of carbon for E–E′ may be taken as the theoretical amount of oxygen necessary for the formation of white cast iron. This equivalent amount of oxygen may be assumed as 0.010 wt per cent, as each atom of carbon and oxygen interstitially enters the quasi-crystalline face-centered cubic lattice. The theoretical oxygen content for white cast iron formation is expressed as 0.010% = total dissolved $O_2 \times (1 - f_0)$, and if the value of f_0 is negligibly small, as in the case of cast iron, the theoretical percentage of required oxygen will be nearly equal to the total dissolved oxygen content. If f_0 is taken at 0.1, the total oxygen in solution will become 0.011 wt. percent. The value of 0.011 wt per cent of oxygen is the general criterion, a deficiency in this oxygen content tending to form grey cast iron and an excess thereover causing white cast iron formation.

The experimental verification of the theoretical quantity of oxygen necessary for the formation of white cast iron will be reported in the subsequent paper. The above mentioned value of 0.011 wt. per cent of oxygen is the dissolved oxygen content in melt just above the solidification point. Direct analysis for the oxygen content in such a state is experimentally impossible, but as the clusters are presumably turned in most cases, into FeO on solidifying, (and partially into sand (ferrous silicate and aluminate) in the presnece of silicon, aluminium or manganese), the analytical quantity of FeO may be taken for the study. It must be pointed out that the experimental quantity of oxygen in white cast iron formation varies according to cooling rate and other factors as explained below, and since the theoretical value of oxygen percentage of 0.010 per cent in the white cast iron formation has been deduced from the double diagram in disregard of cooling rate, special consideration is called for in collating the two values of theory and experiment. Other points to be mentioned are that the oxygen in solution in our study refers to free oxygen atoms in relation only with iron atoms and those in Fe–C–O–Fe clusters and in Fe–C alloys as well as in commercial cast iron, but oxygen atoms in Fe–Si–O–Fe clusters mentioned hereunder will not be considered.

There is no perfect analytical method to determine FeO contents. Among acid process, electrolysis and chlorine process used for analysis of FeO content, chlorine process may be handy for white cast iron, but for grey cast iron the obtained value is too high. We have no need to touch on the respective merits of these several processes and will only give a few examples of analytical values available hereunder.

Example (1)

The FeO values obtained by chlorine method in Fe–C alloys are shown in the rightmost column in Table 1. The iron samples Nos. 121–1 and 121–2 were melted with addition of strongly basic slag of CaO, borax and glass, while to the specimens Nos. 122–1 and 122–2 Na_2CO_3 was further added. 2 kg of each specimen was melted in high frequency furnace and cast in chill mould, 25 mm in diameter, into white cast iron. Judging from the nature of the slag and the type of furnace, the cast iron should contain a high percentage of oxygen. As the theoretical percentage of oxygen forming white cast iron has been deduced from the double diagram in disregard of cooling rate, it cannot be compared off-hand with experimental values, but the table will show what is the approximate percentage of oxygen in oxygen-rich cast iron.

Table 1. Chemical Composition of Fe–C Alloy

No. of Specimen	C	Si	Mn	P	S	FeO (=0)
121 – 1	3.66	0.070	0.16	0.008_3	0.058	0.037(0.0082)
121 – 2	3.65	0.12	0.18	0.005	0.020	0.059(0.013)
122 – 1	4.06	0.11	0.13	0.012	0.024	0.041(0.0091)
122 – 2	3.70	0.08_4	0.20	0.009	0.039	0.036(0.008)

Example (2)

The Table 2 shows the chemical composition, FeO percentage, oxygen percentage and melting process. These specimens are rich in metal elements other than iron and oxygen but these are deemed to have no effect on Fe–C–O–Fe clusters. Manganese and sulphur if present in large percentage, will exert their own influence on the formation of white cast iron, so that a smaller amount of oxygen will suffice to get white cast iron. As for silicon, Fe–Si–C clusters are not conceivable, while Fe–Si–O–Fe clusters have no direct relation to the crystalliza-

Table 2. Chemical Composition, FeO, Melting Process of Cast Iron

No. of Specimen	C	Si	Mn	P	S	FeO	O	Composition of Slag	Melting Time mn.	Furnace
630 – 1	2.66	1.46	0.31	0.578	0.068	0.040	0.009	$SiO_2 : Na_2O = 60 : 40$	30	High Frequency Induction Furnace
630 – 2	2.77	1.78	0.35	0.563	0.055	0.039	0.009	〃	60	
630 – 3	2.85	1.14	0.23	0.598	0.057	0.063	0.014	〃	90	
630 – 4	2.86	1.50	0.35	0.543	0.039	0.064	0.014	〃	120	

tion of carbon. These clusters are deemed to become the main component of sand in the solid. Silicon may be present, in free state, in special clusters as Fe_3-Si, Fe-Si, as well as in compounds such as SiO_2 as non-metallic inclusions, but the presence of silicon does not affect the white cast iron forming activity of Fe-C-O-Fe clusters. But in the meaning that silicon and manganese act as deoxidizers, the oxygen content in the melt will be lowered and the tendency to white cast iron formation will be weakened. The Fe-C-O-Fe clusters, which become FeO in Fe-C alloys on solidification, cannot take the shape of FeO in cast iron rich in silicon and manganese and are changed into sand. Thus, the FeO percentage in such cast irons obtained by chlorine process will be the sum of FeO and sand from Fe-C-O-Fe clusters and FeO from sand derived from Fe-Si-O clusters, as well as Fe-Mn-O and Fe-Al-O clusters if present. There is no way to know the oxygen percentage only from Fe-C-O-Fe clusters. It may be surmized that in case the percentage of oxygen obtained by chlorine or HNO_3 process is high, the number of Fe-C-O-Fe will be correspondingly large.

Example (3)

The specimen was of an Fe-C-Si alloy composed of 3.16 per cent of carbon, 2.22 per cent of silicon, 0.001 per cent of manganese 0.006 per cent of phosphorus and 0.052 per cent of sulphur, which was turned into nearly white cast iron by oxidation in melting. A dry sand mould, 15 mm in diameter, was used in casting. The FeO value under chlorine process shown in Table 3 is partially too high, owing to the partial presence of grey cast iron.

Analysis of cast iron showing unusual characteristice, owing to the presence of excessive oxygen, has been undertaken by Kinoshita, Nakajima(12) and Maekawa(13) among others.

Table 3. FeO of Fe-Si-C Alloy

Method of Analysis	FeO	O
Electrolysis	0.084	0.019
Chlorine	0.322	0.072
Chlorine after Electrolysis	0.076	0.017
〃	0.068	0.015

2. Fffect of cooling rate on the oxygen percentage forming white cast iron

(1) When the cooling rate is abnormally low

In such cases, owing to the large difference of solubility of oxygen in liquid and solid iron, a part of oxygen is thrown out at solidification as inclusion and CO, which means a diminution of oxygen content and the consequent break-up of some clusters, so a percentage of oxygen content higher than 0.01 per cent is required for white cast iron formation.

(2) When the cooling rate is abnormally high

(The effect of supercooling will not be considered in this case).

In this case, the clusters are not broken at all and solidify intact. Consequently, the white cast iron formation is strengthened in tendency, even if the oxygen content is somewhat lower than the theoretical amount corresponding to E-E′.

---

(12) Kinoshita, Nakajima, J. Iron and Steel Inst. Japan, 37 (1951) 420; 461.

(13) Maekawa, ditto, **36** (1950), 246.

The influence for invalidating the lever relation E′C′F′ is enhanced and white cast iron results. In practice, the use of sand mould in casting grey cast iron and chill mould for white cast iron is exploiting the cooling rate factor, together with the effect of supercooling. After all, the theoretical percentage of 0.010 per cent of oxygen applies only to the case in which the cooling rate is kept at a certain fixed value. It must be pointed out that the accuracy of the analytical results of oxygen contents is expected to improve, resulting in a more accurate position of the points E and E′ on the double diagram. In considering the accuracy of experimental researches by C. Wells, we decided to adopt the diagram proposed by him, but we must point out that on the diagrams drawn up by Norbury and other experts, the difference between E and E′ are generally represented as larger.

Summary

(1) White cast iron is formed either by the presence of oxygen in the melt, or supercooling or by the presence of carbide forming metallic elements.

(2) In the melt of cast iron, a small number of oxygen atoms are in free state in relation only with iron atoms, and a large number of them are inactive state forming Fe–C–O–Fe clusters. Where the oxygen content is excessively large, special groups of Fe and O atoms may be assumed to exist, though not in the form of compound melecules. This applies equally to carbon atoms.

(3) The presence of such Fe–C–O–Fe clusters interferes with the crystallization and solidification according to the lever relation at the eutectic point C′, and the solidification point necessarily drops to the lower eutectic point C. It is impossible to prove the existence of Fe–C–O–Fe clusters in the cast iron melt with experimental methods available at present, but it is beyond doubt that with the increase of carbon content in the melt, oxygen atoms become mutually fixed. This fixing of O atoms in clusters interferes with the free crystallization of carbon atoms at the eutectic point C′.

(4) The theoretical amount of oxygen necessary for the formation of white cast iron was estimated to be 0.010 wt per cent, basing on the position of E and E′ in the double diagram.

In conclusion, let us express our gratitude to Prof. Tsunezo SAITO, the Research Institute of Mineral Dressing and Metallurgy, Tohoku University, for his many helpful suggestions. Let us also mention with thanks that a part of this study was made possible by the allocation of Scientific Research Fund from the Education Ministry.