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# Refining Method for Refining Cast Iron by the Electrolysis of Slag\*

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## Synopsis

Original researches on the refining method of cast iron by the electrolysis of slag will be described in this paper. Cast iron is not so easily reduced as steel that strong deoxidizing reagents, such as alkali, alkali earth metals and Mg, are necessary to reduce cast iron melts satisfactorily.

Charging positive voltage to slag and negative voltage to melt, the electrolysis was made of slag which covered the surface of cast iron melt; then, the melt could be reduced, resulting in the nodular graphite structure.

The electrolysis was performed for 10~30 minutes at 1,250°C~1,350°C.

Slag such as fluorides, chlorides, carbonates, oxides of alkali, alkali earth metals or Mg, seem to be applicable to the refining method.

## I. Introduction

It was pointed out by the authors that the deoxidation of cast iron was a little different from and more difficult than that of steel. The reason for this was that dissolved oxygen was almost free and in high-active state in the dilute solution of C and Si as molten steel. Therefore, it is possible to deoxidize molten steel by the deoxidizing power of Mn, Si and Al. However, in the concentrated solution of C and Si such as molten cast iron, the great part of dissolved atoms is in low-active state. In other words, they are in chemically less-active state by the mutual attractive forces of adjacent C and Si atoms. Therefore, the deoxidizing power of Mn, Si and Al are not sufficient for the deoxidation of molten cast iron. The deoxidizing refining by white slag and carbide slag was also not sufficient to accomplish that object. This was obvious from the fact that electric furnace cast iron refined by white slag and carbide slag had characteristics which were dependent upon high occluded oxygen content. For the purpose of deoxidizing molten cast iron, strong deoxidizing elements, such as alkali, alkali earth metals or Mg are required.

By using the characteristic of the carbon atoms that they increase in affinity with oxygen atoms with rising temperature, deoxidation by super-heated melting in unoxidizing atmosphere was carried out with carbon, and oxygen in molten cast iron was deoxidized to CO gas. Another special deoxidizing refining process

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by a slag forming method was also considered. These problems were described in detail in the previous report.<sup>(1)</sup>

In this paper, a fundamental study on a deoxidizing method completely different from the above one is reported. The molten metal was deoxidized by alkali, alkali earth metals and Mg which were deposited on the interface between slag and molten metal, by charging positive voltage to commonly-used slag and flux and negative voltage to the molten metal.

## II. Change in structure of cast iron by oxygen content

It is necessary in a study of deoxidation of cast iron to judge the degree of deoxidation or the quantity of oxygen content. For this purpose, analytical determination of oxygen content is the best. But oxygen atoms in cast iron exist in many complex states and the existing form in liquid state of cast iron is completely different from that in solid state. The collectable amount of oxygen differs with analytical methods. A very small change in oxygen content gives a remarkable effect on characteristics of cast iron. Therefore, an analytical determination cannot be considered to be a proper method, unless it is made by future study sufficient by correct in the determination of the specific oxygen atoms.<sup>(2)</sup> It is considered that the oxygen atoms which have direct effect on the structure of cast iron are those which are adjacent to one another with carbon atoms by attractive force in the liquid cast iron. It was found that cast iron structure would under go changes with changes in the quantity of oxygen as follows: (Cooling velocity was 100°~400°C/min near the freezing point, which corresponds to the cooling velocity of 15~30mm $\phi$  green sand molded casting). With gradual increase in oxygen content, the structure changes from (I) coarse flake graphite structure which is the most common structure in cast iron to  $\rightarrow$  (II) rose graphite structure  $\rightarrow$  (III) eutectic graphite structure  $\rightarrow$  (IV) inverse chilled structure  $\rightarrow$  (V) oxidized white cast iron structure. These changes could be explained by the action of white-cast-ironizing by oxygen. On the other hand, with gradual decrease in oxygen content, the structure changes from (I) coarse flake graphite to (II') rose graphite structure  $\rightarrow$  (III') eutectic graphite structure  $\rightarrow$  (IV') fine granular graphite structure  $\rightarrow$  (V') inverse chilled structure  $\rightarrow$  (IV') super-cooled white cast iron structure. These changes depend on an increase in the supercooling character of molten cast iron due to deoxidation. Nitrogen had little effect on these structure changes in the normal range of its content. The cast iron smelted by usual type cupola (tapping temperature was below 1,450°C) using coke pig iron as raw material corresponded to (I)  $\rightarrow$  (II). That smelted in the electric furnace corresponded to (II) $\rightarrow$ (IV). Both that smelted in unoxidizing atmosphere with by using charcoal pig iron of good quality as raw material and even by using low grade pig iron and that super-heated above 1,550°C of tapping temperature are corres-

(1) M. Homma, J. Japan Inst. Metals, 16 (1952), 486 ; 547 ; 607 ; 666.

(2) Kinoshita, I. Iron and Steel Inst. of Japan, 37 (1951), No. 7, 8. Satô, J. Iron and Steel Inst. of Japan, 35 (1949), 11, p. 5.

ponded to (II') ~ (III'). If it is deoxidized by calcium compound, e.g., Ca-Si alloy at temperature at which the reaction proceeds sufficiently, (III') → (V') range is reached. Nodular cast iron may be considered as that deoxidized to (VI') super-cooled white cast iron by Mg which is graphitized from molten metal by treatment of graphitization, for example, by Fe-Si inoculation.

There are many hypotheses for nodular graphite formation in cast iron by Mg treatment. The main reason is considered to be a strong deoxidation and desulfurization by Mg. Mg is alloyed to cast iron during Mg treatment, but this is a secondary phenomenon in the treatment and hardly considered to be the essential problem in the spheroidizing of graphite. However, the spheroidal shape of nodular graphite became better by alloying with B, Mg, alkali, and alkali earth elements.

### III. Experimental method and results of electrolytic reducing refining of molten slag

The principle of electrolytic reducing refining method of molten slag is that on performing electrolysis by charging positive potential to molten slag and negative potential to molten cast iron, Na, Ca, Ba and Mg are to deposit on the surface of molten cast iron or molten steel and to deoxidize and desulfurize molten metals.

As the electrolysis proceeds, the structure changes gradually from (I) coarse flake graphite structure to (II) rose graphite structure (III') → eutectic graphite structure → (IV') fine granular graphite structure → (V') inverse chilled structure → (VI') super cooled white cast iron structure. Wormy flake graphite is crystalized by the graphitizing acceleration in the deoxidation stage (II')~(III') and also nodular graphite is crystalized and precipitates in the graphitization from liquid in the last (VI') stage. Through these procedures, mechanical and other properties are improved. Sufficiently deoxidized molten cast iron is accompanied with such a strong super-cooling effect, that excellent mechanical properties do not appear only by deoxidation treatment. Inoculation is required to eliminate the super-cooling phenomenon, by which the properties of deoxidized cast iron are improved remarkably. The behavior of inoculation differs greatly with oxygen content in cast iron. In the case of cast iron with high oxygen content, a better result cannot be expected from inoculation.

Sulfur in cast iron behaves differently with different oxygen content. Sulfur is believed to be a white-cast-ironizing element, but its action is essentially different from that of Cr, Mo and W. For instance, the behavior of sulfur in cast iron differs with the change in the oxygen content. Another report will be published on this problem in the future.

In the electrolytic refining method, there was no restriction in chemical composition, melting temperature was optional and it was not necessary to use specially high or low temperature. The present experiment was carried out between 1,250°C and 1,350°C for cast iron.

## (1) Electrolytic refining apparatus

The apparatus for the electrolytic reducing refining experiment are shown in Fig. 1 (a)~(d). We can carry out the experiment without any trouble by any method if the apparatus are so constructed that the positive potential charge is

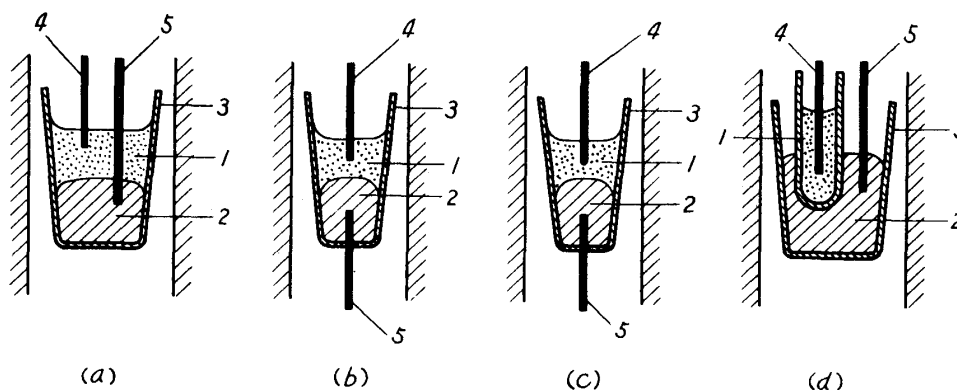


Fig. 1. Experimental arrangements for electrolytic refining.

given to molten slag and negative potential charges to molten cast iron (or molten steel) and electrolysis of molten slag is performed for necessary duration. In Fig. 1, 1 is an electrolytic bath, 2 is molten cast iron, 3 is a crucible, 4 is an anode, and 5 is a cathode. Electrodes 4 and 5 are connected to the electric source. Of these, Fig. 1 (a) and (b) are suitable equipments for electrolysis of molten slag, and heating is done from outside of the crucible. Fig. 1 (c) shows the same type as (b), but heating is used as the resistance heat of molten slag. If the alternating current is overlapped with the direct current, heating becomes more economical. For the equipment shown in Fig. 1 (d), good fluid salts e.g., KCl, NaCl, CaCl<sub>2</sub>, MgCl<sub>2</sub> or their mixtures, may be used as an electrolyte. A vessel containing salt plays the role of diaphragm. At any rate, carbon can be used as electrodes as well as silicon carbide. Silicon carbide has higher electric resistance than carbon electrode, but it can be used for a longer time. For the application of the principle described above to industry, the forehearth of cupola may be available for the construction of a furnace.

## (2) The condition of electrolysis

It is not easy to perform correct measurement of the lowest voltage of electrolysis, but about 6V is sufficient for electrolysis of Na or Ca compound. When current density of cathode is about 0.3 A/cm<sup>2</sup>, the structure can be improved by refining for about 10 minutes. When electrolytic voltage is sufficiently high, the progress of electrolysis can be observed well as gas is discharged from the anode and begins to burn, when carbon electrode is used.

## (3) Electrolytes

Electrolytes used were fluoride, oxide and carbonate of alkali, alkal earth elements, and Mg. From the viewpoint of economy or of optional control of acidity, basicity, reducing capacity, fluidity and slag forming, the addition of other oxides (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, etc.) was advantageous. Use of rare metal compounds, e. g., cerium compound is conceivable, but they are not economical.

## (4) Examples of experiment on electrolytic reducing refining.

Many laboratory-scale experiments were carried out by using kinds of electrolytic bath mentioned above in accordance with electrolyte. The results are summarized in Table 1. The specimens of cast irons were synthetic cast iron (3.60% C, 2.03% Si, 0.005% Mn, 0.005% P, and 0.008% S), and cupola cast iron (3.87%

Table 1. Examples of electrolytic refining of molten slags.

Temperature (°C)	Electrolyte	Voltage (V)	Ampere (A)	Cathode current density (A/cm <sup>2</sup> )	Electrolytic time (min.)	Structure	Photo. No.
1250	NaCl	>5	about 6	0.29	10-30	Spheroidal graphite and fine granular graphite structure	1
1350	CaCl <sub>2</sub>	about 5	about 5	0.25	10	Fine granular graphite structure	2
1250	Na <sub>2</sub> O-SiO <sub>2</sub>	>9	2-3	0.12-0.2	10-30	Ditto	
1250	K <sub>2</sub> O-SiO <sub>2</sub>	>9	2-3	0.12-0.2	10-30	Ditto	
1350	CaO-Al <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub>	about 5	8	0.5	40	Spheroidal graphite and fine granular graphite structure	3, 4, 5

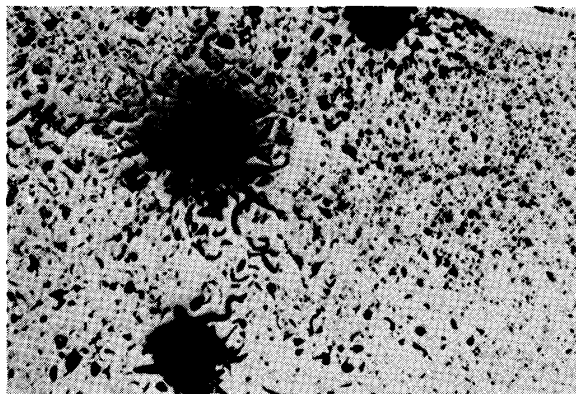
C, 2.74% Si, 0.38% Mn, 0.355% P, 0.021% S, and 0.007% N). In Photos. 3, 4, and 5, the structures obtained by electrolytic refining of ordinary oxide slag (CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>) are shown. Photos 3 and 4 show the degree of deoxidation in which the synthetic cast iron specimen proceeded to (III)~(IV') and at which kish graphite crystallized from graphite solubility curve C' D' was spheroidized (Photo. 1 is also similar). Photo. 5 shows the reducing refining structure of cupola cast iron, namely semi-nodular graphite structure. If oxidation from the surrounding could be protected during electrolytic refining, the degree of deoxidation would progress furthers and it is possible to get perfect nodular graphite cast iron.

## (5) Degree of desulfurization

In this experiment, the desulfurization was from 0.13-0.03% S before treatment to 0.009-0.005% S after treatment. Materials having desulfurizing efficiency was used originally as electrolyte, the electrolyte itself was desulfurized so that the desulfurizing refining by electrolysis deserved a special mention. However, the application of electrolytic desulfurizing refining to a special high desulfur cast iron is effective.

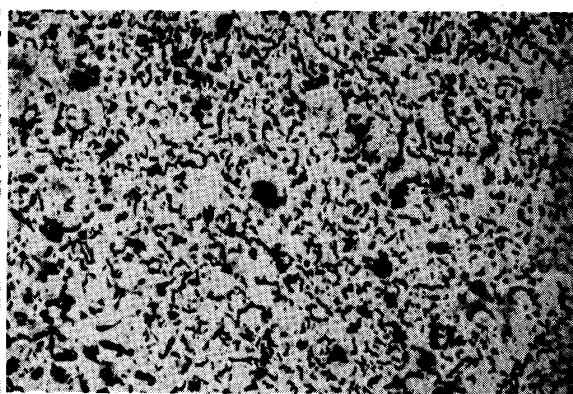
## (6) Industrialization of electrolytic refining process.

Electrolytic refining process of molten slag may be applied to industrial manufacturing of high grade cast iron of low mass effect. For this purpose, the electric furnace, fore-hearth of cupola, and crucible furnace can be used. This method can be applied not only to the reducing refining of cast iron but also to that of steel, copper alloy and other metals and alloys in molten state. Further, if the charged potential on slag-metal interface are reversed, it would be possible



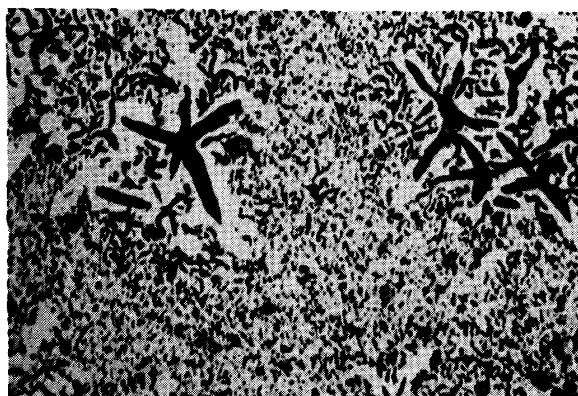
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Photo. 1. Nodular graphite (kish graphite)  
and fine granular graphite structure



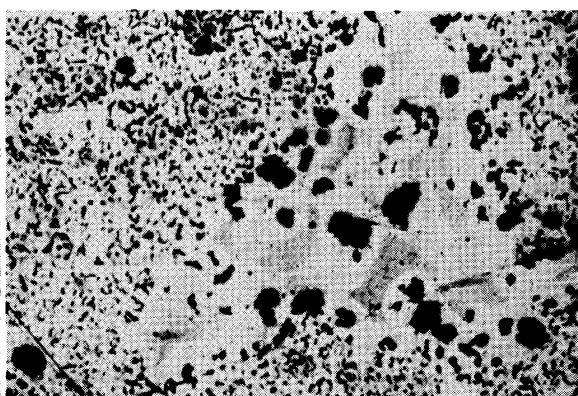
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Photo. 2. Fine granular graphite structure.



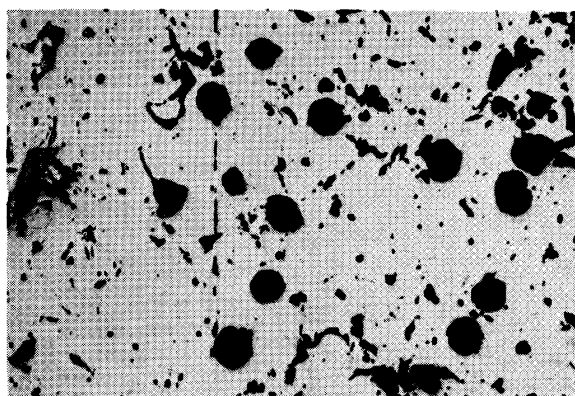
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Photo. 3. Star-like graphite (kish graphite)  
and fine granular graphite structure



×300

Photo. 4. Nodular graphite (kish graphite)  
and fine granular structure.



×100

Photo. 5. Semi-nodular graphite structure.

to do oxidizing refining by depositing oxygen and chlorine gas on the surface of molten metal.

#### IV. Conclusion

The electrolytic reducing refining method of molten slag is described as an effective deoxidizing method of molten cast iron. This method determines correctly and simply the degree of deoxidation of cast iron. An account is given for the manufacturing of strong cast iron. Examples of electrolytic refining are shown in detail and the industrialization of this process is also mentioned.

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