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Effect of the Additions of Barium-bearing Calcium Alloys  
on the Dissolved Oxygen and Sulphur of Liquid Iron\*

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Synopsis

In order to investigate the effect of barium-bearing calcium alloys on the oxygen and sulphur content of liquid iron, deoxidation of liquid iron with CaBa, CaSi, and CaSiBa deoxidizers was studied at 1600°C using a high frequency induction furnace, a lime crucible and mechanically mixed basic powder. The results indicate that barium in the calcium alloy enhances the deoxidation of liquid iron in the early time and then CaO type inclusions with very small concentrations of barium are possible to identify by a microprobe analyser. By Al plus CaSiBa addition decreases final total oxygen levels in the range of 10 ppm to 20 ppm. The sulphur content of the melt is reduced from 50 ppm to below 3 ppm.

I. Introduction

Barium-bearing calcium alloys such as CaSiBa and CaSiBaAl which have been practically used in steelmaking are expected to be more effective for deoxidation purposes than calcium silicon alloy without barium. It has been reported<sup>1,2,3)</sup> that barium in calcium alloy lowers the vapor pressure of calcium, suppresses the violent reactivity and raises the yield of calcium during the addition of calcium alloy into liquid steel, and then improves the effect of calcium on the formation of inclusions.

Boiling point of barium is 1637°C (2979°F) and within the nominal range of temperatures for steelmaking. Since the vapor pressure of barium at 1600°C is 0.7 atm<sup>2)</sup>, it is considerably less than 1.8 atm of

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calcium. As a study of the free energy of formation of the oxides and sulphide-forming elements  $\Delta G^\circ_{1600^\circ\text{C}}$  of barium oxide is of the order of  $-180 \text{ kcal/g.mol O}_2$  in comparison with  $-203 \text{ kcal/g.mol O}_2$  of calcium oxide. It can be inferred that barium oxide is more stable than the formation of silicon or aluminum oxide, and also the formation of barium sulphide should be fairly stable. However, there are still many unresolved problems regarding the deoxidation and desulphurization potential of barium in liquid iron. The purpose of the present work was to determine if the presence of barium in calcium alloy deoxidants would influence the oxygen and sulphur content of liquid iron.

## II. Experimental procedure

500g or 2kg of electrolytic iron was melted in a laboratory-made lime crucible<sup>4)</sup> using a high frequency vacuum induction furnace. When the charge had melted under vacuum at  $10^{-2}$  Pa completely, the furnace was filled with argon to atmospheric pressure and a constant flow was maintained throughout the experiment to avoid the ingress of air. The initial oxygen and sulphur content of the melt were controlled. After a fixed waiting period CaBa (42.2%Ba), CaAl (41.7%), CaSi (29%Ca, 55.6%Si), and CaSiBa (14.9%Ca, 60%Si, 15.7%Ba) which was wrapped in a pure iron foil tied to an end of a soft iron wire was plunged into the liquid iron covered with or without a mechanically mixed powder containing  $70\% \text{CaO} + 30\% \text{CaF}_2$ . Temperature of the melt was measured with a Pt/30pctRh - Pt/6pctRh thermocouple or an optical pyrometer and held constant at  $1600^\circ\text{C}$ . Samples were taken by suction with a non-transparent quartz tube at regular intervals up to 10 min and quenched in water. Portions of the suction sample were used for oxygen analyses. Chemical analyses for sulphur, calcium, and barium were carried out on part of the remaining sample. A representative inclusions were selected and their analyses determined using microprobe analysis. Oxygen analyses were made by the argon carrier gas fusion colorimetric method, and sulphur analyses by the combustion-alkalimetric method and the reduction distillation methylene blue-nitrobenzene extraction method<sup>5)</sup>. Chemical analyses for calcium and barium concentrations were determined by the atomic absorption method.

## III. Results and Discussion

Each 500g of electrolytic iron was melted in a lime crucible with the inside diameter of 48 mm. The experiments were designed under ar-

gon atmosphere to examine the effects on deoxidation and desulphurization with Ca, CaBa, and CaAl<sup>6)</sup>. The changes in total oxygen and total sulphur content of each melt are shown in Figure 1. The addition of 0.1%Ca and 0.2%CaBa corresponds to the equivalent amount of calcium. As seen from the figure the oxygen content in the melt immediately after 0.2%CaBa addition decreases abruptly and reaches a constant level of 300 ppm.

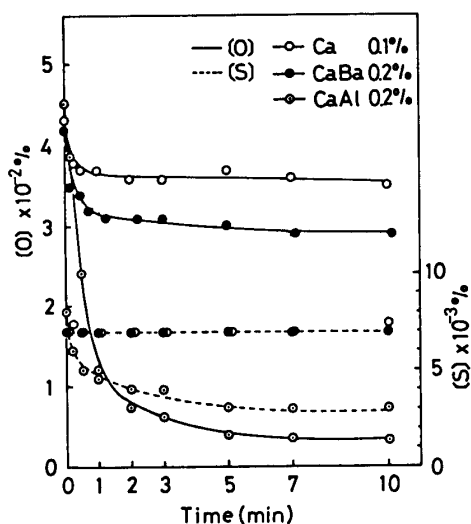


Fig. 1 Effect of various deoxidation additions upon oxygen and sulphur residuals in liquid iron.

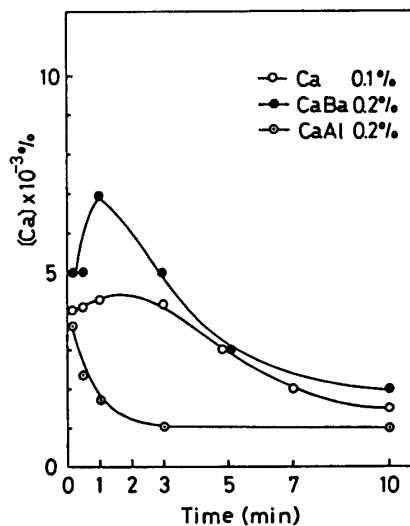
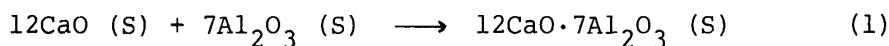


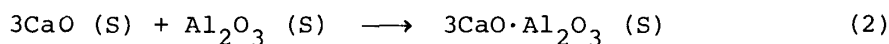
Fig. 2 Effect of various deoxidation additions upon calcium residuals in liquid iron.

The deoxidation of the melt by 0.2%CaBa addition indicates a relatively lower level in comparison with that of the melt by 0.1%Ca addition. Barium reduces presumably the activity and the vapor pressure of calcium, because calcium and barium completely soluble in each other in the liquid state<sup>7)</sup>. The fact that the desulphurization by the addition of these deoxidants didn't occur during the elapsed time of 10 min indicating approximately 70 ppm S may be attributed to the high oxygen level of the melts, because the sulphur transfer between the liquid metal and slag is strongly affected by the dissolved oxygen potential in the melt. Then it can be seen from this figure that in the case of the addition of 0.2%CaAl to compare with other deoxidants the desulphurization does occur simultaneously with the deoxidation resulting in a greater decrease in the total sulphur content from 80 ppm to 30 ppm and in the total oxygen content from 450 ppm to 30 ppm. This experiment indicated the beneficial effect of together addition with aluminum and calcium in lowering the total oxygen and sulphur content within 10 min.

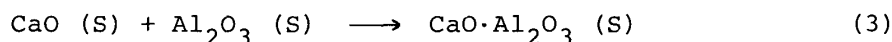
Thermodynamically, calcium oxide has a high affinity for aluminum oxide at steel making temperatures and should therefore form a series of calcium aluminates<sup>8)</sup>:



$$\Delta G^\circ \text{ at } 1700 \text{ K} = -102,260 \text{ cal/mol}$$



$$\Delta G^\circ \text{ at } 1800 \text{ K} = -15,290 \text{ cal/mol}$$



$$\Delta G^\circ \text{ at } 1800 \text{ K} = -11,910 \text{ cal/mol}$$

Calcium aluminate slags have high sulphur capacity. This also explains why after CaAl addition, the desulphurization reaction proceeds extremely. The deoxidation and desulphurization of liquid steel with aluminum containing calcium alloys have been studied in detail<sup>9,10,11)</sup>.

In order to study more clearly the deoxidation process, the changes of residual calcium with time were obtained on liquid iron, in which different calcium alloys were added, as shown in Figure 2. As seen from the figure, in the case of 0.2%CaAl addition the residual calcium in the melt decreases to 10 ppm within 3 min and reaches the lowest level of about 10 ppm at the elapsed time of 10 min. This suggests that the deoxidation products such as  $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaS}$  type are separated quickly and removed away from the melt in the early time. In the case of 0.2%CaBa addition a maximum residual calcium of 70 ppm appears within 1 min and the calcium content in the melt reduces to 20 ppm within 10 min. Compared with the case of CaBa addition, 0.1%Ca addition shows the lower value of a maximum residual calcium of 40 ppm and the calcium content reduces to less than 20 ppm within 10 min. The different curves between the two cases are because the vapor pressure of CaBa alloy containing about equal parts of calcium and barium is presumably less than that of metallic calcium alone<sup>1)</sup>.

Figure 3 illustrates a microprobe analysis of representative inclusions. CaO type inclusions with very small concentrations of barium were only observed in the sample taken within 10 sec after 0.4%CaBa addition. No barium could be observed in the inclusions appearing after 30 sec had elapsed since the CaBa addition, although microprobe analyses did mainly reveal inclusions containing CaO-FeO type.

2kg of electrolytic iron was prepared for the experiment of Al plus Ba deoxidation. The melt was predeoxidized with 0.15%Al at 1600°C. After a waiting period of 3 min a metal sample was taken and the bath

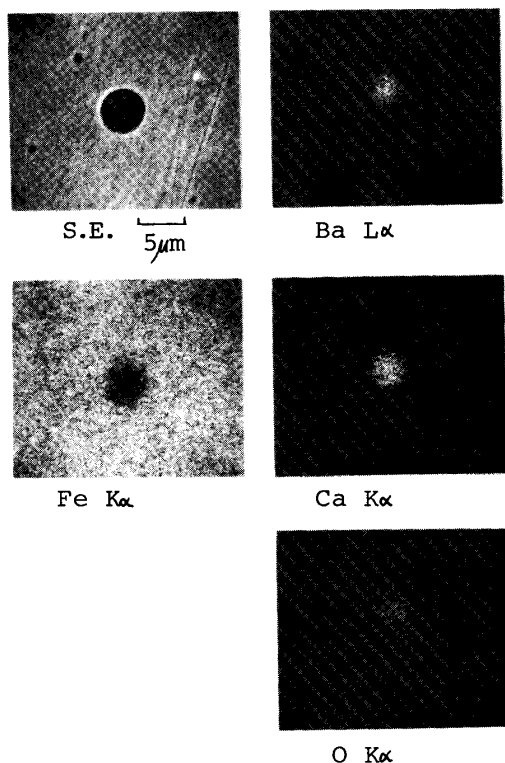


Fig. 3 EPMA images of typical inclusion appearing in the specimen taken from liquid iron within 10 sec after the CaBa addition.

was covered with mechanically mixed powder containing 70%CaO + 30%CaF<sub>2</sub> 80g in total. Immediately after the barium addition of 0.3%, metal samples were taken at regular intervals to observe changes in total oxygen and total sulphur concentrations. The changes in total oxygen and sulphur content of the melt before and after aluminum and following barium addition are shown in Figure 4<sup>12)</sup>.

After the addition of aluminum the oxygen content of the melt decreased sharply from initial 400 ppm to 13 ppm during the first 3 min, as many of the aluminous deoxidation products floated out. The sulphur content decreased simultaneously from initial 50 ppm to 20 ppm. Details of the experiment which the aluminum addition into the liquid iron with a lime crucible fosters the desulphurization are described in an earlier paper<sup>13)</sup>. After the Ba addition the oxygen content reached a constant level of 10 ppm. Simultaneously with the oxygen decrease, the Ba addition also reduced the sulphur content to an extremely low value of 2 ppm at the elapsed time of 10 min. The sulphur decrease may be interpreted as follows: In the first case, the added Ba reacts directly with sulphur in the melt and the resulting BaS inclusions separate out more rapidly. Secondly the added Ba is fluxed together with the mechanically mixed powder materials, and this slagging phase, because of the increase of sulphide capacity plays an important role of desulphurization at the slag/metal interface<sup>14)</sup>. No barium could

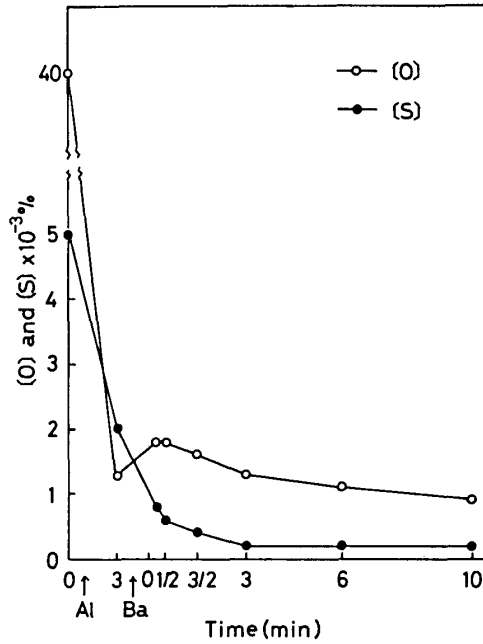


Fig. 4 Effect of 0.15%Al plus 0.3%Ba addition upon oxygen and sulphur residuals in liquid iron.

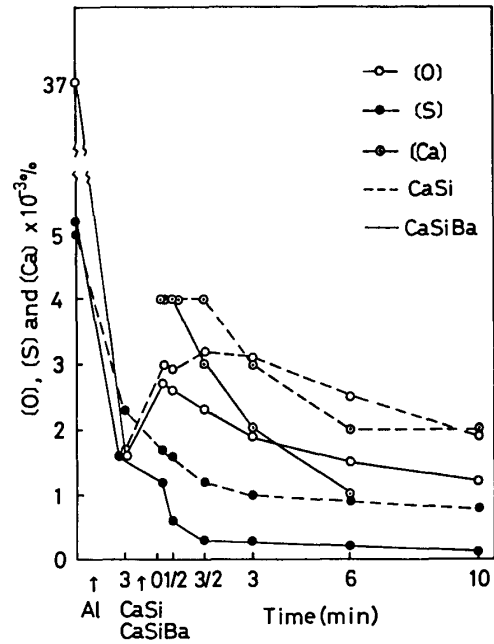


Fig. 5 Effect of 0.15%Al plus 0.25%CaSi or 0.15%Al plus 0.5%CaSiBa addition upon oxygen, sulphur and calcium residuals in liquid iron.

be detected either by a microprobe analysis of nonmetallic inclusions or by chemical analyses of the samples taken 15 - 180 sec after the Ba addition.

Two heats were made to establish the combined effect of Al plus CaSi or Al plus CaSiBa on the oxygen and the sulphur removals in liquid iron at 1600°C. Each 2kg of electrolytic iron was melted in the lime crucible with the inside diameter of 80 mm. Heats were predeoxidized with 0.15%Al. After a waiting period of 3 min a metal sample was taken and then the bath was covered with mechanically mixed powder of 70%CaO + 30%CaF<sub>2</sub> 100g in total. Furthermore, after 0.25%CaSi or 0.5%CaSiBa addition metal samples were taken at regular intervals. The changes in total oxygen, sulphur, and calcium content of the melt before and after Al plus CaSi or Al plus CaSiBa addition are shown in Figure 5.

As seen from the figure, the oxygen content of the melt within 3 min after the addition of aluminum decreases sharply from 370 ppm to 16 ppm. Simultaneously the sulphur content decreases from 50 - 52 ppm to 16 - 23 ppm respectively. The addition of the mixed powder and the following CaSi or CaSiBa causes temporarily a reoxidation of the melt. Within 10 min, however, the oxygen content in the melt indicates a continuous decrease to 19 ppm or 12 ppm. The sulphur content in the melt treated with the CaSi follows by a gradual decrease towards a steady

state below 10 ppm. On the other hand, the sulphur content in the melt immediately after the CaSiBa addition decreases abruptly less than 10 ppm and reaches an extremely low value of 1 ppm at the elapsed time of 10 min. Comparison between the curves obtained by the Ca alloy deoxidation with and without Ba reveals a beneficial effect of Ba in promoting inclusion removal and also in lowering the dissolved oxygen and sulphur content.

It can be presumed that the formation of a basic slag at the surface of the melt and also the floatation of calcium alumina silicate inclusions having a sulphide capacity plays a significant role in desulphurization of the melt. In particular, the low oxygen potential in the melt which can be attained by the deoxidation of Al plus CaSiBa may increase the coalescence and the chemical affinity among the CaO-CaF<sub>2</sub> slagging phase, the lime crucible, and the sulphide inclusions, and thereby allow a rapid inclusion removal rate.

Difference in residual calcium between the curves obtained by the CaSi and the CaSiBa deoxidation may be attributed to a beneficial effect of Ba in promoting the removal of inclusions, judging from the lower levels of the total oxygen and sulphur concentrations.

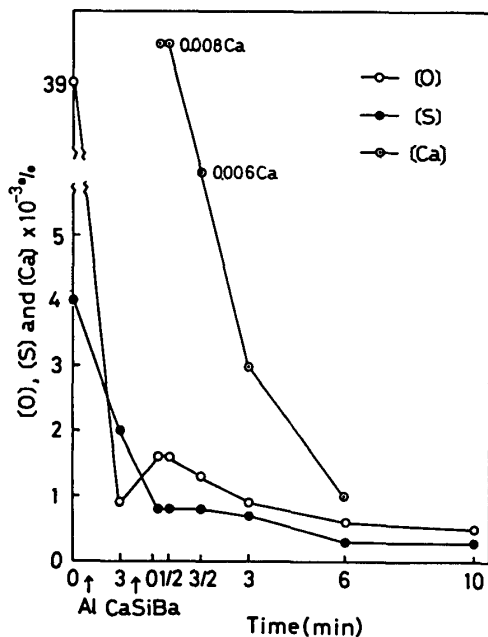


Fig. 6 Effect of 0.15%Al plus 0.5%CaSiBa addition upon oxygen, sulphur and calcium residuals in 3%NiFe liquid alloy.

2kg of 3%NiFe alloy was melted and predeoxidized with 0.15%Al at 1600°C. After a time, the melt covered with mechanically mixed powder of 70%CaO + 30%CaF<sub>2</sub> 100g in total was deoxidized with 0.5%CaSiBa. The changes in total oxygen, sulphur, and calcium content of the melt are shown in Figure 6. The oxygen content of the melt within 3 min after



the addition of aluminum decreased abruptly from 390 ppm to 9 ppm. Simultaneously the sulphur content decreased from 40 ppm to 20 ppm. The addition of the mixed powder and the following CaSiBa caused temporarily a reoxidation of the melt. Thereafter, the oxygen content continued to reduce showing a drop to 5 ppm within 10 min. The sulphur in the melt after the CaSiBa addition continued to decline in quite a gradual fashion and registered 3 ppm as the final content. Residual calcium indicated a maximum amount of 80 ppm within 30 sec with the CaSiBa addition, and the lowest amount of it, 10 ppm was detected at the elapsed time of 6 min. Compared with the case of liquid iron, the nickel-containing liquid iron indicated a higher amount of the maximum residual calcium, because the solubility of calcium in liquid is increased by nickel<sup>15)</sup>.

#### IV. Conclusions

An examination has been made of the progress of deoxidation and desulphurization in liquid iron and liquid iron nickel alloy with the addition of barium-bearing calcium alloys. On the basis of the present investigation, the following conclusions may be drawn.

- (1) The CaBa alloy addition into the bared liquid iron enhances the deoxidation in the early time and brings the higher yield of calcium in comparison with that of the addition of equivalent metallic calcium alone. Very small concentrations of barium in the non-metallic inclusions formed immediately after the CaBa alloy addition is possible to identify by a microprobe analyser.
- (2) When the oxygen potential in the melt is lowered by Al predeoxidation the subsequent Ba addition under the CaO + CaF<sub>2</sub> cover promotes the desulphurization to extremely low value of 2 ppm.
- (3) By Al plus CaSiBa addition decreases the final total oxygen levels in the range of 10 ppm to 20 ppm. The content of sulphur in the melt is reduced from 50 ppm to below 3 ppm.

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