Influence of Ca-Al Deoxidizer on the Morphology of Inclusions*

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Synopsis

In order to make clear the influence of Ca-Al deoxidizer on the shape control of Al_2O_3 and MnS inclusions which cause the anisotropy of the steel deoxidized by aluminum, experiments have been performed on the Ca-Al deoxidation for the steel predeoxidized by aluminum. And a formation mechanism of the inclusions characteristic to this deoxidation is discussed. The results are summarized as follows:

(1) Inclusions in the molten steel change to low melting ones consisted of Al_2O_3 -CaO-CaS in which CaS distributed uniformly.

(2) Inclusions in the ingot change to complex type ones consisted of Al_2O_3 -CaO-(CaS) in which CaS deposits peripherally. These complex inclusions are thought to be formed by the precipitation of CaS due to the solubility drop during the solidification process.

(3) The anisotropy of the steel is improved by this shape control of inclusions.

I. Introduction

When steel is deoxidized with aluminum which is widely used as the deoxidant, Al_2O_3 clusters, which often appear in the sedimental zone of ingots, sometimes have chances to become sand marks in the steel products. It is thought to be an effective countermeasure to make their melting points as low as possible, because they are formed by the collision of Al_2O_3 inclusions during the solidification process¹⁾ of ingot. At the same time, MnS inclusions also exist in the steel. These inclusions, elongated by the hot working, cause the anisotropy of the steel deoxidized by aluminum and the decrease in their amounts as well as the shape control are considered to be very important. So, some studies on the calcium^{2,3)} or REM^{4,5)} treatment of the steel have been reported recently.

Though calcium is considered to be very effective for the shape control of inclusions owing to its strong affinity for oxygen and sulfur, it has unusual characters of gaseous state at the steelmaking temperature and a small solubility in the molten steel, compared with other deoxidants. Accordingly, in spite of many studies on the calcium treatment, the consensus has not so far been obtained on its effect influenced by many factors such as kind, amount, adding method of Ca-deoxidant or test scale.

Then, in order to clarify the effect of calcium on the shape control of Al_2O_3 and MnS inclusions, ex-

periments have been done for 3 kg and 25 t molten steel. And, some discussions have also been made on the formation mechanism of oxysulfide complex inclusion characteristic to the Ca-deoxidation.

II. Experimental

The Ca-Al deoxidants used for this experiment are wires of 7 and 4.8 mm diameter manufactured by protecting the mixture of metallic calcium and aluminum with steel plate of 0.2 mm thickness, and the chemical composition is shown in Table 1.

1. Experiment of the 3 kg Steel

An experiment was carried out by adding Ca-Al deoxidant to 3 kg molten steel, which was melted in a high frequency induction furnace in the air and predeoxidized with 0.06%Al at 1 610°C, and by casting immediately into a metal mold of 60 mm diameter. When the Ca-Al deoxidant, tied up to a steel rod, was dipped into the steel bath, the steel was splashed due to the evaporation of calcium. The experimental conditions and the chemical composition of the steel are shown in Tables 2 and 3, respectively. Here, only Heat No. 1 was not predeoxidized by aluminum. The content of soluble aluminum in molten steel after the predeoxidation by aluminum was 0.023 to 0.047% for carbon steel of Heat Nos. 2 to 8 and 0.014% for

Table 1. Chemical composition of Ca-Al deoxidizer

	Composition (%)			Diameter (mm)
	Ca	Al	Fe	
A	19.5	22.3	57.3	7
B	33.3	9.1	56.7	
C	31.8	7.8	57.0	4.8

Table 2. Experimental conditions

Heat No.	1	2	3	4	5	6	7	8	9
Deoxidizer	A	A	A	A	B	B	B	B	A
Addition (%)	1	1	0.5	0.15	1	0.5	0.3	0.15	1

Table 3. Chemical compositions of 3 kg ingots

Heat No.	C	Si	Mn	P	S	Ni	Cr
1~8	0.27/0.30	0.15/0.30	0.38/0.46	0.008/0.012	0.010/0.013	0.08/0.14	0.10/0.14
9	0.05	0.49	1.10	0.010	0.017	8.0	18.3

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stainless steel of Heat No. 9, and their oxygen contents were 120 to 190 ppm and 310 ppm, respectively. On the other hand, the aluminum content in the ingot was 0.05 to 0.22%, and the oxygen content was 210 ppm for Heat No. 1 and 90 to 125 ppm for Heat Nos. 2 to 9.

Samples taken from the ingot were subjected to the EPMA analysis of the oxide inclusions.

2. Experiment of the 25 t Steel

Another experiment was carried out by adding 0.17%Ca–Al wire into the 0.02%Al predeoxidized melt of 25 t in a ladle through the machine which enables the wire of 4.8 mm diameter feed continuously at the speed of 30 m/min. During the addition of Ca–Al deoxidant, the splash of molten steel due to the evaporation of calcium was also observed. This steel was bottom poured into a slab mold of about 800 mm thickness, and the ingot obtained was rolled to a steel plate of 120 mm thickness as shown in Fig. 1. The chemical composition of the ingot is shown in Table 4.

The samples taken from the molten steel in a ladle before and after the addition of Ca–Al deoxidant as well as the ones taken out of the top and bottom of the plate were subjected mainly to the determination of the composition and morphology of inclusions.

III. Experimental Results

1. Experimental Results of 3 kg Steel

Several oxide inclusions of relatively large size in each 3 kg ingot were analyzed by EPMA, and the representative inclusion as well as their chemical compositions are shown in Photo. 1 and Table 5, respectively. Thus, two types of inclusions were recognized, the one is uniform and the other is a two-phase type with the precipitated part of CaO rich. And, most

inclusions were consisted mainly of Al_2O_3 and CaO, and did not contain such components as SiO_2 and MnO.

The relation between the CaO/ Al_2O_3 ratio of each inclusion analyzed and the amount of calcium added is shown in Fig. 2, in which the ratio in the precipitated part is also plotted. It was seen from this figure that in spite of the scattered values of the CaO/ Al_2O_3 ratio against the amount of calcium added it grew larger with increasing amount of calcium added and became constant for more than 0.2%Ca. But, the influences of deoxidant and nickel, which were expected to be effective in raising the CaO/ Al_2O_3 ratio due to the increase in the solubility of calcium in steel,⁶⁾ was not so clear. And based upon the relation between the composition of inclusions and the melting point shown in Fig. 2 which is obtained from the CaO– Al_2O_3 phase diagram,⁷⁾ the melting point of inclusion decreases with the increase in the CaO/ Al_2O_3 ratio and some of them are considered to be liquid at 1 600°C. On the other hand, the melting points of the precipitated inclusions are higher than 1 800°C. Accordingly, it is necessary to maintain the CaO/ Al_2O_3 ratio at about unity in order to keep its melting point low. Furthermore, the compositions of inclusions in a ladle and those of steel plate of the 25 t plant test, which will be mentioned later, are also plotted together in Fig. 2.

2. Experimental Results of 25 t Steel

The electron beam scanning images of representative inclusions in the samples taken from the molten steel in a ladle before and after the Ca–Al addition are shown in Photo. 2. It is seen from this that the Al_2O_3 inclusions formed after the predeoxidation by alu-

Table 4. Chemical composition of 25 t ingot

C	Si	Mn	P	S	Ni	Cr	Mo	Al
0.21	0.34	1.37	0.009	0.008	0.16	0.16	0.07	0.021

Table 5. Chemical compositions of inclusions (%)

		CaO	Al_2O_3	FeO	Total
(a)		45.5	53.2	1.9	100.6
(b)	A	60.2	27.1	1.9	89.2
	B	47.7	41.7	2.0	91.4
(c)		25.6	74.6	0	100.2

Fig. 1. Sampling position from the steel plate

- (a) Heat No. 5
- (b) Heat No. 6
- (c) Heat No. 7

Photo. 1. Inclusions in the 3 kg ingots deoxidized with Ca–Al ($\times 600$) ($\times 4/5$)

minum change to those of $\text{Al}_2\text{O}_3\text{--CaO--CaS}$ containing CaS almost uniformly after the Ca–Al addition. Here, manganese was not contained in the inclusions at all. Next, the inclusions existing near the surface and center of the plate, which correspond to the chilled and slowly cooled zones of the ingot, are shown in Photos. 3 and 4, respectively. In this way, inclusions existing near the surface region were found to be consisted of $\text{Al}_2\text{O}_3\text{--CaO--CaS}$ containing CaS almost uniformly or a little higher near its surface, while inclusions existing near the center were mainly of $\text{Al}_2\text{O}_3\text{--CaO--(CaS)}$ in which CaS deposited peripherally and MnS was also seen

partly. The complex inclusion inside the ingot is thought to be characteristic to the Ca–Al deoxidation. The $\text{CaO}/\text{Al}_2\text{O}_3$ ratios of inclusions in the molten steel just after the Ca–Al deoxidation and in the ingot were analysed by EPMA to be plotted in Fig. 2. It was found from this that the Al_2O_3 inclusions also change to those of $\text{Al}_2\text{O}_3\text{--CaO}$ with the melting point lower than $1\,500^\circ\text{C}$ in the plant test. The superior effect of Ca–Al on the $\text{CaO}/\text{Al}_2\text{O}_3$ ratio of the 25 t steel to that of the 3 kg steel is assumed to be due to the longer residence time of calcium vapor in the molten steel.

Because of the change of oxide inclusions to those of globular type C as shown in Photo. 4, the Al_2O_3 cluster of type B characteristic to the deoxidation by aluminum was not observed. Further, sulfide inclusions were mainly CaS deposited peripherally around the oxide, though MnS partly existed. Accordingly, calcium is considered to be effective in the shape control of inclusions. And, according to the tensile test of specimens taken from the top and bottom ends of the steel plate, the ratio concerning the elongation and reduction of area in the through thickness to the rolling direction approached unity and the anisotropy of the steel was much improved. Here, the oxygen contents of molten steel and steel plate were about 60 to 90 ppm and the effect of calcium on the decrease in the oxygen content was not observed. But, the desulfurization effect of calcium was recognized, judging from the change in the sulfur content from 0.010% in the molten steel before the Ca–Al deoxidation to 0.006% in the steel plate.

Fig. 2. Effect of Ca on the $\text{CaO}/\text{Al}_2\text{O}_3$ ratio of inclusions

Photo. 2. Inclusions in the molten steel in a ladle before and after the Ca–Al addition ($\times 4/5$)

Photo. 3. Inclusions observed at the surface of the bottom sample in the Ca-Al deoxidized steel plate

(a) Oxy-sulfide inclusion

(b) Sulfide inclusions

Photo. 4. Inclusions observed at the center of the bottom sample in the Ca-Al deoxidized steel plate ($\times 350$) ($\times 4/5$)

IV. Discussion

From the experimental results mentioned above, it was found that calcium was effective in decreasing the amounts of Al_2O_3 cluster and MnS by changing them to those of $\text{Al}_2\text{O}_3\text{-CaO}$ and CaS deposited around the oxide when Ca-Al was added to the steel predeoxidized by aluminum. And, it was also found that the anisotropy of the mechanical properties such as elongation and reduction of area was much improved due to the morphology control of inclusions. Accordingly, the formation mechanism of this complex inclusion characteristic to the Ca-Al deoxidation is thought to be very important, while its systematic studies have not been done yet.

It is well known that calcium has a potent effect when it is added to the melt predeoxidized by aluminum and that the Al_2O_3 inclusion is reduced to the one of $\text{Al}_2\text{O}_3\text{-CaO}$ by the calcium⁸⁾ vapor. So, it is necessary to add calcium into the melt as deeply as possible so as to make the residence time of calcium

vapor longer for the higher deoxidation efficiency. For that reason, adding methods of calcium such as shooting the metal capsule holding Ca-Si and blowing Ca-Si or CaC_2 through the aperture of the stopper-like rod inserted into the steel bath are adopted and the shape control of inclusions have been achieved industrially. But, the complex inclusion surrounded by CaS is assumed to be formed during the solidification process of steel, because they are recognized in steel ingot after completion of solidification when the deoxidation by calcium was undertaken in an industrial scale. As shown in Photos. 2 to 4, CaS is distributed relatively uniformly in the inclusions in the molten steel as well as in the chilled surface of the steel plate, while it deposited peripherally on the oxide surface in the slowly cooled center of the steel plate. Accordingly, it is assumed that CaS deposited on the surface of the oxide inclusion is formed by the precipitation from the inclusion containing CaS uniformly due to the decrease in the solubility of CaS

in the inclusion during the solidification process. On the other hand, though there is a theory that the complex inclusion is formed by the reaction of calcium with sulfur on the surface of Al_2O_3 -CaO inclusion, it is not based on the experiment and is unable to explain the behavior of inclusion without inconsistency. Then, the formation mechanism of the complex inclusion was studied experimentally.

1. *The Formation Mechanism of CaS due to the Reaction between Calcium and Sulfur at the Nucleation Site of Oxide Surface*

First, the formation mechanism of peripheral CaS due to the reaction between calcium and sulfur dissolved in the molten steel at the nucleation site on the surface of oxide inclusion is discussed.

Fe-1%P alloy having a wide liquid-solid coexistence range and little influence on the inclusions was held at a liquid-solid coexisting temperature in order to reproduce the practical solidification conditions experimentally. The mother alloy used, Fe-1%P-0.2%Mn-0.02%S, was melted in a high frequency induction furnace and deoxidized with 0.05%Al and 0.8%Ca entrapped by a thin steel plate to be cast into a 30 mm ϕ metal mold. The obtained Fe-1%P alloy, enclosed in a silica tube of 28 mm diameter,

was kept at 1460°C which is a temperature of liquid-solid coexistence for 1 hr in an argon atmosphere by dipping it into a Ni-40%Sn bath as shown in Fig. 3 and cooled rapidly. Then, the morphology of inclusions in the samples before and after heating was investigated metallographically by SEM.

The representative inclusions in the sample before heating are shown in Photo. 5. Thus, it has been turned out these inclusions are similar to those in the molten steel just after the deoxidation by Ca-Al, be-

Fig. 3. Experimental apparatus

Photo. 5. Inclusions in the Fe-1%P alloy deoxidized with Ca-Al and cast into a 30 mm ϕ steel mold

cause they are mainly consisted of Al_2O_3 , CaO and a small amount of CaS or MnO , and contain no MnS . The absence of CaS in the inclusion in the calcium deoxidized steel as shown in Photo. 5 (b) is thought to be caused by the non-uniform effect of calcium on sulfur due to the short reaction time, compared with that of the plant scale test. On the other hand, characteristic inclusions in the sample held at a liquid-solid coexisting temperature are shown in Photo. 6. It is found that sulfides coexisting with oxide as well as those existing individually are both MnS and that the latter is the same as that shown in Photo. 4 (b). And, the inclusion, the surface of which is covered with MnS , shown in Photo. 6 (a) corresponds to that of Al_2O_3 - CaO - MnO without CaS in Photo. 5 (b). It is assumed that the sulfide formed during the solidification process of the steel treated with calcium is MnS , judging from the fact that MnS is not observed in the mother alloy before heating. Accordingly, it is not considered to be valid to explain the formation mechanism of complex inclusion by the reaction between calcium and sulfur dissolved in the molten steel on the oxide surface.

2. The Formation Mechanism of CaS due to the Precipitation from the CaS Containing Inclusion

Next, the formation mechanism of peripheral CaS due to the precipitation from the inclusion containing CaS is discussed.

Though it is necessary to deoxidize the molten steel containing sulfur and oxygen with calcium and aluminum in order to obtain Al_2O_3 - CaO inclusion containing CaS uniformly, it is difficult to investigate only the change in the inclusion due to the reaction between inclusions and mother alloy during holding in the liquid-solid coexisting state. Then, the experiment was done by dipping a silica tube of 20 mm diameter, which held the mixture of the granular particles of Fe-1%P alloy without elements such as Ca, S, Mn, etc., and slag containing CaS uniformly, into the Ni-Sn bath kept at 1460°C. Here, the air among the particles was replaced with argon before dipping. Fe-1%P alloy containing about 30 ppm oxygen was prepared by melting the electrolytic iron in a vacuum induction furnace and casting it into a metal mold of 30 mm diameter after the 0.05%C deoxidation. The alloy, crushed into particles smaller than 0.84 mm, was used by 50 g at a time. And, the slag was also prepared by melting the mixture of 45% Al_2O_3 -45% CaO -10% CaS in a graphite crucible by the use of a high frequency induction furnace and casting it into a metal mold. The slag, also crashed into particles of 0.105 to 0.074 mm size, was used by 0.1 g at a time. The distribution of sulfur in the slag analyzed by EPMA is shown in Fig. 4. In this way, sulfur was distributed uniformly in the slag and it was considered that sulfur also distributed uniformly in the slag particle obtained. According to the chemical analysis, the sulfur content in the slag was 2.54%, which corresponded to 5.72% CaS .

The electron beam scanning image of a representa-

Photo. 6. Inclusions in the Fe-1%P alloy held at solid-liquid coexisting temperature of 1460°C for 1 hr ($\times 300$) ($\times 4/5$)

Fig. 4. Distribution of sulfur in the slag

Photo. 7. Inclusion observed in the Fe-1%P alloy held at solid-liquid coexisting temperature of 1 460°C for 2 hr and cooled rapidly ($\times 350$) ($\times 4/5$)

Photo. 8. Inclusion observed in the Fe-1%P alloy held at solid-liquid coexisting temperature of 1 460°C for 1 hr and cooled at 5°C/min ($\times 500$) ($\times 4/5$)

tive inclusion in the sample, obtained by keeping the mixture of the alloy and slag particles at liquid-solid coexisting temperature of 1 460°C for 2 hr and then by rapid cooling, is shown in Photo. 7. Thus, the inclusion did not become quite the same as that in the center of the steel plate shown in Photo. 4, because CaS is present in the periphery and the inside of the inclusion. Next, the inclusion in the slow cooled sample, which was cooled at about 5°C/min after keeping the mixture at 1 460°C for 1 hr so as to simulate the actual solidification condition, is shown in Photo. 8. In this way, the complex inclusion surrounded by CaS, identical to that shown in Photo. 4, was obtained by the slow cooling. The precipitation of CaS from the inclusion was considered to be due to the elimination of solubility accompanied with the temperature drop, while the solubility of CaS in the Al_2O_3 -CaO melt has not been reported yet. So, it was measured experimentally.

The solubility of CaS was measured by adding 35% Al_2O_3 -35%CaO-CaS slag onto the 10 g of 50% Al_2O_3 -CaO slag melted in a graphite crucible of 16 mm diameter by the use of a charcoal resistance furnace and making CaS diffuse into the lower slag. Here, the experimental temperature was 1 450°, 1 500° and 1 550°C, and the weight of slag added was 5 g for 1 450°C and 10 g for 1 500° and 1 550°C, respectively. The longitudinal cross section of the slag chilled from the experimental temperature was roughly divided into two regions corresponding to the weight ratio of the slags added. So, the slag taken from the lower part of the boundary line was analyzed for sulfur.

The sulfur content increased with the holding time and reached constant after 60 min from the preliminary experiment done at 1 450°C. So, the sulfur content after keeping for 2 hr at each temperature is shown as CaS in Fig. 5.

Fig. 5. Solubility of CaS in 50%CaO- Al_2O_3 slag

It is found that the solubility of CaS in the 50% CaO- Al_2O_3 melt decrease with the temperature drop. According to the work on the solubility of CaS in the CaO- SiO_2 ⁹⁾ slag, the solubility of CaS depends largely on the temperature and is assumed to be relatively small under 1 550°C. And, the solubility of CaS in the current slag is expected to be smaller than that of CaO- SiO_2 slag, judging from its small solubility in the slag with strong desulfurizing power. From these facts, the result shown in Fig. 5 is considered to be adequate.

Considering from the fact that the solubility of CaS in the slag at 1 460°C is about 1.8% from Fig. 5, the inclusion containing about 5.7%CaS at first changes to the one which contains 1.8% soluble CaS in it and 3.9% precipitated CaS around it during holding at 1 460°C. On the other hand, all the CaS contained in the inclusion precipitate peripherally around it as shown in Photo. 8 due to the solubility drop to almost zero during the slow cooling from 1 460°C.

Consequently, the complex inclusion characteristic to the deoxidation by Ca-Al is thought to be formed by the precipitation of CaS from the inclusion containing CaS uniformly due to the solubility drop during the solidification process. Hence, CaS is thought to be precipitated peripherally due to its surface active nature.

V. Conclusions

In order to control the shape of Al_2O_3 and MnS inclusions, which cause the anisotropy of the mechanical properties as well as the rejection of steel product in a remarkable case, 3 kg and 25 t of aluminum pre-deoxidized steel were deoxidized with Ca-Al. And, the formation mechanism of the complex inclusion characteristic to the Ca-Al deoxidation was discussed experimentally. The results obtained are summarized as follows.

(1) In the 3 kg experiment, the Al_2O_3 inclusion changed to the inclusion which has a low melting point and consisted of Al_2O_3 -CaO. And, the CaO/ Al_2O_3 ratio of this inclusion increased with the increase in the amount of calcium added.

(2) In the 25 t experiment, the inclusions existing in the molten steel and ingot changed to those of Al_2O_3 -CaO-CaS in which CaS was distributed uniformly and of Al_2O_3 -CaO-(CaS) in which CaS deposited peripherally, respectively. As the result, the Al_2O_3 and MnS inclusions decreased remarkably.

(3) These complex inclusions characteristic to the deoxidation by Ca-Al were thought to be formed by the precipitation of CaS due to the solubility drop during the solidification process.

(4) The anisotropy of the steel was much improved by this shape control of inclusions.

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