

THE FORMATION OF ALUMINA INCLUSION IN ALUMINUM KILLED STEEL
CONTACTING WITH THE FeO CONTAINING SLAG

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Synopsis: Reformation of non-metallic inclusions with the reaction between FeO containing slag and aluminum killed steel was investigated through the laboratory scale test. The reformation behavior was evaluated by counting the number of the inclusions under the slag-metal interface. The number of inclusions increases with the increasing FeO content of the slag. And the critical condition for the inclusion reformation is described with the supersaturation degree of aluminum and oxygen under the slag-metal interface through the experiment with the two kinds of steel that contain different amount of aluminum, respectively.

Key words: Aluminum killed steel, slag, slag-metal reaction, inclusion, supersaturation degree, clean steel, diffusion, FeO activity, re-oxidation

1. Introduction

The highly deformable steel sheets are required high qualities without inclusion defect. In the recent continuous casting process, there are few defects due to non-metallic inclusions in the steady cast region. But in the unsteady cast region, just like ladle exchange period, many non-metallic inclusions are contained in the steel. The reformation of inclusion by the oxygen supply through the FeO containing slag is considered to be one of the major reasons of contamination. In this report, we tried to evaluate the critical value in practical operation of FeO content of the slag to prevent the contamination of steel through the oxidized slag.

2. Experimental procedure

The experiments were carried out with the Tammann furnace. The experimental apparatus is shown in Figure 1. Two kinds of metal of different aluminum content were used as the specimen. Table 1 shows the chemical composition of the metal specimens.

The FeO content of the slag was varied to evaluate its effect on the oxygen potential of the slag. Table 2 shows the chemical composition of slag specimens. The high basicity and the low MnO content were selected to prevent the effect of SiO₂ and MnO on the oxygen potential of the slag.

Table 1. Chemical composition of metal specimens (wt%)

	C	Si	Mn	P	S	Al
Low-Al	0.03	0.04	0.19	0.008	trace	0.17
Hi -Al	0.04	0.05	0.22	0.008	trace	0.39

Table 2. Chemical composition of slag specimens (wt%)

FeO	CaO	SiO ₂	Al ₂ O ₃	MnO	MgO	P ₂ O ₅	S
0.5 ~ 3	44	6	48	0.1	1	0.01	0.08

The 60g of metal specimen was melted in the high alumina crucible at 1873K. The slag was melted in the furnace at the same time. The molten slag was pumped up using the high alumina tube and poured onto the molten metal. After 60 sec. reaction, the crucible for metal was picked out of the furnace and was water-quenched.

The inclusions reformed by the reaction between slag and metal were evaluated by counting the number of the inclusions under the slag-metal interface.

3. Results

The metal specimen was etched with the SPEED (Selective Potentiostatic Etching by Electrolytic Dissolution [1]) method to observe the shape of the inclusions and to measure their chemical composition by EPMA. Fig. 2 shows one of the SEM image of the inclusion. Most of the inclusions observed were in the size less than 5 μm.

Major component of the inclusion were Fe and Al. Al content of the inclusion varied from 30 to 96 % with EPMA, and the rest was Fe. Because the inclusions are surrounded with iron, the analysis by the EPMA may include the background of iron. Therefore, these inclusions are considered to be alumina or hercynite.

The number of inclusions under the slag-metal interface was counted in the longitudinal section of the specimen. Fig. 3 shows the distribution of the inclusions in the direction of depth at half radius of the specimen. The number of inclusions does not differ in this direction. It is considered that the inclusions move from the slag-metal interface to the inner region with the metal flow by convection during solidification. Therefore, the number of inclusions in 4 mm from the slag-metal interface is adopted to represent the experimental condition.

Fig. 4 shows the relation between FeO content of the slag and the number of inclusions under the slag-metal interface.

A large number of inclusions are reformed with slag in the FeO content more than 1 %. But only a few inclusions are reformed with the slag in FeO content less than 1 %.

4. Consideration

4-1. Equilibrium between slag and metal

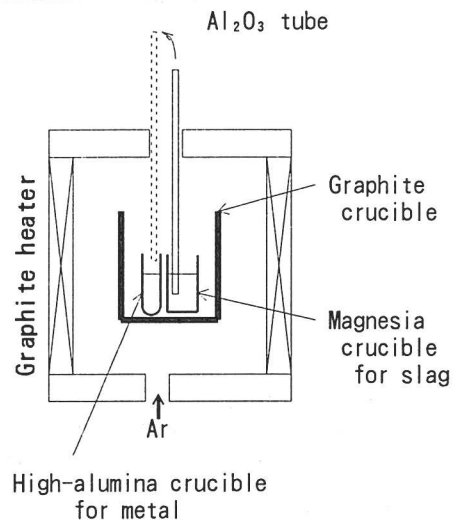


Fig. 1. Experimental apparatus.

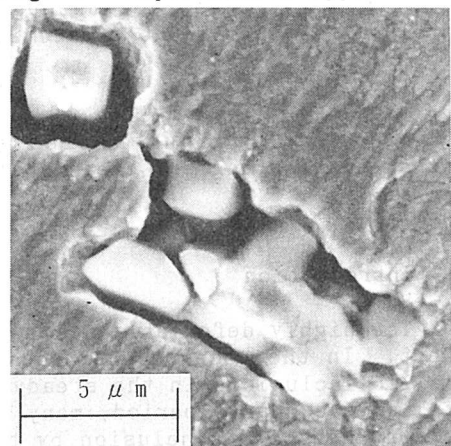


Fig. 2. Inclusion observed in the metal.

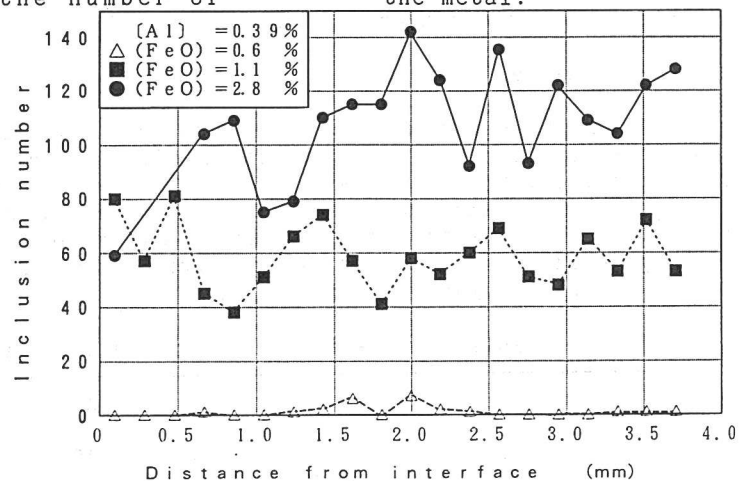
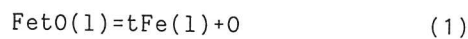
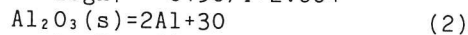


Fig. 3. Distribution of inclusions in the depth direction.

The equilibrium relation between slag and metal is considered to be expressed by the equations (1) and (2)[2].



$$\log K_1 = -6150/T + 2.604$$



$$\log K_2 = -64000/T + 20.57$$

The equation (1) gives the relation between FeO content of the slag and oxygen content in the steel. And the equation (2) gives the relation between oxygen and aluminum content in the steel. From these equations, the FeO content in equilibrium with aluminum in the steel can be obtained. Fig. 5 shows this relation. From this figure, the FeO content in equilibrium with the steel is in the order of 10^{-2} %. This value is much lower than the critical value observed in the experimental results. This suggests that the reformation of inclusion can be prevented even with higher FeO containing slag than the equilibrium value with the aluminum content in the steel.

4-2. Estimation of aluminum and oxygen distributions in the steel

The critical FeO content is higher than the equilibrium value. This is considered to be explained in terms of supersaturation. To estimate the supersaturation condition of aluminum and oxygen under the slag-metal interface, the distribution of aluminum and oxygen in the steel is calculated by unsteady diffusion model of oxygen and aluminum in the steel.

In the following estimation of aluminum and oxygen distribution, it is postulated that the equilibrium relation is achieved both at the slag-metal interface and in the bulk of the steel.

The unsteady diffusion is expressed by the equation (3).

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (3)$$

where C is the content of the solute, x is the distance from the slag-metal interface, and D is the diffusion coefficient of the solute in the molten iron.

The initial and the boundary conditions are given as followed.

Initial condition :

$$t = 0, x > 0, C = C_B \quad (4)$$

$$t = 0, x < 0, C = C_I \quad (5)$$

Boundary condition:

$$t > 0, x = 0, C = C_I \quad (6)$$

$$t > 0, x = \infty, C = C_B \quad (7)$$

The subscript "B" represents the value in the bulk of the steel, and "I" represents the value at the slag-metal interface.

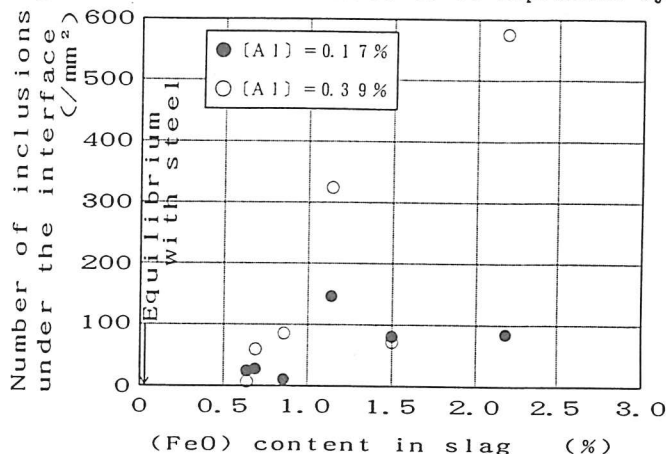


Fig. 4. Relation between (FeO) content in the slag and the inclusion number in the metal.

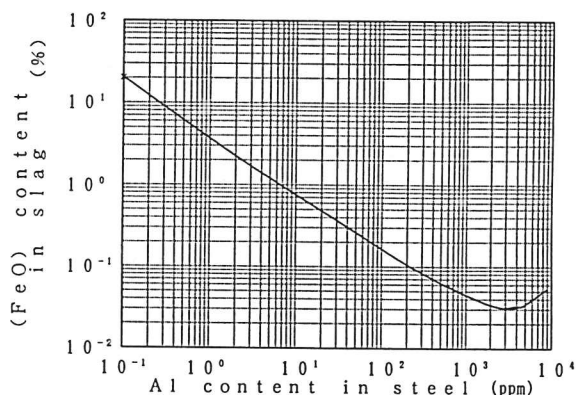


Fig. 5. Equilibrium relation between FeO in slag and aluminum in steel.

The diffusion coefficient of 3×10^{-5} (cm²/sec)[3] was used to both of aluminum and oxygen. The oxygen and aluminum content at the interface were calculated using equation (1) and (2), respectively.

Fig. 6 shows the example of the distribution of aluminum and oxygen content under the slag-metal interface. From this figure, the diffusion distance from the slag-metal interface in the contacting time of 60 sec. is about 1.5 mm.

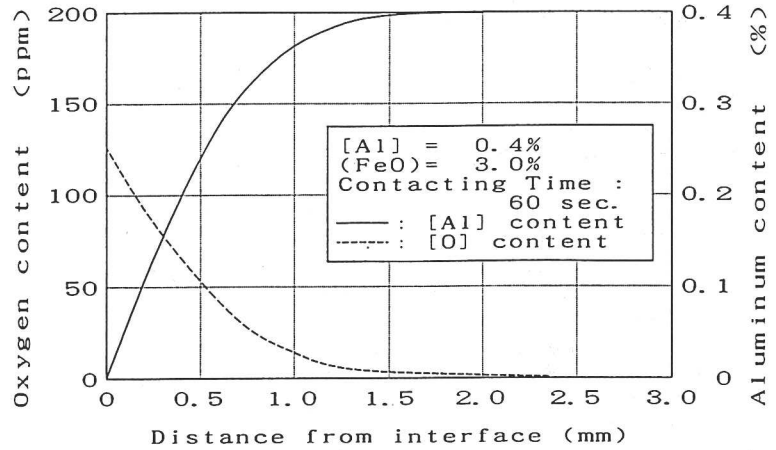


Fig. 6. Distribution of aluminum and oxygen content in the region under the slag-metal interface.

4-3. Estimation of supersaturation degree of aluminum and oxygen near the slag-metal interface.

The composition of inclusion reformed by slag-metal reaction is considered to be either alumina or hercynite. The equilibrium equation of alumina formation is expressed by the equation (2), and that of hercynite formation is expressed by the equation (8)[3].



$$\log K_3 = -165227/T + 53.6$$

From the equations (2) and (8), the equilibrium relation between aluminum and oxygen in the steel is shown in Fig.7. In this figure, the calculated aluminum and oxygen content under the slag-metal interface is also shown. The oxygen content under the interface is higher than the value equilibrated with both alumina and hercynite. Therefore, both of them can be reformed in this region. The supersaturation condition for the reformation both of alumina and of hercynite is calculated in the following consideration.

If the inclusions are alumina, the supersaturation degree of aluminum and oxygen in the steel, S , is expressed by the equation (9).

$$S_{\text{alumina}} = \frac{a_{\text{Al}}^2 \cdot a_{\text{O}}^3}{(a_{\text{Al}})_e^2 \cdot (a_{\text{O}})_e^3} = \frac{(f_{\text{Al}}[\% \text{Al}])^2 \cdot (f_{\text{O}}[\% \text{O}])^3}{(f_{\text{Al}}[\% \text{Al}]_e)^2 \cdot (f_{\text{O}}[\% \text{O}]_e)^3} \quad (9)$$

$$\begin{aligned} \log f_{\text{Al}} &= -1.98 [\% \text{O}] + 0.043 [\% \text{Al}] \\ \log f_{\text{O}} &= -0.174 [\% \text{O}] - 1.17 [\% \text{Al}] \end{aligned}$$

where "a" represents the activity, "f" represents the activity coefficient, and the subscript "e" represents the equilibrium state.

On the other hand, if the inclusions are hercynite, the supersaturation degree is expressed by the equation (10).

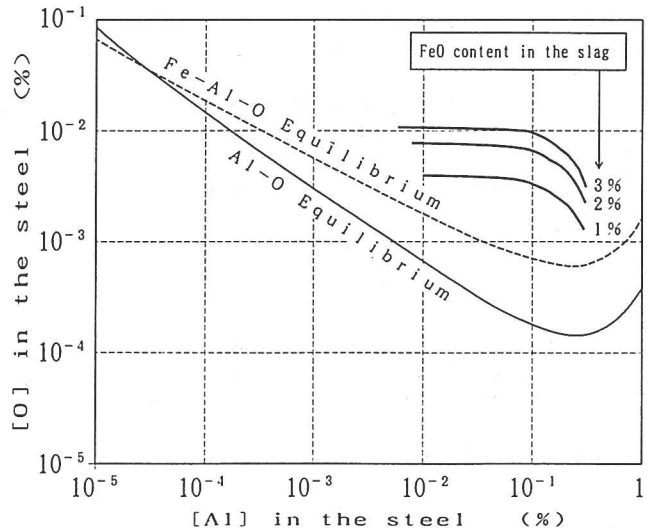


Fig. 7. Equilibrium relation between Al and O in Al-O and Fe-Al-O system.

$$S_{\text{hercynite}} = \frac{a_{\text{Al}}^2 \cdot a_{\text{O}}^4}{(a_{\text{Al}})_e^2 \cdot (a_{\text{O}})_e^4} = \frac{(f_{\text{Al}}[\% \text{Al}])^2 \cdot (f_{\text{O}}[\% \text{O}])^4}{(f_{\text{Al}}[\% \text{Al}]_e)^2 \cdot (f_{\text{O}}[\% \text{O}]_e)^4} \quad (10)$$

Fig. 8 shows the distribution of supersaturation degree under the slag-metal interface calculated by the equation (9). The "S" value have a peak under the slag-metal interface, and decrease with increasing distance. If the reformation of inclusion requires some supersaturation degree, the inclusions are expected to be formed only in the region where the "S" value exceeds the particular value. Therefore, the inclusions can be considered to be reformed not only at the interface but also in the steel.

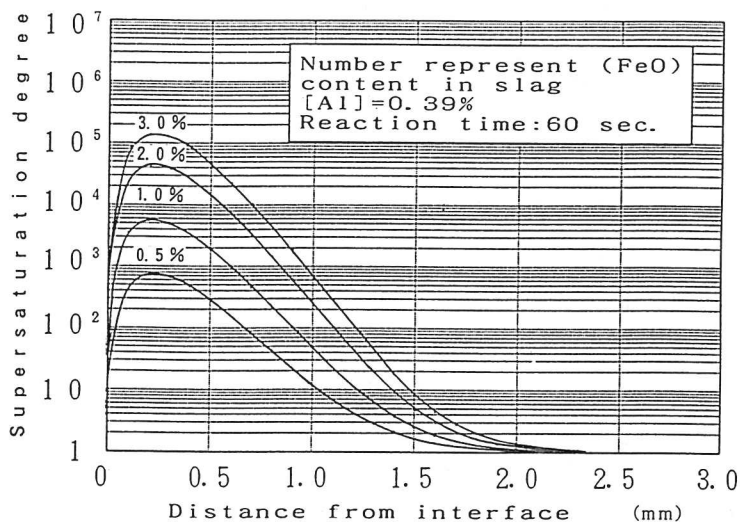


Fig. 8. The distribution of supersaturation degree of Al and O under the slag-metal interface.

Fig. 9 shows the relation between the peak value of the supersaturation degree " S_{alumina} " under each experimental condition and the number of inclusions observed under the slag-metal interface. This figure shows that only a few inclusions can be observed with the "S" value less than 10^3 . This suggests that 10^3 is the critical value of supersaturation degree for the reformation of inclusions by the contact of slag with metal.

If the inclusions are hercynite, the relation between the peak value of " $S_{\text{hercynite}}$ " and the number of inclusions slightly changes as shown in Fig. 10. In this case, the critical value to prevent the inclusion reformation is considered to be 10^2 .

In both systems, it is clear that the condition for inclusion reformation by slag-metal reaction can be described in terms of supersaturation degree under the slag-metal interface.

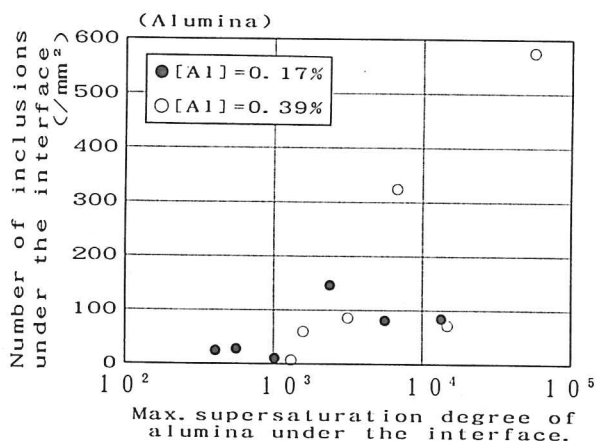


Fig. 9. The relation between peak value of " S_{alumina} " and the number of inclusions.

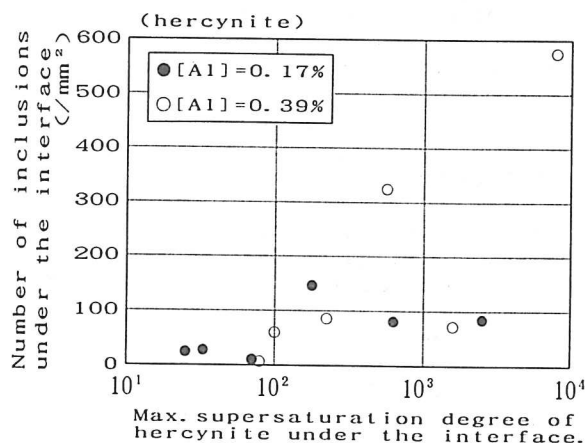


Fig. 10. Relation between peak value of " $S_{\text{hercynite}}$ " and the number of inclusions.

4-4. Discussion by nucleation theory.

The critical supersaturation degree of alumina (S_{alumina}) is expected to be 10^5 to 10^{11} from nucleation theory[5]. This value depends on the interfacial tension (σ_{alumina}) between alumina and molten steel. Fig. 11 shows the relation between the critical supersaturation degree and the interfacial tension for alumina and hercynite,

respectively. σ_{alumina} decreases with the increasing oxygen content in the molten steel. But S_{alumina} calculated at high oxygen content is three order higher than the experimental one.

On the other hand, the range of measured $\sigma_{\text{hercynite}}$ is wide between 1000 to 1700 (erg/cm²)[6]. Therefore, the calculated $S_{\text{hercynite}}$ is in the order of 10² to 10⁵, which is relatively close to the experimental value, 10², for hercynite formation.

Suito et al. investigated the Al-O system in equilibrium with the molten CaO-Al₂O₃ slag by laboratory experiment, and obtained the critical supersaturation degree (S_{alumina}) as about 10³.

In this time, it is not clear sufficiently what the supersaturation degree, 10³ for alumina or 10² for hercynite, means. But it is considered to be useful for practical operation.

4-5. Critical FeO content for commercial grade aluminum killed steel.

The experiments were carried out using aluminum killed steel containing higher amount of aluminum. If the critical supersaturation degree is independent of the aluminum content, it is considered that the critical FeO content to prevent the reformation of inclusions depends on the aluminum content. Fig. 12 shows this relation. The critical FeO content increases with the decreasing aluminum content. In the case of commercial grade steel containing about 0.05%[Al], the FeO content of the slag required to prevent the reformation of inclusions is 1.7 wt% in the case of alumina reformation, and 1.4 wt% in the case of hercynite reformation, respectively.

5. Conclusion

The critical condition to prevent the inclusion formation in the aluminum killed steel was investigated through laboratory scale experiment. The critical FeO content for the commercial grade aluminum killed steel was also estimated from the results.

6. Reference

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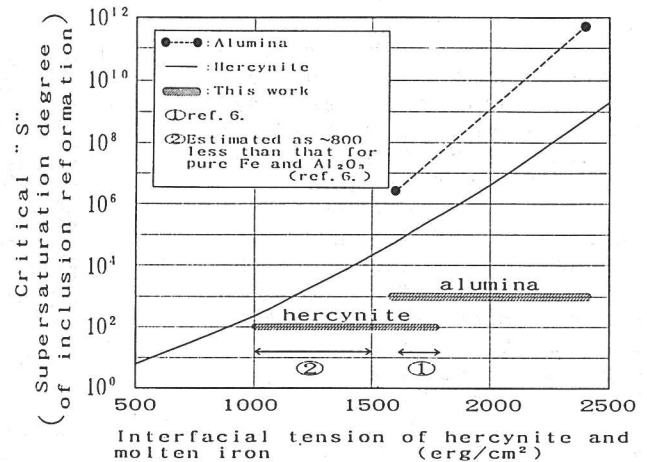


Fig.11. Effect of interfacial tension between steel and inclusion on critical supersaturation degree.

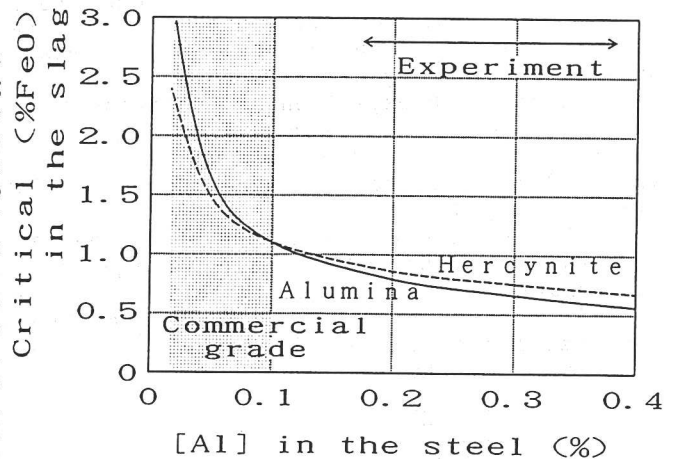


Fig.12. Relation between [Al] content in the steel and the critical FeO content in the slag.