Liquid Steel Treatment in the Ladle with Non-oxidizing Synthetic Slag*

By Kazuo OKOHIRA,** Nobuo SATO,** and Hisashi MORI***

Synopsis

Synthetic slags with low FeO content were produced by way of trial with a view to purifying liquid steel by preventing its reoxidation by the slag in the ladle. Using the 1-ton E.F., low-carbon aluminium-killed steel was tested on a semi-industrial scale.

The effects of slags and lining materials by types were investigated, and the following results were obtained:

(1) If the FeO content in slag in the ladle is decreased to less than 2%, liquid steel is purified and the total oxygen decreases to below 40 ppm. Large inclusions ($\geq 100 \mu$) are eliminated.

(2) Loss of sol. Al in liquid steel is caused not only by slag but also by lining material. In the case of treatment with synthetic slag, relative contribution of lining material to the loss of sol. Al is greater than in the case of treatment with normal slag. However, this contribution can be suppressed by the use of a lining material with high Al_2O_3 content.

(3) The velocity of sol. Al loss is controlled by the diffusion of oxygen in the slag.

I. Introduction

It is known that when liquid steel in the ladle is stirred by blowing argon gas therein from the bottom of the ladle or by any other methods, floatation and separation of suspending inclusions are promoted, thereby to purify the liquid steel and to decrease the total oxygen content¹⁾ therein. However, in the case of low-carbon aluminium-killed steel for which the slag flowing out of the LD-converter into the ladle has a very high oxidizing potential, the total oxygen in the liquid steel is hardly decreased, because of the oxidation of liquid steel by slag, even if argon bubbling is performed.²⁾ With a view to reducing oxidation of liquid steel, therefore, the purifying effect to be obtained by replacing this slag with a non-oxidizing synthetic slag with low FeO content and the effect of ladle lining material on low-carbon aluminium-killed steel were investigated by conducting semi-industrial tests on 1-ton scale using the synthetic slags produced by way of trial.

II. Test Methods

The steel selected for testing is low-carbon aluminium-killed steel, having the desired composition as shown in Table 1, which is most likely to be re-oxidized by slag on account of the properties of slag and the composition of liquid steel.

Table 1. Aim compositions of test heat

Compositions (%)	C	Si	Mn	P	S	sol. Al
Low C-Al-killed steel	0.03		0.30			0.030
	λ	<0.02	λ	<0.02	<0.02	λ
	0.05		0.40			0.070

1. Selection of Composition of Synthetic Slag

The slag which is most suitable for the above-mentioned objective must have the following characteristics:

- (i) Low oxygen potential
- (ii) Ease of absorption of inclusion (Al_2O_3)
- (iii) Low melting point and high fluidity.

The slag having these characteristics is of the $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system. The physical properties of this slag were controlled by adding AlF_3 , NaAlF_4 , Na_2CO_3 , and others thereto in small quantities. To suppress its oxygen potential, it is desirable to reduce the amount of FeO and MnO contents of it as much as material blending can permit. In Fig. 1, the synthetic slags mentioned in the references,³⁻⁸⁾ LD-converter slag and blast furnace slag having the typical compositions and refractories for ladle and powder for continuous casting are plotted on the phase diagram of the $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system. When assumed that the melting point of slag is preferably lower than 1300°C , the composition of the slag will be limited to three ranges with the following three points.

I: $\text{CaO}-\text{SiO}_2-\text{Al}_2\text{O}_3=38:42:20$

II: $\text{CaO}-\text{SiO}_2-\text{Al}_2\text{O}_3=50:7:43$

III: $\text{CaO}-\text{SiO}_2-\text{Al}_2\text{O}_3=22:63:15$

According to the iso-activity lines of Al_2O_3 and SiO_2 , which are shown in Fig. 2, the slag compositions I and II, excluding III, are suitable for suppressing the activity of SiO_2 as much as possible in the range where the activity of Al_2O_3 , the main constituent of

Fig. 1. Phase equilibrium diagram of $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system⁹⁾

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** Technical Research Institute, Yawata Works, Nippon Steel Corporation, Edamitsu-cho, Yawata-higashi-ku, Kitakyushu 805.

inclusions in aluminium killed steel, is low. As plotted in Fig. 1, any equivalent of composition I approximates that of powder (*F*) used for continuous casting and of blast furnace slag (⊙).

The composition of slags such as *C*,⁶⁾ *D*,⁷⁾ and *E*⁸⁾ mentioned in the references resembles composition II.

With a view to lowering the melting point even if the composition is changed due to enrichment of Al_2O_3 , SiO_2 , and others, the synthetic slag I (*S*-slag I) containing $\text{CaO}/\text{SiO}_2 \sim 1$ and basic synthetic slag II (*S*-slag II) containing $\text{CaO}/\text{SiO}_2 \sim 4$, both having the desired composition as shown in Table 2, were produced by way of trial. Experiments were conducted mainly using *S*-slag I having a wide range of low melting points.

2. Test Procedure

After the steel to be tested was melted down in the 1-ton E.F., oxygen was blown into it so that its carbon content became 0.03 to 0.04% and its total oxygen content became 600 to 700 ppm before tapping. At the time of tapping, Fe-Mn and Al were charged so that the steel attained the desired composition after slag off. Synthetic slag was added at the end of tapping and argon gas blown in from the early stage of tapping, while the hourly changes in composition of slag and liquid steel as well as the amount of inclusions were examined.

Slag samples were taken by a steel spoon at intervals of 3 to 5 min. Liquid steel samples were taken

at intervals of 0.5 to 2 min by means of a steel bomb of $40\phi \times 70$ mm in inner size and 10 mm in thickness. The analysis and observation of inclusions by microscope was conducted at the cross section at a height of 20 mm above the bottom of the bomb.

The main dimension of the ladle used for test are shown in Fig. 3. The liquid steel-slag interface is 600 mm in diameter and the liquid steel head is 500 mm. Synthetic slag is required an amount of 6 to 15 kg to suppress the rising of melting point occurring in accordance with changes in slag composition caused by Al_2O_3 (about 1.5 kg) to be formed on the assumption that the whole amount of oxygen content of liquid steel at the tapping, is converted into Al_2O_3 . In testing, therefore, the slag was used in a quantity of 10 to 20 kg per heat. If the liquid steel is stirred at a high flow rate of argon gas, the surface of liquid steel is exposed. The test, therefore, was conducted with the argon flow controlled at 3 to 10 Nl/min so as to avoid exposure of the liquid steel. To protect the surface of molten steel in case when the flow rate of argon gas is high, carbonized chaff was added in an amount of 2.5 to 5 kg to prevent air oxidation of liquid steel which, however, could not be sufficiently prevented. A considerably large amount of carbon pick-up on the other hand was observed, and so addition of carbonized chaff was limited to a small number of heats. To further decrease the amount of FeO in the synthetic slag, deoxidizers such as Al, Si, or Ca-Si may be added to the synthetic slag. Because, however, of the limitation imposed on the steel that Si content should be low, powdered aluminium was added and its effect was investigated.

Fig. 2. Isoactivity lines of Al_2O_3 and SiO_2 on the system $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ at 1630°C^{10,11)}

Table 2. Properties of slags

Properties Kinds of slag	Chemical composition										Physical properties		
	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaF ₂	Na ⁺	I _g loss	CaO/SiO ₂	ρ	ρ'	m.p
Synthetic slag I	43.8	36.1	7.7	0.6	—	0.6	5.5	2.1	3.4	1.21	2.95	0.95	1 150
	46.0	37.9	8.1				5.8	0	0.7	1.21	2.97	0.89	1 250
„ II	41.0	9.6	38.1	0.8	—	0.3	9.8	tr.	0.7	4.27	3.40	0.95	1 300
Normal slag	45	15	2	20	6	5	5	—	—	3			

The chamotte refractory (low Al_2O_3) having the composition as shown in Table 3 was used as a ladle lining material. Further, a coating material with high Al_2O_3 content was used to prevent silicon pickup during treatment, and the results were compared.

III. Test Results

Table 4 shows the analytical values of metal and slag in test heats as classified according to the test conditions. The heat asterisked in the "Note" column indicates that in which the liquid steel was exposed by about 10% of the area of liquid steel-slag interface, and that in which the liquid steel was presumably in direct contact with the carbonized chaff judging from the large quantity of carbon pick up formed at the time of its addition. These heats are the ones in which the N-pick up (ΔN) is large and the degree of air oxidation of liquid steel presumably is considerably high. In the heat in which powdered aluminium was added to the synthetic slag, the amount of FeO contained therein was the lowest.

1. Contribution of Various Reactions to Oxidation of Aluminium in Liquid Steel

The causes of the decrease in the amount of sol. Al due to the reoxidation of liquid steel in the ladle to be caused at the time of argon bubbling are presumably the following:

- (i) Air oxidation of sol. Al
- (ii) Oxidation by FeO, MnO and the like contained in the slag
- (iii) Oxidation of sol. Al by SiO_2 .

Based on the amount of pickups of Si and N and the decrease in sol. Al, which are shown in Table 4, loss of sol. Al was estimated by causes on the following assumptions:

(1) By the reduction of SiO_2 , Al is lost in an amount which is stoichiometrically equivalent to the amount of Si-pick up (ΔSi).

- ① Al-loss caused by SiO_2 -reduction 0.012(%)Al
- ② Al-loss caused by slag 0.008(%)Al
- ③ Al-loss caused by air-oxidation 0.034(%)Al

Fig. 3. Ladle dimension

(2) The amount of sol. Al oxidized by air is proportional to the amount of ΔN . (Fig. 4.)

(3) The loss due to reaction with slag is obtained by subtracting the sum of the losses mentioned in the assumptions 1 and 2 above from the total loss of sol. Al.

The heats were divided into two groups, *i.e.*, the group in which the amount of ΔN was small and consequently the loss of sol. Al by air was small, and the group in which the loss of sol. Al was great, and the average value of contribution of each reaction is given in Table 5. When treating with normal slag (N -slag), the loss of sol. Al thereby is decidedly great, *i.e.*, several times as great as the loss due to reaction with SiO_2 . When treating with S -slag, however, the contribution of reaction with SiO_2 is greater than the loss of sol. Al by the slag. In the case of S -slag treated heat for which a ladle lined with high Al_2O_3 material for suppressing its reaction both with SiO_2 and with air is used, loss of sol. Al by slag occupies the most part of the loss. In case air oxidation is so great that the amount of ΔN reaches 7 ppm during the treatment of about 15 min, it is considered that the contribution of air, SiO_2 , and slag becomes smaller in the order mentioned.

As an example, Fig. 5 (see p. 342) shows the hourly changes in sol. Al and total oxygen at the time of argon bubbling, respectively in the heat (No. 9) in which there was no exposure of molten iron surface when treated with S -slag I using a ladle lined with low Al_2O_3 material, in the heat (No. 7) in which the surface of molten iron was exposed by about 10% of the total area, and in the heat (No. 3) in which there was no exposure of molten iron surface when treated with the N -slag. In the N -slag treating heat, the decrease in sol. Al is quick and the total oxygen becomes the lowest when the amount of sol. Al has decreased to below 0.020%. In the S -slag treating heats, there is no example where the amount of sol. Al becomes extremely low during treatment. Accordingly, the point at which the total oxygen became nearly constant as shown in Fig. 5 was taken as the minimum value of total oxygen and was used for subsequent analysis. In the heat (No. 7) in which the exposure of molten iron surface is large, the decrease in sol. Al is great and the value of total oxygen is high. The behaviour of total oxygen is not satisfying the logarithmic law.¹²⁾ The reason may be that the physical properties of liquid steel are changed with the rapid temperature drop during treatment. Another reason may presumably be that new inclusions are formed by the reoxidation of liquid steel, while the inclusions are floating up and being eliminated, and part of them are trapped in the liquid steel.

Table 3. Chemical compositions of lining materials of ladle

Compositions Kinds of lining materials	Al_2O_3	SiO_2	Fe_2O_3	CaO	MgO	TiO_2	Na_2O	K_2O	I_g loss
Low- Al_2O_3	34.7	59.9	2.56	0.3	0.4	1.07	0.47	0.02	0.72
High- Al_2O_3	89.8	1.45	1.75	5.0	0.2	0.44	0.47	0.02	0.72

Table 4. Results

Kinds of slag	Ladle lining	Heat No.	Metal						$\frac{\Delta Si}{Si \text{ initial}}$ (%) $\times 10^3$
			Total O (ppm)		sol. Al (%) + 10 ³				
			initial	at min*	initial	at (T, O) min**	Δ sol. Al	$-\frac{d\text{sol. Al}}{dt}$	
Normal slag	Low-Al ₂ O ₂	1	264	82	150	80	70	17	20/8
		2	226	125	65	8	60	22	0/20
		3	242	95	157	22	153	25	(−18/3)
		4	155	54	120	64	60	9	7/13
	High-Al ₂ O ₃	5	260	192	81	1	80	16	4/6
		6	202	49	189	112	88	11	10/4
Synthetic slag I (S-slag I)	Low-Al ₂ O ₃	7	143	77	73	21	54	10	10/18
		8	99	61	132	77	58	—	12/15
		9	123	69	75	46	28	4	12/15
		10	102	68	96	73	23	—	12/18
		11	155	85	62	32	38	—	11/10
		12	133	42	138	85	58	4	24/10
		13	202	73	4	2	3	—	0
		14	142	92	10	1	9	0	7/6
		15	314	65	37	17	24	4	8/8
	High-Al ₂ O ₃	16	127	42	81	58	30	4	33/7
		17	135	35	110	76	40	3	2/8
		18	166	46	146	110	36	1	0/13
		19	150	47	151	123	40	3	0/18
		20	195	48	146	101	58	5	0/18
S-slag II	Low-Al ₂ O ₃	21	105	44	62	39	26	3	12/36
		22	107	45	49	26	28	2	9/26

* Minimum total-oxygen value during this refining treatment
** Sol. Al value at the point when Total O shows minimum value

Fig. 4. Presumption of Al-loss caused by air-oxidation

2. Effect of Ladle Lining Material on Reduction of SiO₂

Some examples in which $\overline{Si}$ is increased during treatment are as shown in Fig. 6. In the case of lining material with low Al₂O₃ content, $\overline{Si}$ is increased by more than 0.01% in about 15 min. Figure 7 shows the amount of ΔSi by types of ladle lining materials and slags. It is apparent that the ΔSi is decreased

greatly by the use of high Al₂O₃ lining material. It is evident from the study of inclusions, described later, that part of ΔSi exists in the form of oxides. If it is assumed that the whole amount of 0.01% Si exists in the form of SiO₂, the amount of oxygen generated thereby may be calculated as follows:

$$0.01(\%) \times \frac{32(2 \cdot O)}{28(Si)} = 0.0114$$

of experiments

		Slag				wt of metal (kg)	wt of slag (kg)	Note
ΔN (ppm)	Mn (%)×10³	FeO (%)		MnO (%)				
		initial	at (T. O) min	initial	at (T. O) min			
4	33	16.2	5.8	8.5	8.7	1 000	>100	
0	22	25.8	21.2	8.1	6.8	1 000	112	
0	20	22.8	17.3	7.4	4.7	1 000	125	
(0)	31	10.8	7.4	9.5	10.1	1 000	32	
(0)	21	32.2	26.8	6.2	7.6	900	106	
(0)	41	15.6	6.0	11.3	12.0	1 000	>100	
8	32	18.2	4.4	12.5	5.8	1 000	20	***
4	35	—	—	—	—	1 000	10	***
0	33	6.4	6.0	5.5	6.9	1 000	20	
2	36	—	—	—	—	1 000	10	
1	35	—	—	—	—	1 000	20	
9	—	0.7	0.7	1.8	1.8	800	10	c.c. 2
5	—	2.0	1.7	3.9	3.3	900	10	{c.c. 2****
—	33	4.2	3.6	4.5	5.0	1 000	20	{F-Al 400****
—	28	6.9	6.1	5.5	5.8	1 000	20	
12	41	1.1	1.2	1.4	1.4	800	10	c.c. 1****
4	—	1.9	1.3	8.9	4.7	900	20	c.c. 1****
2	43	2.5	1.8	5.4	4.9	900	15	
0	33	4.5	4.4	5.5	5.0	900	15	
0	39	3.6	1.8	3.0	3.1	900	15	
0	42	1.0	0.8	2.4	2.5	1 000	20	
0	39	1.5	1.2	3.7	3.8	1 000	20	

*** With much N pickup, that is, strong oxidation by air
**** c.c.: Carbonized chaff, F-Al: Flake-Al

Table 5. Contribution of repective reaction to sol. Al-loss

Kinds of slag	Kinds of lining	Selected heats	Mean value of variation of elements			Contribution to sol. Al-loss (%)×10 ³			Note
			—Δsol. Al (%)×10 ³	ΔSi (%)×10 ³	ΔN (ppm)	by ΔSi	by air	by slag	
Normal slag	Low-Al ₂ O ₃	No. 14, 19, 26	63	9	1.3	12	5	46	With less Al-oxidation by air
	High-Al ₂ O ₃	No. 23, 25	84	7	0	9	0	75	
S-slag I	Low-Al ₂ O ₃	No. 3, 4, 6	30	12	1	15	4	11	
	High-Al ₂ O ₃	No. 17, 18, 20	45	0	0.7	0	3	42	
S-slag I	Low-Al ₂ O ₃	No. 1, 2, 13	57	5	7	19	28	10	With much oxidation by air

Namely, the amount of oxygen would reach no less than 114 ppm.

In view of the facts that the greater part of inclusions is of Al₂O₃ and that the total oxygen is lowered to several tens ppm, it is presumable that most of the analytical values of Si exist in the form of Si. The reason why the ΔSi differs considerably as shown in Fig. 7 even if the same low Al₂O₃ lining material is used, can be explained by the difference in the composition of the treated liquid steel.

Assuming that the amount of ΔSi corresponds to the brick erosion based on the report⁽¹⁵⁾ that brick erosion is increased with the increase in the amount of excess Mn ($\mu:\mu=Mn-2.15\text{ Si}$) under Fe–O–Mn–Si

deoxidation equilibrium, but is decreased if the amount of Al is high, the relation between ΔSi and μ is shown in Fig. 8. It has been confirmed that the erosion is increased with the increase of μ even in the range where the content of Mn is so low as 0.20 to 0.40%. The influence of the level of Al is shown in Fig. 9, but its effect has not been clarified.

3. Factors that Control the Total Oxygen in Liquid Steel

The total oxygen which showed the lowest value during treatment ((Total O)_{min}) was taken as a guide to the cleanliness of liquid steel, and the relations between the amount of sol. Al and the (Total O)_{min} by types of ladle lining materials and slags have then been

Fig. 5. Change of Total O and sol. Al in liq. steel

Fig. 6. Change of silicon in liq. steel

Fig. 7. Comparison of Si pickup among kinds of slag and ladle lining

shown in Fig. 10 together with the equilibrium values reported so far. The oxygen amount to be balanced

Fig. 8. Relation between Si pickup and μ -factor

Fig. 9. Relation between Si pickup and sol. Al

Fig. 10. Relation between Total O and sol. Al

increases rapidly as the amount of sol. Al decreases to below 0.030%, and the same trend is clearly seen in the measured values. Figure 11 shows the relation between the (Total O)_{min} and the amount of FeO in slag at the corresponding time. It will be seen that the value of (Total O)_{min} decreases with the decrease in the amount of FeO in slag and the liquid steel becomes clean, provided that sol. Al is at the same level. If the amount of FeO is less than 2% and the amount of sol. Al is more than 0.030%, the value of (Total O)_{min} would become lower than 45 ppm. As to the effect of lining material, if the amount of FeO in slag is low, the total oxygen content would be decreased by several ppm., when a high Al₂O₃ material is used and thus the effect of lining material is observed. The difference in effects of synthetic slags I and II depending on their types is hardly observed.

Fig. 11. Relation between minimum values of Total O and FeO content of slag

4. Inclusions

Examples of hourly changes in the number of inclusions per unit area by sizes and types and changes in the total oxygen values are shown in Fig. 12. In heat (No. 17) with *S*-slag addition large alumina-clusters decrease in quality quickly with the lapse of time and the total oxygen values also decrease down to 40 ppm. On the other hand in heat (No. 1) without *S*-slag addition large alumina clusters remain even after argon bubbling of 8 to 10 min.

This presumably is because part of the product formed by the reaction of the slag having a high FeO content (16.3 to 5.8%) with Al contained in the liquid steel is trapped therein. In other words, the decrease in inclusions (ΔI) must be expressed by the difference between the amount of inclusions eliminated through floatation (ΔI_{float}) and the amount of the trapped portion ($\alpha \cdot I_{\text{react}}$) of inclusions reproduced (I_{react}).

$$\Delta I = \Delta I_{\text{float}} - \alpha \cdot I_{\text{react}} \dots \dots \dots (1)$$

As liquid steel is stirred uniformly, the trapping coefficient α may well be considered as being constant. Accordingly, if the decrease of inclusions is small, this means that I_{react} is great. The above-described fact means that I_{react} is greatly affected by the amount of FeO in slag.

IV. Discussion

1. Behaviour of Sol. Al and Total Oxygen (T. O) during Treatment

While the liquid steel is being stirred in a ladle, various chemical reactions as described below will occur at points ①, ② and ③ shown in Fig. 3.

① Oxidation of Al by air and absorption of nitrogen.

② Oxidation of Al by FeO and MnO in slag and trapping of Al₂O₃ in the liquid steel. Absorption of floating inclusion.

Fig. 12. Variation of inclusions and Total O during Ar-gas bubbling

③ Erosion of lining and reduction of SiO₂ by Al

So far, special attention has been paid to the behaviour of total oxygen from the standpoint of purification of liquid steel. If the content of sol. Al is more than 0.030%, changes in the amount of free oxygen are small. Consequently, the amount of T. O is presumably determined by the floating separation of inclusions being suspended in liquid steel, coupled with the phenomenon wherein the oxidation product of Al produced by various reactions is trapped in liquid steel and is newly suspended. Accordingly, the rate of decreasing of T. O can be expressed by the equation

$$-\frac{d(T.O)}{dt} = k(T.O) - \beta \cdot \left(-\frac{dAl}{dt} \right) \dots \dots \dots (2)$$

where, β : trapping coefficient of Al₂O₃, including coefficient of conversion from Al to O
 k : floating separation coefficient.¹⁶⁾

The oxidation reaction of Al on the other hand may be expressed by the following formula:

The rate of oxidation ($-dAl/dt$) of Al which is the basis of Eq. (2) was calculated, using the constant mentioned in the references, from the standpoint of the double boundary film theory for the following two cases: the case in which the oxidation rate of Al is controlled by the supply of Al to the reaction site, and the case in which the rate is controlled by the supply of oxygen from slag:

(1) Control by Diffusion of Al

In the case where the oxidation of Al is assumed to be controlled by the diffusion of Al, the oxidation rate of Al is expressed by the equation.

$$-\frac{d[\%Al]}{dt} = \frac{D_{Al}}{\delta_M} \cdot \frac{A}{V} [\%Al] \dots \dots \dots (4)$$

Fig. 13. Dependence of kinds of reaction control step on FeO content in slag and Al content in liq. steel

Fig. 14. Relation between $(-d \text{ sol. Al}/dt)$ and FeO, (FeO+MnO) in slag

Fig. 15. Relation between $(-d \text{ sol. Al}/dt)$ and sol. Al

where, V : liquid steel volume $1.36 \times 10^5 \text{ cm}^3$
 A : reaction surface
 $2.8 \times 10^3 \text{ cm}^2$ (only liq. steel-slag interface)
 $1.5 \times 10^4 \text{ cm}^2$ (plus liq. steel-lining interface)
 D_{Al} : diffusion coefficient of Al in steel
 $2 \times 10^{-4} \text{ }^{17)} \sim 3.5 \times 10^{-5} \text{ }^{18)} \text{ cm}^2 \cdot \text{sec}^{-1}$
 δ_M : thickness of diffusion layer in liq. steel side
 $3 \times 10^{-3} \text{ }^{19)} \text{ cm}$

Substituting the values mentioned in the references, Eq. (4) can be rewritten as follows:

$$-\frac{d[\% \text{ Al}]}{dt} = (8.0 \times 10^{-2} \sim 1.4 \times 10^{-2})[\% \text{ Al}] \dots \dots (4)'$$

(2) Control by Supply of Oxygen from Slag

The mole content of FeO to be supplied from slag per unit time is as follows:

$$\begin{aligned} \dot{n}_{\text{FeO}} &= A \frac{D_o}{\delta_s} (C_{\text{FeO}} - C_{\text{FeO}}^i) \\ &\approx A \frac{D_o}{\delta_s} \cdot C_{\text{FeO}} \dots \dots \dots (5) \end{aligned}$$

where, $\dot{n}_{\text{FeO}}$: mole flux of FeO ($\text{mol} \cdot \text{sec}^{-1}$)
 C_{FeO} : mole content of FeO in slag bulk ($\text{mol} \cdot \text{cm}^{-3}$)
 C_{FeO}^i : mole content of FeO in slag bulk at liq. steel-slag interface
 $C_{\text{FeO}}^i \approx 0$ by sufficient Al content
 D_o : diffusion coefficient of oxygen in slag

$4.9 \times 10^{-5} \text{ cm}^2 \cdot \text{sec}^{-1} \text{ }^{20)}$
 δ_s : thickness of diffusion layer in slag $1.0 \times 10^{-2} \text{ cm}^{20)}$

x : wt% FeO in slag $C_{\text{FeO}} = 3.9 \times 10^{-4} \cdot x$

The following Eq. (6) can be established from the mass balance of aluminium and oxygen to be reacted.

$$-\frac{V \cdot \varphi}{100} \cdot \frac{48}{54} \cdot \frac{d[\% \text{ Al}]}{dt} = 16 \cdot \dot{n}_{\text{FeO}} \dots \dots \dots (6)$$

where, φ = density of liquid steel ($7.2 \text{ gr} \cdot \text{cm}^{-3}$)

Substituting the constant described above, Eq. (6) can be rewritten as follows:

$$-\frac{d[\% \text{ Al}]}{dt} = 5.94 \times 10^{-4} \cdot x \dots \dots \dots (6)'$$

From Eqs. (4)' and (6)', the following equation can be obtained as the critical condition:

$$\begin{aligned} 5.94 \times 10^{-4} \cdot x &= 8.0 \times 10^{-2} [\% \text{ Al}] \\ x &= 1.35 \times 10^{-2} [\% \text{ Al}] \dots \dots \dots (7) \end{aligned}$$

Comparing Eqs. (4)' and (6)' and based on the quantitative relation between the sol. Al content and the FeO content (x) in slag, these reaction systems are divided into the range where it is controlled by the diffusion of Al and the range where it is controlled by the supply of oxygen. The critical conditions for these ranges are given by Eq. (7). In Fig. 13, Eq. (7) is shown in solid lines and the initial values obtained by way of experiments are plotted therein. (Mark "O" indicates the range in which the oxidation rate is controlled by the diffusion of Al ; mark "●", the range in which oxidation is controlled by the supply of oxygen; and mark "◐", the intermediate range.) Plotting sol. Al against time for each heat, the oxidation rate of Al at the early stage of reaction was obtained from the slope of plotted curve. Its relations with the amount of FeO or (FeO+MnO) in slag as well as to sol. Al are shown in Figs. 14 and 15. The effects of heats with large pickups of Si and N, which are marked with "v" in the figures, are not clear. Although these effects must be further studied, it may be appropriate in our experiment to consider that in the heats treated the oxidation rate is controlled by the supply rate of oxygen from slag.

Furthermore, the linearity of lines as shown in Fig.

16, illustrating the hourly changes in FeO content in slag, endorses that the oxidation rate of Al is controlled by the supply of oxygen from slag in these heats. From Eq. (8), it is considered that the difference in the slope is caused by the difference of slag amount (V_{slag}).

$$-\frac{d(\text{FeO})}{dt} = \frac{D_o}{\delta_s} \cdot \frac{A}{V_{\text{slag}}} \cdot (\text{FeO}) \dots\dots\dots(8)$$

$$\log(\text{FeO}) = -\frac{1}{2.75} \cdot \frac{D_o}{\delta_s} \cdot \frac{A}{V_{\text{slag}}} \cdot t \dots\dots\dots(8)'$$

Based on Eq. (8) D_o was calculated backwards from the slope of the line shown in Fig. 16, the results of which being given in Table 6. $5.62 \times 10^{-5} \sim 3.67 \times 10^{-5} \text{ cm}^2 \cdot \text{sec}$ was obtained as D_o . This value agrees nearly with $D_o = 4.9 \times 10^{-5} \text{ cm}^2 \cdot \text{sec}^{-1}$ which was used in Eq. (5). Consequently, it is considered that the boundary line indicated by Eq. (7) and shown in Fig. 13 is moved upward as shown by dotted lines, for the reason that the value used in Eq. (4) in estimating the diffusion rate of Al was not appropriate.

Furthermore, as the second term on the right side of Eq. (2) is proportional to the amount of FeO in slag, the relation between $(\text{Total O})_{\text{min}}$ and the amount

of FeO which is shown in Fig. 11, can be introduced as follows:

$$-\frac{d(\text{T. O})}{dt} = k \cdot (\text{T. O}) - \beta'(\text{FeO}) \dots\dots\dots(2)'$$

As $(\text{T. O})_{\text{min}}$ is the amount of T. O at the time of $d(\text{T. O})/dt \rightarrow 0$, the following formulas can be obtained from Eq. (2)' :

$$k(\text{T. O})_{\text{min}} - \beta'(\text{FeO}) \doteq 0 \quad (\text{T. O})_{\text{min}} \doteq \frac{\beta'}{k}(\text{FeO}) \dots\dots\dots(2)''$$

Thus, the linear relationship between $(\text{T. O})_{\text{min}}$ and the amount of FeO can be explained by these equations.

2. Effect of Ladle Capacity on Loss of Al

Limiting the discussion now to cases where the amount of slag is sufficiently great and hence air oxidation of liquid steel can be ignored, the speed of Al loss by slag and the speed of Si-pick up, in two ladles of greatly different capacities, were compared on the following assumptions:

(1) Technical data of ladle

Dimension Ladle	Inner diameter (mm)	Liq. steel head (mm)
1 t	600	500
150 t	3 000	3 000

(2) The oxidizing rate of Al conforms to that given in Eq. (4).

(3) Si-pick up per unit interface of ladle wall is constant regardless of the ladle size.

The results of calculations are given in Table 7.

In a 150-ton ladle, the oxidation of Al by slag is decreased to about 1/6 of that in a 1-ton ladle and the Si-pick up is also decreased to about 1/5. When a large ladle is used, the contribution of SiO_2 becomes

Fig. 16. Variation of FeO content in slag

Table 6. Calculation of diffusion coefficient

	Slag-weight W_s (kg)	Slag-volume $V_{\text{slag}} = \frac{W_s}{\rho_s} \times 10^3$ (cm^3)	Tangent = $\frac{d(\log \text{FeO})}{dt}$ (min^{-1}) (from Fig. 16)	$K = \frac{-1}{2.75} \times \frac{A}{\delta \cdot V_{\text{slag}}}$ (cm^{-2})	$D_o = \frac{\text{tangent}}{K} \cdot \frac{1}{60}$ (cm^2/sec)
●	106	35.4×10^3	8.0×10^{-3}	2.88	4.6×10^{-5}
△	72	24.0×10^3	1.0×10^{-2}	4.24	3.9×10^{-5}
○	64	21.3×10^3	1.0×10^{-2}	4.78	3.5×10^{-5}
□	32	10.7×10^3	3.1×10^{-2}	9.26	5.6×10^{-5}

Diffusion layer thickness $\delta = 10^{-2} \text{ cm}$, Density of slag $\rho_s = 3$, Reaction area $A = 2.83 \times 10^3 \text{ cm}^2$

Table 7. Comparison of sol. Al-loss and Si-pick up between different heat sizes

Heat size		1T (Ladle dia. 600 ϕ) (liq. steel head 500)	150T (Ladle dia. 3 000 ϕ) (liq. steel head 3 000)
Sol. Al loss or Si-pick up			
Sol. Al loss (%/10 min)	When slag contains 15%FeO	0.089	0.015
	When slag contains 1.0%FeO	0.006	0.001
Si-pick up (%/10 min), (Al equivalent)		0.010 (0.0124)	0.002 (0.0025)

small if the amount of FeO in slag is extremely high. When a synthetic slag is used, however, said contribution becomes relatively large, making it necessary therefore to give due consideration to the selection of ladle lining material.

V. Conclusion

In low-carbon aluminium-killed steel, the total oxygen content in the liquid steel is hardly decreased even if argon bubbling is performed, owing to reoxidation by the slag flowing from the LD-converter into the ladle. To prevent reoxidation of liquid steel by slag, synthetic slag with a low FeO content was produced and the purifying effect to be derived by substituting the LD-converter slag with this synthetic slag was studied, and the following results were obtained:

(1) Two systems of synthetic slags were considered usable: *i.e.*, CaO: SiO₂: Al₂O₃=38.42: 20 (S-slag I), and CaO: SiO₂: Al₂O₃=50: 7: 43 (S-slag II). However, studies were conducted chiefly using S-slag I having a wider range of low melting points.

(2) The lower the FeO content in slag, the lower the total oxygen in liquid steel. If the FeO content in slag is lowered to 1 to 2%, the total oxygen decreases to less than 40 ppm after argon bubbling of about 15 min. Further, almost all of inclusions of more than several tens microns in size disappear.

(3) If the amount of sol. Al is lowered to less than 0.030%, the total oxygen is rapidly increased. If the amount of FeO in slag is increased, the total oxygen is thereby markedly increased.

(4) When treatment with the synthetic slag is done using a ladle lined with low-Al₂O₃ material, Si is picked up in an amount of 0.01 to 0.02%. The zero to 60% of Al-loss is presumably caused by its reaction with SiO₂. A close relationship is observed between the increase in Si-amount and the amount of excessive Mn (μ), but Si-pick up can be prevented by using a high-Al₂O₃ lining material.

(5) It is considered that the oxidation rate of sol. Al in liquid steel by slag can be controlled by the supply of oxygen.

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