

Rate of reoxidation of ultra-low carbon steel in contact with slag of various compositions

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Laboratory-scale experiments were carried out to investigate the effect of ladle slag composition on the decreasing behaviour of aluminum content in steel, i.e., reoxidation of molten steel in contact with slag, using a vertical tube furnace. The steel composition and the slag system chosen were for ultra low carbon and CaO-Al₂O₃-FeO-MnO-MgO based to simulate ULC steel grades. It has been observed that the reoxidation rate shows a good relationship with (T.Fe) content in slag. In case of (T.Fe) content higher than 1.5 weight per cent, the reoxidation rate increases linearly with increasing (T.Fe) content. For a given (T.Fe) content, it decreases with the increasing (CaO)/(Al₂O₃) ratio of the slag. However, in the case of (T.Fe) content lower than 1.5 weight per cent, no particular relationships are observed between the reoxidation rate and (T.Fe) content or the (CaO)/(Al₂O₃) ratio of the slag. These results were used to propose for an aim a slag composition for the ULC steel grades in a steelmaking plant.

Keywords: slag deoxidation, slag killing, slag composition control, IF steel, ULC steel grade

Introduction

ULC (ultra low carbon) steel is widely used for various applications where good formability and surface quality are required. To secure the required qualities, the oxide cleanliness of steel should be high enough not to cause a defect during rolling and forming operations. Steel cleanliness is affected by the physico-chemical properties of slag in contact with molten steel in the secondary metallurgy ladle. Use of slag, which has a large capacity for alumina absorption and a small tendency towards oxidation, is known to be effective in the production of clean ULC steel¹⁻⁴.

The ladle slag of the ULC steel is composed mainly of CaO, Al₂O₃, MgO, Fe₂O and MnO. In this slag system, the alumina absorption capacity increases as the (CaO) content increases to a certain value. Oxidation tendency increases with increasing (Fe₂O+MnO) content. From an economical point of view, POSCO's Gwangyang Works used to aim at the ladle slag having a (CaO)/(Al₂O₃) mass ratio of 1.0 ~ 1.6 and the (T.Fe+MnO) lower than 5 mass per cent³. However, there are still arguments that the (T.Fe+MnO) of 5 mass per cent is not low enough to produce clean ULC steel. In addition, in producing manganese containing ULC steel, due to the addition of a large amount of manganese alloy, the slag tends to have such a high (MnO) content that the intended (T.Fe+MnO) value could not be met. The oxidation tendency of (MnO) needs to be assessed so that the slag composition for that steel grade can be determined.

Laboratory-scale experiments were carried out to investigate the reoxidation rate of molten ULC steel in contact with CaO-Al₂O₃-FeO-MnO-MgO based slag having various compositions. Referring to results from the experiments, a slag composition was proposed and tested in a steelmaking plant for the ULC steel grades. The details are described in this paper.

Experiments

Laboratory-scale experiments were carried out to measure the oxidization rate of aluminum in molten steel in contact with molten slag using a vertical tube furnace equipped with an LaCrO₃ heating element. The primary concern was to assess the effect on the oxidizing tendency of the slag composition, such as (FeO), (MnO), (CaO) and (Al₂O₃) contents. A master slag of 50 weight per cent CaO-50 weight per cent Al₂O₃ was prepared following the procedure: melting CaCO₃ and Al₂O₃ reagent in a graphite crucible charged in a box furnace → cooling → crushing → decarburization by reheating to 1200°C for 24 hours.

The treated master slag was mixed with dried reagent grade CaO, Al₂O₃ and MgO to make slag material. ULC steel produced at Gwangyang Works was used for the metal phase. The 30 g of materials for slag and 600 g of metal, which had been charged in a crucible having a inner diameter of 60 mm, were heated up to 1600°C under a purified argon atmosphere. After maintaining the metal and slag in contact with each other for an hour, aluminium sealed in a copper pipe was plunged in the metal phase. The amount of aluminium was determined for the steel to have the initial aluminium content of 0.08 ~ 0.10 weight per cent. The metal and slag were sampled at a predetermined time interval using a quartz tube and a copper plate, respectively. After being weighed, the samples were for chemical analysis following adequate treatment. Crucibles of lime, alumina and magnesia were used to meet various compositions of (CaO) and (Al₂O₃), including a lime- and alumina-saturated one.

In order compare the results from the laboratory-scale experiments with plant data, samples were taken for the ULC steel produced at Gwangyang Works. The conditions for the steelmaking processes for the steel grades can be obtained in more detail in another report⁴⁻⁵.

Results and discussion

Measurement of reoxidation of ULC steel in contact with slag

As ULC steel is widely used for various applications where a low level of oxygen is required, aluminium is used as a primary deoxidizing element. After deoxidation, in general, the steel has a smaller oxygen potential than the slag. Oxygen is transferred from the slag to the liquid steel, leading to the reoxidation of steel. Reoxidation results in a decrease of the contents of soluble elements, particularly of the aluminium. With the increasing amount of the transferred oxygen, the extent of the soluble aluminium decreases becomes larger, leading to an assumption that the decreasing rate of the soluble aluminium content can be used as a measurement for the reoxidation of steel by slag or the oxidizing tendency of slag.

In the steelmaking process, the ULC steel after the deoxidation and the secondary refining remains unstirred in the ladle for a long period of time. The decrease of soluble aluminium, then, can be assumed to be determined by Ficks' law, Equation [1].

$$\begin{aligned} -\frac{d[Al]}{dt} &= \frac{D}{\delta} \frac{A}{V} ([Al] - [Al]^*) \\ &= \frac{\rho DA}{\delta} \cdot \frac{([Al] - [Al]^*)}{W} \end{aligned} \quad [1]$$

where $[Al]$, D , ρ , V , W , A , δ , t are the aluminum content (weight per cent), the diffusion coefficient (cm^2/min), the density (g/cm^3), the volume (cm^3), the weight of the steel (g), the area (cm^2), and the thickness of the interfacial area (cm) between the metal and slag phases, and $[Al]^*$ is the aluminum content of steel at the slag-metal interface.

Theoretically, the value of $[Al]^*$ can be obtained using the thermodynamic data for the following chemical reaction.



$$K_2 = \frac{a_{(Al_2O_3)^*}}{a_{[O]^*}^3 \cdot a_{[Al]^*}^2} = \frac{a_{(Al_2O_3)^*}}{a_{[O]^*}^3 \cdot f_{[Al]^*}^2 \cdot [Al]^*{}^2} \quad [3]$$

where the notation follows the general terminology in thermodynamic textbooks. Introduction of a new variable, $k_{[Al]}$, leads to Equation [4].

$$-\frac{d[Al]}{dt} = k_{[Al]} \cdot \frac{([Al] - [Al]^*)}{W} \quad [4]$$

The variable $k_{[Al]}$, which is given by Equation [3], can be considered a mass transfer coefficient. As it represents the decreasing rate of the soluble aluminium content in the molten steel in contact with slag, the value of $k_{[Al]}$ can be considered to be a measurement for the reoxidation potential, i.e., the oxidizing tendency of the slag.

$$k_{[Al]} = \frac{\rho DA}{\delta} \quad [5]$$

Integration of Equation [4], assuming that $[Al]^*$ remains constant, results in

$$\ln \frac{[Al]_o - [Al]^*}{[Al] - [Al]^*} = k_{[Al]} \int_{t=0}^t \frac{1}{W} dt \quad [6]$$

where $[Al]_o$ means the initial concentration of the soluble aluminum in steel. It should be mentioned here that, as a

considerable amount of steel is removed at each sampling, W should be treated as a time-dependent variable. However, $k_{[Al]}$ can be considered to be an time-independent variable for the whole period of the experiment. In addition, $[Al]^*$ has been assumed to be constant, even though it may change somewhat.

Graphical representations for an experimental heat using Equation [6] gives the value of $k_{[Al]}$ as the slope of a straight line for the relationship between $\ln \frac{[Al]_o - [Al]^*}{[Al] - [Al]^*}$ and $\int_{t=0}^t \frac{1}{W} dt$. In this research, the value of $\int_{t=0}^t \frac{1}{W} dt$ was obtained by an approximation because the steel weight was assumed to change step by step only with each sampling.

$$\int_{t=0}^t \frac{1}{W} dt \approx \sum_i \frac{1}{W_i} (t_{i+1} - t_i) \equiv \sum \frac{1}{W} \quad [7]$$

where t_i is a time for the i -th sampling.

An example of the graphical representation for an experimental heat is given in Figure 1, which shows the variation of soluble aluminum content in steel with time, which is set at zero at the time of the aluminium addition. Compositions of the molten slag in contact with the steel at the initial and final states of the experiments are given in Table I. The aluminium content decreases very quickly from the initial stage.

Rearrangement of the previous data in a $\sum_i \frac{1}{W_i} (t_{i+1} - t_i) - \ln \frac{[Al]_o - [Al]^*}{[Al] - [Al]^*}$ plot gives Figure 2. The linear relationship between the two variables is clear, indicating that the assumptions suggested in the procedure to measure the $k_{[Al]}$ value, the values of the $k_{[Al]}$ and the $[Al]^*$ remain constant during the experiment. From the slope of the line, the value of $k_{[Al]}$ is 35.13 g/min, which can be chosen as a measurement to represent the reoxidation tendency of the slag.

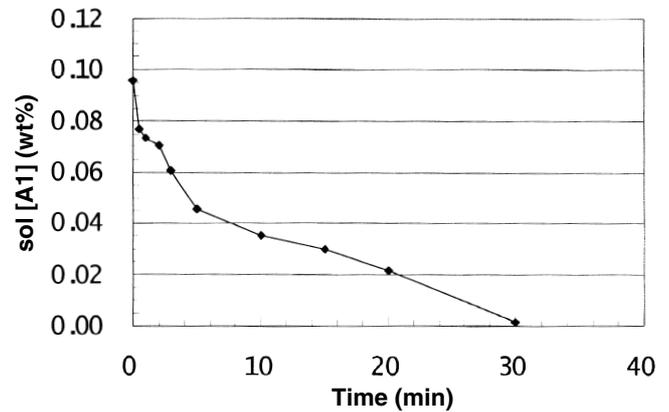


Figure 1. Example for the change of the soluble aluminium content with time

Table I
Chemical composition, weight per cent, of slag for the experimental heat in Figure 1

Component	CaO	Al ₂ O ₃	T.Fe	MnO	MgO	(CaO)/(Al ₂ O ₃)
Initial	51.58	35.95	0.85	0.23	6.85	1.43
Final	50.34	36.76	0.29	0.06	8.72	1.37

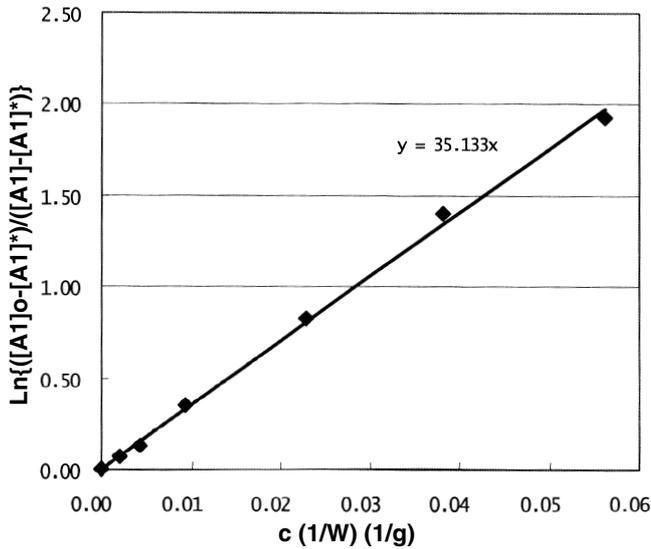


Figure 2. $\ln \frac{[Al]_o - [Al]^*}{[Al] - [Al]^*}$ vs. $\int_{t=0}^t \frac{1}{W} dt$ for data shown in Figure 1

Effect of slag composition on the reoxidation of ULC steel

In manner similar to that explained in the previous section, the value of $k_{[Al]}$ for slags having various compositions has been measured and summarized in Table II.

Using the values of $k_{[Al]}$, the effect of the slag composition on the reoxidation of ULC steel has been investigated. Equations [2] and [3] show that $[Al]^*$ is dependent on the activities of $[O]$ and (Al_2O_3) at the slag/metal interface. In $CaO-Al_2O_3-FeO-MnO-MgO$ based slag, oxygen potential is often determined by the activities of very reducible oxides such as (FeO) and (MnO) . Activity of (Al_2O_3) is largely affected by that of (CaO) in the slag. Hence, referring to Equation [6], a decreasing rate, $k_{[Al]}$, of the soluble aluminium content will be a function of these variables.

Figure 3 shows the relationship between the $k_{[Al]}$ and the initial value of the $(T.Fe)$ content in slag. Here the experimental data are grouped for the slag having a certain range of the $(CaO)/(Al_2O_3)$ mass ratio and the (MnO) content to study the role of the other components in more detail. The results can be summarized as follows:

- The general behaviour of $k_{[Al]}$ changes depending on the $(T.Fe)$ content
- In the case of $(T.Fe) > 1.5$ weight per cent, the value of $k_{[Al]}$ increases with increasing $(T.Fe)$ content for a given $(CaO)/(Al_2O_3)$ mass ratio. For a given $(T.Fe)$ content, $k_{[Al]}$ decreases with increasing value of the $(CaO)/(Al_2O_3)$ ratio. No distinct effect of (MnO) on the behaviour of $k_{[Al]}$ has been observed in this relationship
- On the other hand, in the case of $(T.Fe) < 1.5$ weight per cent, the $k_{[Al]}$ value remains almost constant even with varying $(T.Fe)$, (MnO) contents and $(CaO)/(Al_2O_3)$ mass ratio.

It is not too difficult to understand the behaviour of $k_{[Al]}$ in a qualitative way. Increase of the $(T.Fe)$ content causes an increase of $[O]^*$ and a decrease of $[Al]^*$, leading to an increase of the difference of $[Al]$ content between the bulk metal and the interface. As a result, the value of $k_{[Al]}$ increases with increasing $(T.Fe)$ content. In the case of $(T.Fe) < 1.5$ weight per cent, however, $[O]^*$ reaches a value close to one at equilibrium with the bulk metal. Then a

remarkable amount of the soluble aluminium is not deoxidized by the iron oxide in slag. As a result, the $k_{[Al]}$ value remains almost constant in that $(T.Fe)$ range.

According to the previous report including Figure 46, for a given content of (FeO) in slag, the higher level of the $(CaO)/(Al_2O_3)$ ratio exerts lower activity on the iron oxide⁶⁻⁷, leading to a decrease of $[O]^*$. In the same manner as described for the $(T.Fe)$ content, the $k_{[Al]}$ value decreases with increasing value of the $(CaO)/(Al_2O_3)$ ratio.

It has been frequently stated that, as the (MnO) in slag acts as an important supply of oxygen into the molten steel⁸, it should be lowered to a certain level. This has a logical background to the concept that $(T.Fe+MnO)$ content should be used as an index for slag control. At first glance at Figure 3, however, the $k_{[Al]}$ value for a given $(T.Fe)$ content does not seem to change with the variation of the (MnO) content. In order to understand this phenomenon, the chemical reaction between FeO and MnO , given in the following Equations, has been analysed.

$(CaO)/(Al_2O_3)$	<1.0	1.0~1.2	1.2~1.4	1.4~1.6	>1.8
$(MnO) > 3 \text{ wt\%}$	i p	i à	i â	i 0	+
$(MnO) < 3 \text{ wt\%}$	i ß	i á	i ä	i Ü	*

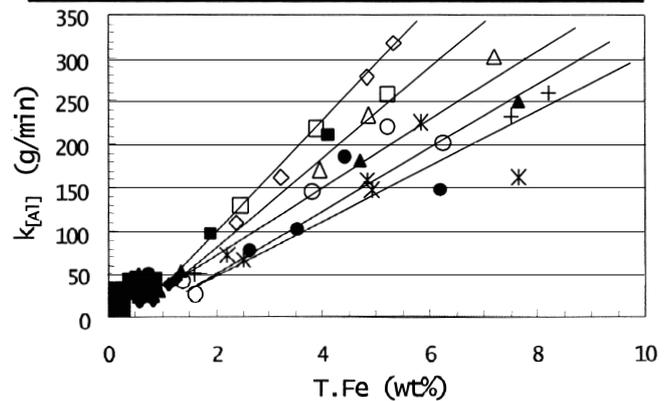


Figure 3. Value of $k_{[Al]}$ vs. $(T.Fe)$ content in slag

Table II
Summary of the $k_{[Al]}$ value for various slag compositions (g/min)

$T.Fe(wt\%)$	$MnO(wt\%)$	≤ 3.0	$3 \sim 6$	> 6
≤ 1.5	$C/A \leq 1.0$	31.49		
	$1.0 < C/A \leq 1.2$	32.64		
	$1.2 < C/A \leq 1.4$	69.93		
	$1.4 < C/A \leq 1.6$	36.89	34.86	
	$C/A > 1.6$	29.49		
$1.5 \sim 3$	$C/A \leq 1.0$		109.84	
	$1.0 < C/A \leq 1.2$		129.09	
	$1.2 < C/A \leq 1.4$	96.64		
	$1.4 < C/A \leq 1.6$	77.68		
	$C/A > 1.6$	70.09	50.2	
$3 \sim 5$	$C/A \leq 1.0$			161.46
	$1.0 < C/A \leq 1.2$	210.36	184.93	62.41
	$1.2 < C/A \leq 1.4$	181.65	170.54	235.22
	$1.4 < C/A \leq 1.6$	186.54	123.70	
	$C/A > 1.6$	153.1		
> 5	$C/A \leq 1.0$			317.14
	$1.0 < C/A \leq 1.2$	248.75		258.7
	$1.2 < C/A \leq 1.4$	175.41		
	$1.4 < C/A \leq 1.6$	193.79	220.12	
	$C/A > 1.6$		260.0	266.89

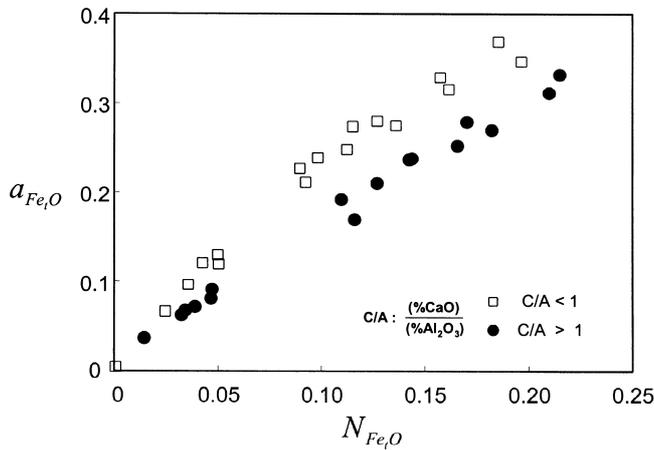
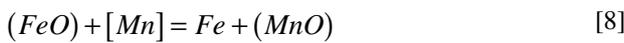


Figure 4. Activity of iron oxide in the secondary metallurgy slag for ULC steel



$$\frac{[wt\% MnO]}{[wt\% Mn]} = K_8 f_{[Mn]} \alpha_{(FeO-MnO)} \frac{\gamma_{(FeO)}}{\gamma_{(MnO)}} (wt\% FeO) \quad [9]$$

where $\alpha_{FeO-MnO}$ is a conversion factor for the slag composition from mole fraction to a weight per cent. Equation [9] implies that there is a certain relationship between the (T.Fe) and the (MnO) contents. In Figure 5, (MnO)/[Mn] in weight per cent is plotted as a function of the (FeO) content. Although there is a large margin of error, a linear relationship has been observed between them, indicating that the (FeO)-(MnO) reaction reaches a point close to equilibrium. Then the oxygen potential exerted by Mn-MnO equilibrium will be at a similar level as that by Fe-FeO. As a result,) mass ratio. For a given (T.Fe) content, $k_{[Al]}$ decreases with increasing value of the (CaO)/(Al₂O₃) ratio. No distinct difference will be observed with $k_{[Al]}$ having a varying amount of (MnO) for a given (T.Fe) content.

Summarizing the experimental results, the following are suggested for slag control of the ULC steel. Firstly, (MnO) content does not need to be controlled to reduce the oxidizing tendency of the slag. Secondly, if the reoxidation by slag is completely avoided, the (T.Fe) content of slag should be lowered to the level 1.5 weight per cent. Such a (T.Fe) level is not so easy with a conventional operation so that a compromise is necessary from the economical point of view in the plant operation. Lastly, not only the (T.Fe) content, but also the (CaO)/(Al₂O₃) ratio should be considered to improve the cleanliness of the ULC steel. A higher value of the (CaO)/(Al₂O₃) ratio alleviates the adverse effect of higher (T.Fe) content on the steel cleanliness.

Application of the experimental result to the plant operation

In the steelmaking process for the ULC steel, decarburization precedes the deoxidation of steel. To this end, four RH units are under operation at No. 1 and No. 2 steelmaking plants at Gwangyang Works, POSCO. Slagging materials—lime and slag deoxidant—are added at tapping from BOF, at bubbling stand, and at departure from the RH station to secure the oxide cleanliness. Ladle transfer and waiting time from the RH station to the start of

the continuous casting has been extended. More detailed information on the plant operation is available in another report. During the transfer and waiting time, the steel melt remains unstirred and protected from the air by the slag layer. It can be assumed that the decrease of the soluble aluminium content can be attributed to reoxidation by the slag. The observed value of the decreasing rate of the soluble aluminium content during the period is plotted as a function of (T.Fe) content for the ULC steel treated in the No. 2 steelmaking plant for 2 months (Figure 6). The data are grouped for the slag having a certain range of the (CaO)/(Al₂O₃) mass ratio in the same way as in Figure 3. The figure shows a general trend that the decreasing rate increases with increasing (T.Fe) content. In addition, the slag having a higher value of the (CaO)/(Al₂O₃) ratio shows a smaller decreasing rate than the other case.

In the previous sections, the reoxidation tendency of slag has been discussed with both the laboratory- and the plant-scale tests. The topic has been investigated to establish the aim of the slag killing practice to secure the cleanliness of the ULC steel. However, steel cleanliness is affected not only by the reoxidation but also by the inclusion absorption capacity of slag. Steel cleanliness is affected by chemical and physical properties of slag in contact with molten steel in the ladle after deoxidation. As the non-metallic inclusions in ULC steel are mainly alumina, the slag for clean steel practice should have good absorption capacity for alumina. However, it is very difficult to assess alumina

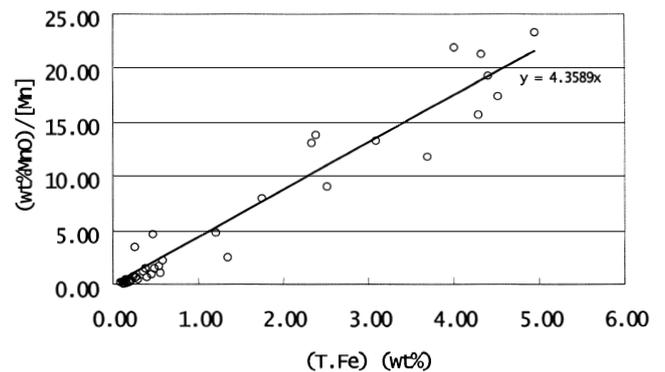


Figure 5. (T.Fe) vs. (MnO)/[Mn] for the slag and metal at the final stage of the experiment

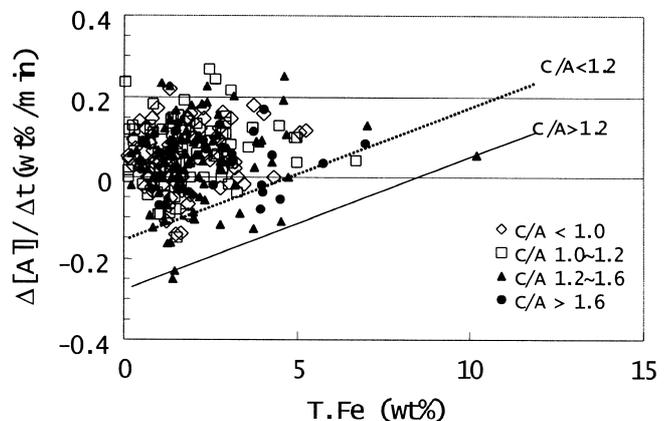


Figure 6. Decreased of the soluble aluminium content in steel vs. (T.Fe) for ULC grade

absorption capacity directly in the slag-metal reaction. Several methods have been suggested as indirect ways to estimate the absorption capacity including the 'rotating bar' experiment. According to H.G. Lee⁹, the alumina absorption rate increases with increasing (CaO) content in the CaO-Al₂O₃ binary slag, as shown in Figure 7. It is very fortunate that the inclusion absorption is favoured by higher (CaO) content, which reduces the reoxidation tendency of slag. It can be concluded that the steel cleanliness will be favoured by lower (T.Fe) content and a higher (CaO)/(Al₂O₃) ratio.

The previous sections describe how the steel cleanliness is favoured by lower (T.Fe) content and higher (CaO)/(Al₂O₃) ratio in a certain range. It is more practical to correlate the cleanliness of steel produced in the plant with the slag composition to establish the aim of slag control practice. There have been various types of index to represent the level of steel cleanliness. Of them all, total oxygen content in steel, T.[O], is one of the most frequently used index. In Figure 8, the T.[O] content of steel slab is shown for various values of the (T.Fe) content and the (CaO)/(Al₂O₃) ratio. The numbers near the symbols denote the T.[O] content and the lines represent approximate iso-T.[O] compositions. It is clear that the T.[O] content decreases with decreasing (T.Fe) content and with increasing (CaO)/(Al₂O₃) ratio. In addition, the same level of the T.[O] content for a given slag composition can be obtained with a slag having higher (T.Fe) content by increasing the (CaO)/(Al₂O₃) ratio. The slag composition for good steel cleanliness can be established as the shaded area.

Conclusion

The reoxidation rate of CaO-Al₂O₃-FeO-MnO-MgO slag was investigated in a laboratory to establish the ladle slag composition needed to secure the oxide cleanliness of the ultra low carbon steel produced at Gwangyang Works, POSCO. As an index for the reoxidation rate or the oxidizing tendency, the mass transfer coefficient, $k_{[Al]}$, of the soluble aluminium between the slag and melt was used. It has been observed that $k_{[Al]}$ shows a good relationship with (T.Fe) content in slag but its general behaviour changes depending on the (T.Fe) content.

In case of (T.Fe) content higher than 1.5 weight per cent, the reoxidation rate increases linearly with increasing (T.Fe) content. For a given (T.Fe) content, it decreases with the increasing (CaO)/(Al₂O₃) ratio of the slag. No distinct effect of (MnO) on the behaviour of $k_{[Al]}$ has been observed in this relationship. However, in the case of (T.Fe) content

lower than 1.5 weight per cent, no particular relationships are observed between the reoxidation rate and (T.Fe) content or (CaO)/(Al₂O₃) ratio of the slag. These results imply that the (T.Fe) content and the (CaO)/(Al₂O₃) ratio of slag can serve as a good parameter to represent the oxidizing tendency of the slag.

Plant tests were carried out to compare the experiment result with a large-scale one and to establish the operational standard for slag control practice. The T.[O] content of steel, which was chosen as an index to represent its cleanliness, was correlated with the (T.Fe) content and the (CaO)/(Al₂O₃) ratio of slag. The T.[O] content has been observed to decrease with decreasing (T.Fe) content and with increasing (CaO)/(Al₂O₃) ratio. In addition, the same level of the T.[O] content for a given slag composition can be obtained with a slag having higher (T.Fe) content by increasing the (CaO)/(Al₂O₃) ratio. An intended slag composition for good steel cleanliness can be established.

References

1. MAEDA, M. Y., TAKEOKA, H.M., and KURIHADA, K. Improvement of steel cleanliness in LD converter-RH-Slab casting process. *CAMP-ISIJ*, vol. 4, 1991, p. 1245.
2. TAGO, Y., HIGUCHI, Y., FUKUGAWA, S., KANAI, T., TANI, Y., and MUTOH, A. Reoxidation behaviour of molten steel from RH to tundish. *CAMP-ISIJ*, vol. 9, 1996, p. 706.
3. HIGUCHI, Y., TAGO, Y., TAKATANI, K., and FUKAGAWA, S. Effect of stirring and slag condition on reoxidation of molten steel. *Tetsu-to-Hagané*, vol. 84, 1998, pp. 333-338.
4. LEE, K., CHOI, S., and JEE, K. Optimization of ladle slag composition for ultra low carbon steel. *ASIA STEEL—2000. Proceedings ASIA Steel International Conference—2000*, Beijing China. The Chinese Society for Metals, 2000. vol. C, pp. 444-452.
5. AHN, S., CHOI, H., KIM, J., YIM, C., and KIM, Y. A new slag making method for ultra low carbon steel. *Proceedings of 83rd Steelmaking Conference*, Pittsburgh, PA, Iron and Steel Society, 2000, pp. 107-116.

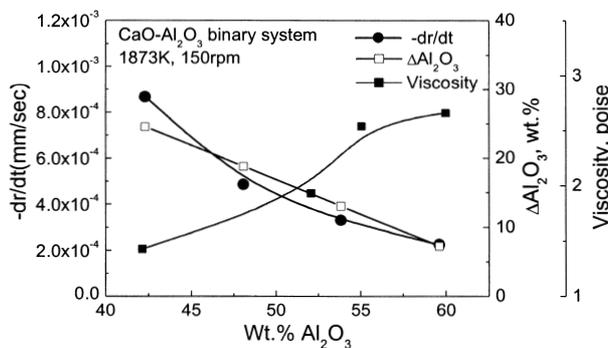


Figure 7. Alumina absorption rate and viscosity of CaO-Al₂O₃ slag at 1600°C

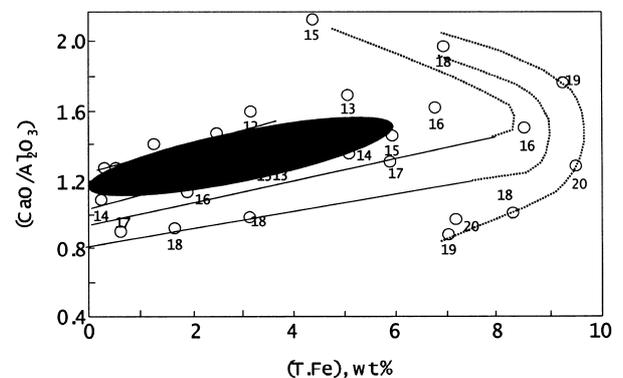


Figure 8. T.[O] content of slab vs. (T.Fe) and (CaO)/(Al₂O₃) ratio of the secondary metallurgy slag

6. PARK, J., and KANG, S. Equilibrium of slag metal reaction. *Proceedings Annual Autumn Meeting*, Seoul, Korea. The Korean Institute of Metals and Materials, 2000, p. 56.
7. OHNUKI, K., ISONO, T., and UMEZAWA, Y. Effect of slag composition on the activity coefficient of FeO. *CAMP-ISIJ*, vol. 6, 1993, p. 220.
8. SUN, H., and MORI, K. Reoxidation mechanism of aluminum in iron by slag. *CAMP-ISIJ*, vol. 9, 1996, p. 769.
9. LEE, H. Development of computer software for prediction of inclusions chemistry in steels, POSCO Technical Report 2000Y902, Pohang Korea, June, 2001.