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Manganese Loss during the Oxygen Refining of High-Carbon Ferromanganese Melts

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Decarburization tests of high-carbon ferromanganese melts by oxygen refining were successfully carried out in a model converter with 2-ton production capacity. During the oxygen refining, the manganese loss was inherently accompanied by oxidation and evaporation. The oxidation loss of manganese into slag was affected by slag composition, melt temperature and slag weight. The oxidation loss of manganese into slag was minimum at a slag basicity of about 1.5 and it increased with temperature and slag weight. The amount of manganese evaporation loss was comparable to that of oxidation loss. An empirical equation for the evaporation loss of manganese was derived as a function of process variables. The apparent vaporization coefficient, β, was significantly affected by the oxygen mixing ratio in bottom blowing gas and the fraction of top blown oxygen.

Key words : medium-carbon ferromanganese, oxygen refining, manganese loss, oxidation, evaporation

1. INTRODUCTION

The source of manganese used for industrial purposes includes ferromanganese alloys and electrolytic manganese. Electrolytic manganese is used only for special purposes due to its high cost. Ferromanganese alloys are generally used for deoxidation and alloying of molten steel in conventional steelmaking processes. Ferromanganese alloys can be classified into high-carbon ([C]~7.0%), mediumcarbon ([C]≤2.5%), and low-carbon ([C]≤0.5%) grades depending on their carbon contents.

Ferromanganese alloys are usually added to molten steel in the final stage of the refining process, and most impurities in ferromanganese alloys dissolve in steel and can affect the quality of the final products. Moreover, recently there is a trend for increased production of low- and ultra low-carbon steel grades. This situation increases the demand for low-carbon ferromanganese alloys.

Conventionally, medium- and low-carbon ferromanganese alloys have been produced by the silico-thermic reduction process of manganese ore. However, this process has technical and economical problems, such as high energy consumption, severe refractory attack, generation of a large amount of slag, poor metal yield and so on. Recently, the decarburization process of molten high-carbon ferromanganese using an oxygen-inert gas (N_2 or Ar) mixture was realized as an effective process for the production of low-carbon ferromanganese alloys [1-4]. During oxygen refining, however, a substantial amount of manganese in melt oxidizes into slag and evaporates at high temperatures [5]. Manganese loss should be minimized to increase metal yield during the oxygen refining process.

In this study, features of manganese loss during the oxygen refining of high-carbon ferromanganese melts was investigated through trial tests in a model converter with 2-ton production capacity.

2. EXPERIMENTAL

A model converter with 2-ton production capacity was used for the oxygen refining tests of high-carbon ferromanganese melts. Fig. 1 is a schematic drawing of the converter lined with MgO-C bricks. Three bottom tuyeres were installed on the back wall near the bottom of the converter. Each tuyere consists of inner and outer concentric pipes made of copper and stainless steel, respectively. The mixture of oxygen and inert gas was blown through the inner pipe, and inert gas was blown through the outer pipe.

About 1.8 ton/heat of high-carbon ferromanganese melt was charged into the preheated converter. The temperature of the melt was about 1300°C after charging. Oxygen gas

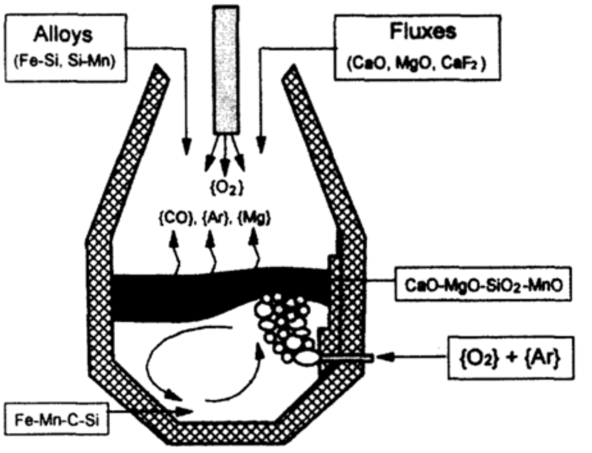

Fig. 1. Schematic view of experimental apparatus.

was introduced into the ferromanganese melts through a top lance and bottom tuyeres for decarburization. About 0.8 Nm^3/min-ton of oxygen was blown onto the melt surface through a top lance for 30 minutes. About 1.5 Nm^3/min-ton of oxygen and inert gas mixture was blown through the bottom tuyeres. The mixing ratio of oxygen in the bottom gas was changed in 4 steps of 0.7→0.6→0.35→0.15 every 20 minutes from the blow start. Fluxes, such as burnt lime, burnt dolomite and fluorspar were added as slag formers during blowing. In the final stage of refining, Fe-Si and/or Si-Mn were added as reducing agents of manganese oxide in the slag, and inert gas was blown through bottom tuyeres to stir the melt. Every 5~15 minutes from the blow start, metal samples were taken by immersion samplers and melt temperature was measured. The slag samples were taken at the blow end.

3. RESULTS AND DISCUSSIONS

3.1. Change of melt composition

Fig. 2 shows the change of carbon and manganese contents in melt depending on the refining time. In the initial stage of refining, the carbon content decreases slightly with the blowing time. The decarburization rate, thereafter, increases due to the increase of melt temperature. In the final stage, the decarburization reaction is diminished due to a low carbon content in melt and a low oxygen ratio in the refining gas.

The manganese content in melt remains nearly constant until the carbon content of initially 6.8% reaches about 3%, and decreases thereafter. At a low carbon content, the oxidation reaction of the manganese is thermodynamically favored over the decaburization reaction [4]. By this time, the oxygen ratio in the refining gas is reduced, and Fe-Si and/or Si-Mn alloys are added to reduce the manganese oxide in the slag. As can be seen from the figure, the manganese content increases again in the final stage of refining. The manganese content at the blow end is almost the same or higher compared to the initial value.

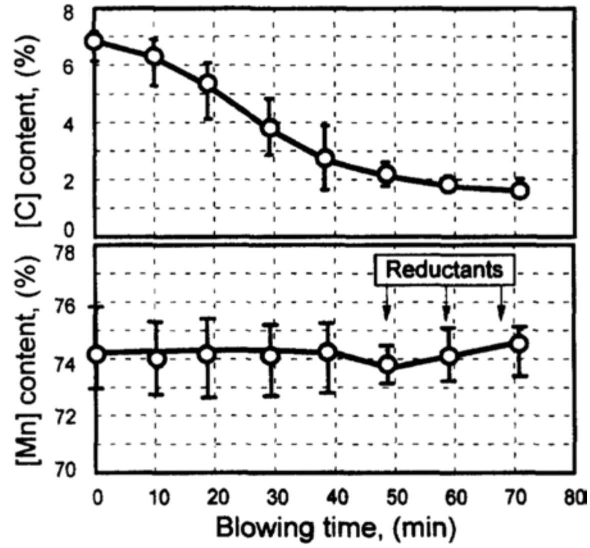

Fig. 2. Change of [Mn] and [C] contents depending on blowing time.

In these trial tests, high-carbon ferromanganese melt was successfully refined to have carbon contents lower than 2% at the blow end. The manganese content in the melt was almost the same as the initial value.

3.2. Manganese yield

In order to assure an economical process in producing low carbon ferromanganese alloys, it is necessary to maximize manganese yield through the minimization of manganese loss during refining. The weight of the ferromanganese melt can be estimated from the mass balance of iron in melt [3,4]. The amount of manganese remaining in melt then can be calculated from the melt weight and the manganese content at the blow end. The amount of manganese input in the converter can be also calculated from the weight and composition of the high-carbon ferromanganese melt, Fe-Si and/or Si-Mn alloys charged.

Fig. 3 shows the relationship between the amount of manganese remaining in melt at the blow end and the amount of manganese charged per ton of melt. The lines of manganese yield are also plotted in the figure. The manganese yields in these trial tests are in the range of 75~95%, which means a manganese loss of 5~25% consisting of oxidation loss into slag and evaporation loss as fume and dust.

3.3. Oxidation loss of manganese into slag

The slag weight at the blow end significantly affects the

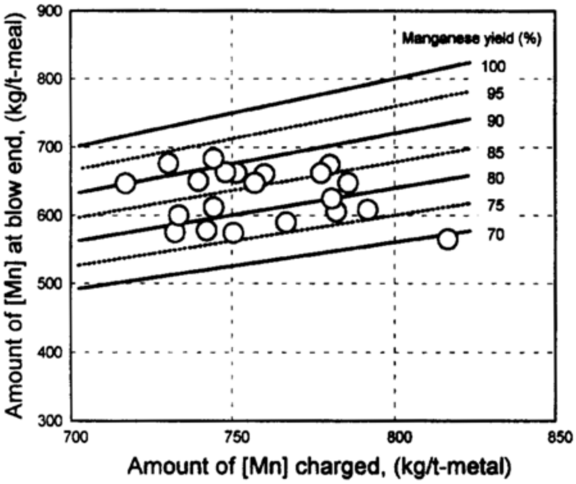

Fig. 3. Manganese yield at blowing end.

manganese loss into slag. The slag weight was estimated from the mass balance of Si in melt and (SiO_2) in slag. The amount of manganese in slag at the blow end can be calculated from slag weight and manganese content in slag. Fig. 4 shows the relationship between the oxidation loss of manganese into slag and the slag weight per ton of hot metal charged into the converter. It can be seen from the figure that the manganese loss into slag increases almost linearly with the slag weight. The slag weight should be minimized as much as possible to reduce manganese loss into slag.

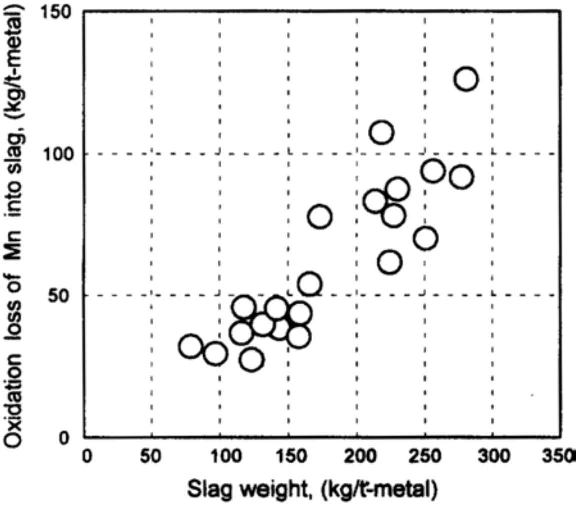

Fig. 4. Manganese loss into slag depending on slag weight.

When the oxygen is blown into the ferromanganese melt, carbon and manganese are oxidized simultaneously. Therefore, a substantial amount of manganese is oxidized and dissolves in slag. To reduce manganese oxide from slag, Fe-Si and/or Si-Mn alloys are added in the final stage of refining. A reaction between the manganese oxide in slag and silicon dissolved in melt can be expressed as follows [6,7]:

$$2\ (MnO)+[Si]=2[Mn]+(SiO_2) \tag{1}$$

$$\log\ K=\log\left(\frac{a_{[Mn]}^2 \cdot a_{(SiO_2)}}{a_{(MnO)}^2 \cdot a_{[Si]}}\right)=\frac{4590}{T}-0.16 \tag{2}$$

where ( ) denotes oxides dissolved in slag and [ ] denotes elements dissolved in metal. K is the equilibrium constant, a_i's are the activities of the "i" component and T means the absolute temperature.

The Eq. 2 can be rearranged as follows:

$$\log\ \left(\frac{[\%Mn]^2 \cdot (\%SiO_2)}{(\%MnO)^2 \cdot [\%Si]}\right)=\log\left(\frac{\gamma_{(MnO)}^2 \cdot \gamma_{[Si]}}{\gamma_{[Mn]}^2 \cdot \gamma_{(SiO_2)}}\right)+\frac{4590}{T}-0.16 \tag{3}$$

where γ_i's are the activity coefficients of corresponding components. The activity coefficient of each component depends on the compositions of melt and slag.

In order to find out the distribution ratio of manganese between slag and melt as a function of process variables, a multiple regression analysis was made by taking the temperature and the compositions of slag and melt as independent variables, and the apparent equilibrium constant as a dependent variable. For convenience, the compositions of melt and slag were simplified as follows:

$$[\%Mn]+[\%C]+[\%Si]+[\%Fe]=100\% \tag{4}$$

$$(\%CaO)+(\%MgO)+(\%SiO_2)+(\%MnO)=100\% \tag{5}$$

The result of regression analysis yields an empirical relationship as follows:

$$\log\ \left(\frac{[\%Mn]^2 \cdot (\%SiO_2)}{(\%MnO)^2 \cdot [\%Si]}\right) = \left[\frac{\{(\%CaO)+(\%MgO)\}^{1.025} \cdot (\%SiO_2)^{1.606}}{[\%Si]^{0.932}}\right] + \frac{380.88}{T}-2.072 \tag{6}$$

Fig. 5 shows the correlation of this equation with the data from the experiments. It can be seen that the equation represents the data very well, and a very high correlation coefficient (R^2) of about 0.98 was obtained.

The distribution ratio of manganese, (%MnO)/[%Mn], can be derived from the Eq. 6 as follows:

$$\log\ \left(\frac{(\%MnO)}{[\%Mn]}\right) = -\log([\%Si]^{0.034} \cdot \{(\%CaO)+(\%MgO)\}^{0.5125} \cdot (\%SiO_2)^{0.303}) - \frac{190.44}{T}+1.036 \tag{7}$$

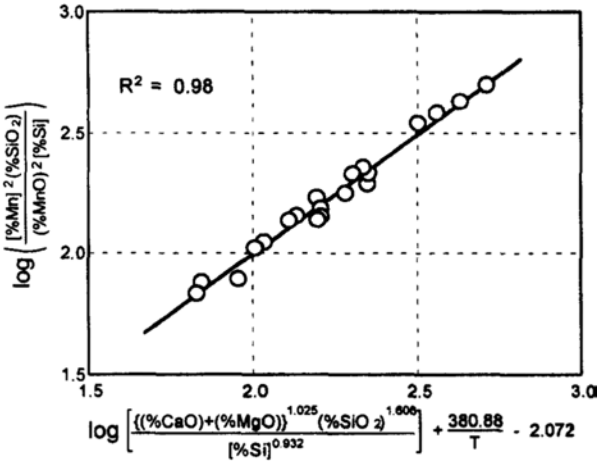

Fig. 5. Comparison of the apparent equilibrium constant with the result of regression analysis.

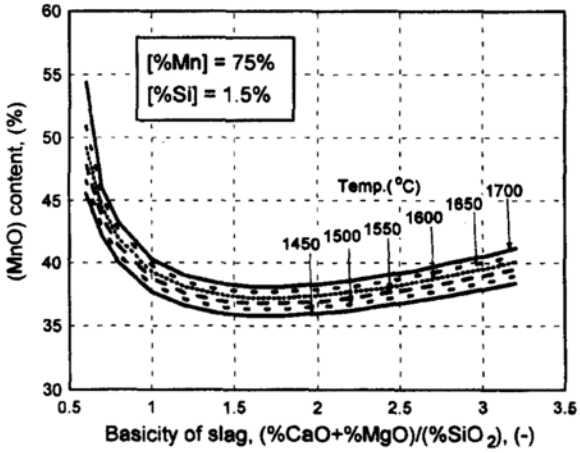

Fig. 6. Change of (MnO) content in slag depending on slag basicity for various temperatures.

Defining the slag basicity as {(%CaO)+(%MgO)}/(%SiO$_2$) in a quarternary slag system of (CaO)-(MgO)-(SiO$_2$)-(MnO), the following relationships are given:

$$\frac{(\%\mathrm{CaO})+(\%\mathrm{MgO})}{(\%\mathrm{SiO_2})}=\mathrm{B(Basicity)}$$

$$(\%\mathrm{CaO})+(\%\mathrm{MgO})=100-\{(\%\mathrm{SiO_2})+(\%\mathrm{MnO})\} \tag{9}$$

A combination of Eqs. 8 and 9 gives

$$(\%\mathrm{SiO_2})=\frac{100-(\%\mathrm{MnO})}{1+\mathrm{B}} \tag{10}$$

$$\text{and } (\%\mathrm{CaO})+(\%\mathrm{MgO})=\mathrm{B}\cdot\frac{100-(\%\mathrm{MnO})}{1+\mathrm{B}} \tag{11}$$

Substituting Eqs. 10 and 11 into 7, the distribution ratio of manganese can be expressed as a function of (%MnO), [%Si], melt temperature and slag basicity as,

$$\log\left(\frac{(\%\mathrm{MnO})}{[\%\mathrm{Mn}]}\right) =-\log\left[[\mathrm{Si}]^{0.034}\cdot\mathrm{B}^{0.5125}\cdot\left\{\frac{100-(\%\mathrm{MnO})}{1+\mathrm{B}}\right\}^{0.8155}\right] -\frac{190.44}{\mathrm{T}}+1.036 \tag{12}$$

Generally, the medium-carbon ferromanganese alloy requires [%Mn]≥75% and [%Si]≤1.5%. Therefore, applying the manganese content of 75% and the silicon content of 1.5% to Eq. (12), a correlation equation of (%MnO) can be obtained as a function of slag basicity and temperature. Fig. 6 shows the relationship between (%MnO) and slag basicity in the temperature range of 1450~1700°C. As can be seen from the figure, (%MnO) decreases sharply with increasing slag basicity at a low slag basicity region. It reaches the minimum value at a slag basicity near 1.5, and increases slightly at higher slag basicity. Although the effect of temperature is not significant, (%MnO) increases with increasing temperature. Consequently, in order to minimize the oxidation loss of manganese into slag, the slag basicity should be controlled near about 1.5 and the temperature should not be too high.

As mentioned above, the oxidation loss of manganese into slag depends on the slag weight at the blow end. The amount of manganese in slag can be calculated from the content of manganese oxide in slag and the slag weight. Fig. 7 shows the relationship between the manganese loss into slag and the slag basicity as a function of slag weight at 1550°C. The effect of slag basicity on manganese loss becomes more predominant with increasing slag weight. Therefore, the process should be carefully controlled to have minimum slag weight and slag basicity of about 1.5 to minimize the manganese loss into slag.

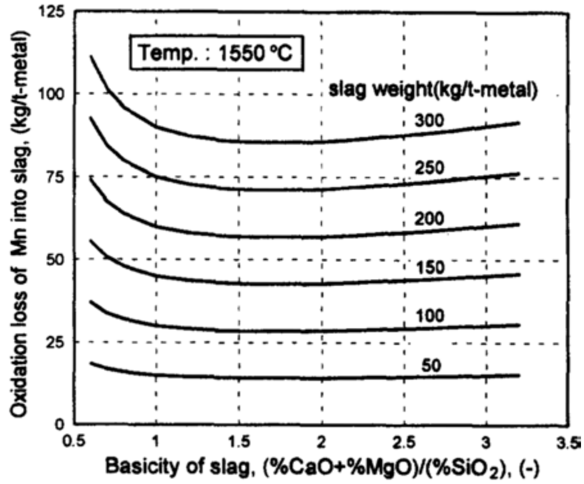

Fig. 7. Change of manganese loss into slag depending on slag basicity for various slag weights.

3.4. Evaporation loss of manganese

The evaporation loss of manganese is unavoidable during the oxygen refining of high-carbon ferromanganese melt because of the relatively high vapor pressure of manganese. The evaporation loss of manganese can be estimated from the difference between the total manganese loss calculated by material balance and the oxidation loss into slag. Fig. 8 compares the amount of evaporation loss and the oxidation loss of manganese in the present tests. Although no notable relationship can be seen, the amount of evaporation loss is comparable to that of oxidation loss.

The evaporation rate of manganese strongly depends on the vapor pressure of manganese and can be expressed by the following general equation [8]:

$$\omega = \alpha \cdot \frac{P_{Mn}}{\sqrt{T}} \qquad (13)$$

Here, ω is the evaporation rate (kg/m^2-min), P_{Mn} is the vapor pressure (atm), T is the absolute temperature (K), and α is the vaporization coefficient. The vapor pressure of manganese in molten alloy is a function of manganese activity and melt temperature [9].

$$\ln\left(\frac{P_{Mn}}{a_{[Mn]}}\right) = 37.67 - 3.02\ \ln T - \frac{33430}{T} \qquad (14)$$

Thermodynamic model equations and parameters for the calculation of manganese activity, $a_{[Mn]}$, in ferromanganese melts are available in the literature [7,9]. However, in real practice it is difficult to estimate the evaporation amount of manganese quantitatively because melt composition and temperature change continuously during the oxygen refining process. Therefore, we attempted to derive an empirical equation for the evaporation loss of manganese as a function of process variables using the experimental results.

For each run, metal sampling and temperature measurement were carried out every 5~15 minutes from the blow start. The manganese activity and vapor pressure in melt at each sampling moment were calculated from the melt composition and temperature using the thermodynamic model developed by Dresler [9] and Eq. 14. The total evaporation loss of manganese per ton of melt was assumed to be proportional to the sum of evaporation loss during time intervals between samplings. That is

$$\frac{(W_{Mn})_{evap}}{W_{metal}} = \beta \cdot \sum_{i=1}^{n} \left\{ \frac{(P_{Mn})_i}{\sqrt{T_i}} \cdot (t_{(i+1)} - t_{(i)}) \right\} \qquad (15)$$

Here, $(W_{Mn})_{evap}$ is the evaporation loss of manganese (kg), W_{metal} is the amount of hot metal charged(ton), "i" is the order of sampling, and $(t_{(i+1)}$-$t_{(i)})$ is the time interval in minutes between samplings. The apparent vaporization coefficient, β, would be a function of process variables such as oxygen and inert gas flow rates. A multiple regression analysis was made by taking β as a dependent variable, and process variables such as mixing ratio of oxygen in bottom gas, fraction of top blown oxygen and carbon content in melt at the blow end as independent variables. The correlation coefficient (R^2) is about 0.81, and the result of regression analysis yields an empirical relationship as follows:

$$\beta = 10^{4.776} \cdot \frac{\left(\frac{Q_{O_2(B)}}{Q_{O_2(B)} + Q_{intert(B)}}\right)^{2.604} \cdot \left(\frac{Q_{O_2(T)}}{Q_{O_2(T)} + Q_{O_2(B)}}\right)^{1.811}}{[\%C]^{0.608}} \qquad (16)$$

where Q_{O2} and Q_{inert} are the flow rates of oxygen and inert

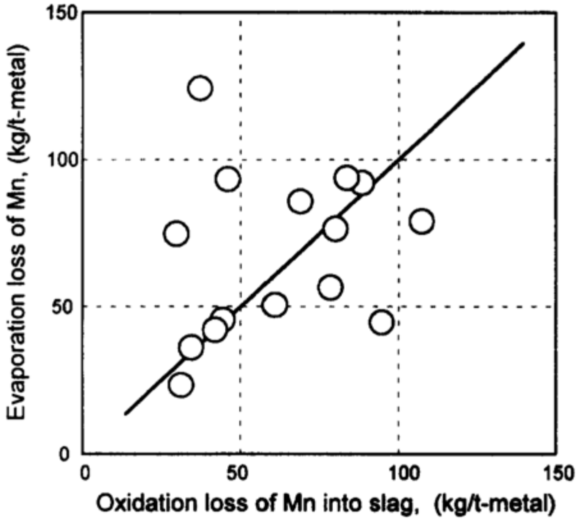

Fig. 8. Comparison of the evaporation loss with oxidation loss of manganese into slag.

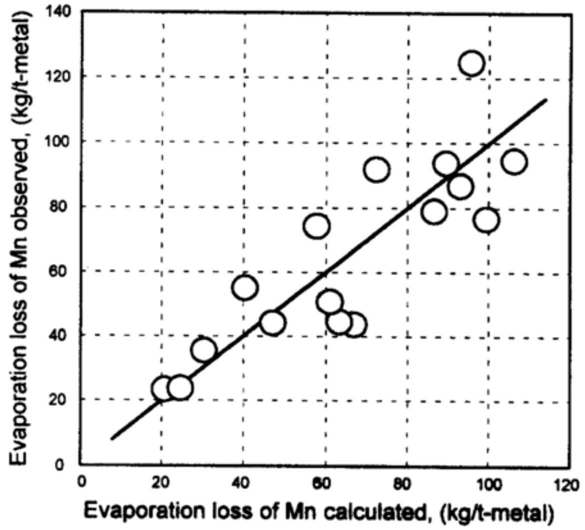

Fig. 9. Comparison of the observed evaporation loss of manganese with the calculated loss.

gas(Nm^3/min), and the subscripts (B) and (T) denote bottom and top blowing, respectively.

Fig. 9 shows the relationship between the evaporation loss of manganese observed in actual tests and the calculated values from Eq. 15. The standard deviation of differences between the observed and calculated values was about ±24 kg/ton-metal. Basically, for the minimization of evaporation loss of manganese, excessively high melt temperature and long refining time should be avoided. We also recommend keeping the oxygen mixing ratio in bottom blowing gas and the fraction of top blown oxygen as low as possible.

4. CONCLUSIONS

For the purpose of developing a decarburization process of molten high-carbon ferromanganese alloy, features of manganese loss during oxygen refining were investigated using a model converter with 2-ton production capacity. The main results can be summarized as follows:

1. The oxygen refining process of high-carbon ferromanganese melts shows a great possibility for the production of a medium-carbon ferromanganese alloy.
2. During oxygen refining, a substantial amount of manganese loss occurs from oxidation and evaporation.
3. The manganese loss into slag is significantly affected by slag basicity and slag weight at the blow end. Therefore, the process should be carefully controlled to have minimum slag weight and a slag basicity of 1.5 to minimize the oxidation loss of manganese into slag.
4. The amount of manganese evaporation loss is comparable to that of oxidation loss.
5. The evaporation loss of manganese is basically due to the high vapor pressure of manganese in ferromanganese melts. Therefore, an excessively high melt temperature and long refining time should be avoided.
6. An empirical equation for the evaporation loss of manganese was derived as a function of process variables. The apparent vaporization coefficient, β, is significantly affected by the oxygen mixing ratio in bottom blowing gas and the fraction of top blown oxygen.

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