Recovery Rate of Chromium from Stainless Slag by Iron Melts

Takamitsu NAKASUGA, Kunihiko NAKASHIMA1) and Katsumi MORI2)

Formerly at Graduate School of Engineering, Kyushu University, now at Research and Development Center, Kakogawa Works, Kobe Steel, Ltd., Ikeda, Onoe-cho, Kakogawa 675-0023 Japan. 1) Department of Materials Science and Engineering, Graduate School of Engineering, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581 Japan. E-mail: nakasima@zaiko.kyushu-u.ac.jp 2) Professor Emeritus, Kyushu University.

(Received on September 5, 2003; accepted in final form on November 21, 2003)

The kinetic behavior of Cr₂O₃ reduction by iron melts containing carbon, aluminum and silicon were investigated at various conditions in order to understand effective slag treatment for recovery of chromium from stainless slag. It was found that the recovery rate of chromium was fairly slow, but it was considerably accelerated by the addition of some fluxes, such as Al₂O₃ and SiO₂ to the slag, which promoted the formation of liquid slag at the early stage of the reaction, and the recovery ratio of chromium was also improved. In addition, SiO₂ addition was more effective for increasing the chromium recovery than Al₂O₃ addition due to the effect of CaO/SiO₂ ratio of slag on the reduction rate of Cr₂O₃ in slag. The experimental results were well simulated by the previous kinetic reaction model based on two-film theory. The modeling study showed that the transfer rate of chromium from slag to metal was controlled by the mass transport in the slag phase.

KEY WORDS: ironmaking; steelmaking; recycle; stainless slag; Cr₂O₃; reduction; slag-metal reaction; kinetics; modeling.

1. Introduction

In recent years, diminution and recycle of a large amount of slag generated during the decarburization period of steelmaking process in the converter has been carried out extensively from both the economical and the environmental points of view. However, there has been an increasing demand for investigation on the characteristics of the slags and improvement of such recycling processes, because iron contents in the slags are relatively high and changes in composition of the slags are large due to the utilization of various kinds of iron ores. In particular, it is necessary to reduce chromium oxide efficiently down to lower chromium content in slag. It was found that the recovery rate of chromium was fairly slow, but it was considerably accelerated by the addition of some fluxes, such as Al₂O₃ and SiO₂ to the slag, which promoted the formation of liquid slag at the early stage of the reaction, and the recovery ratio of chromium was also improved. In addition, SiO₂ addition was more effective for increasing the chromium recovery than Al₂O₃ addition due to the effect of CaO/SiO₂ ratio of slag on the reduction rate of Cr₂O₃ in slag. The experimental results were well simulated by the previous kinetic reaction model based on two-film theory. The modeling study showed that the transfer rate of chromium from slag to metal was controlled by the mass transport in the slag phase.

KEY WORDS: ironmaking; steelmaking; recycle; stainless slag; Cr₂O₃; reduction; slag-metal reaction; kinetics; modeling.

2. Experimental Procedures

2.1. Raw Material

The composition of slag used in this study, which were generated in the stainless steelmaking process, is shown in Table 1. The chromium content in stainless slag is 2.66 mass%. According to the X-ray diffraction analysis and the EPMA mapping analysis given in Figs. 1 and 2, respectively, it was found that most of iron in the slag existed as metal.
and contained a little chromium, whereas chromium existed mainly as MgCr$_2$O$_4$ and dispersed in the slag phase. CaO–SiO$_2$ slag phase was also observed to contain either Al$_2$O$_3$ or MgO.

2.2. Slag Treatment for Stainless Slag

2.2.1. Modification of Nature of Slag Melts

Both the formation of liquid slag and the control of its composition would be important to promote the reduction reaction of Cr$_2$O$_3$ in slag. Therefore, for the purpose of increasing the reactivity of stainless slag, Al$_2$O$_3$ and SiO$_2$ powder reagents were added to the slag, because such oxides lowered the liquidus temperature of slag. Slag weight, CaO/SiO$_2$ ratio, and liquidus temperature of slag measured by Hot-thermocouple technique, are listed in Table 2.

2.2.2. Reduction of Slags by Iron Melts

The same experimental apparatus (SiC resistance furnace) as in the previous work$^6$ was used. At first, about 0.12 kg of Fe–C–Al–Si alloy was contained in an alumina crucible (0.036 m I.D.) and melted at aimed temperature under an argon atmosphere. After the initial metal sample was taken from the metal bulk by a silica tube, a mixture of stainless slag of 0.01 kg and a fixed amount of Al$_2$O$_3$ and SiO$_2$ powder reagents was added onto the metal surface. The moment of this slag addition was taken as the starting time of the reaction. Some metal samples were taken at predetermined time intervals. After a certain reaction time period, the alumina crucible was withdrawn from the furnace and quenched into water. The reacted slag sample was collected from the crucible. The compositions of these metal and slag samples were determined by chemical analysis to follow the progress of the reduction reaction of stainless slag. The structural change was also investigated by the X-ray diffraction and EPMA methods.

Iron alloys were prepared by premelting a mixture of appropriate amount of iron, graphite, aluminum and ferrosilicon in an alumina crucible using an induction furnace under an argon atmosphere.

In the present work, the effects of temperature, Al$_2$O$_3$ and SiO$_2$ addition to stainless slag, and aluminum and silicon addition to iron melt were examined at temperatures from 1400 to 1600°C. The experimental conditions and the experimental results are summarized in Table 3. The alphabetical letter of “Run No.” indicates the slag type shown in Table 2. Initial reduction rate, $k_{i,Cr}$, is calculated from the initial slope of curves in Figs. 3 through 6, defined by $d(Cr)/dt|_{t=0}$, and is taken as the index of Cr$_2$O$_3$ reduction to compare effects of various factors on the reduction rate.

Table 1. Composition of slag from stainless steelmaking process (mass%)

| Slag | CrO$_2$ | FeO | CaO | SiO$_2$ | Al$_2$O$_3$ | MgO | MnO | TiO$_2$ | C/S |
|------|--------|-----|-----|--------|-----------|-----|-----|--------|-----|
| SA   | 2.66   | 5.20| 44.57| 33.06  | 3.59      | 8.33| 0.44| 2.15   | 1.35|

Table 2. Slag weight, CaO/SiO$_2$ ratio, and liquidus temperature of slag, $T_{liq}$, measured by Hot-thermocouple technique.

| Slag | Description | Weight of Mixed Slag (g) | CS | $T_{liq}$ (°C) |
|------|-------------|------------------------|----|--------------|
| SA   | No addition | 10.0 - - -              | 10.0 | 1.35 | 1444 |
| SB   | 5mass% SiO$_2$ | 10.0 0.6 - - | 10.6 | 1.14 | 1387 |
| SC   | 10mass% SiO$_2$ | 10.0 1.2 - - | 11.2 | 0.99 | 1328 |
| SD   | 20mass% SiO$_2$ | 10.0 2.4 - - | 12.4 | 0.78 | 1292 |
| SF   | 10mass% Al$_2$O$_3$ | 10.0 - 1.2 | 11.2 | 1.35 | 1299 |

Fig. 1. X-ray diffraction pattern of stainless slag before reduction.

Fig. 2. EPMA mapping analysis images of stainless slag before reduction.
Recovery ratio of chromium from slag to metal, \( R_{Cr} \), is calculated using the final compositions of slag, obtained from the kinetic analysis discussed later.

3. Experimental Results

3.1. Explanation of Reduction Behavior

Figure 3 shows the variation of chromium and carbon content in iron melt with reaction time, when various kinds of Cr\(_2\)O\(_3\) contacted Fe–C melts at 1 600°C. The slag foaming due to CO gas evolution was observed during the experiment. The chromium content in iron melt increased and the carbon content in iron melt decreased by the addition of the slag samples, however, the initial reduction rate of chromium of stainless slag was smaller than that of synthetic slag. The reason for this is that the formation of liquid slag was not visually observed at the early stage of the reaction. In addition, the reduction reaction of other oxides such as FeO and MnO in stainless slag proceeded simultaneously or preferentially. Therefore, it can be said that the recovery rate of chromium from stainless slag by iron melt is fairly slow, and the effective slag treatment technique is necessary.

3.2. Effect of Temperature

Figure 4 shows the results of the reduction of stainless slag by Fe–C melts at 1 450, 1 500 and 1 600°C. The reduction rate of Cr\(_2\)O\(_3\) in slag increased with increasing temperature, but when the temperature was as low as 1 450°C, little formation of liquid phase was observed. In such a case, the reduction was significantly retarded, so that the final chromium content in iron melt decreased. Some of carbon was used for the reduction of SiO\(_2\) in slag at the later stage of a run, and higher temperature also favors its reduction reaction, and therefore, it is seen that the final silicon content in iron melt was higher in a run at higher temperature.

3.3. Effect of Slag Composition

Figure 5 shows the results of the reduction of stainless slag with different Al\(_2\)O\(_3\) and SiO\(_2\) addition by Fe–C melts at 1 400°C. It is found that the reduction reaction was enhanced by the addition of Al\(_2\)O\(_3\) and SiO\(_2\) addition to the slag due to the formation of liquid slag at earlier stage. However, as the amount of SiO\(_2\) addition increased up to 20 mass%, the initial reduction rate of chromium and the final chromium content in final iron melt were remarkably decreased. The slag volume generated was increased for the run with 20 mass% SiO\(_2\) addition, and it may lead to a decrease in the activity of Cr\(_2\)O\(_3\) in slag. And it may be attributed to an increase of the viscosity of slag. Furthermore, it is found that SiO\(_2\) addition was more effective than Al\(_2\)O\(_3\) addition. According to the previous work, which measured the reduction rate of Cr\(_2\)O\(_3\) in the Cr\(_2\)O\(_3\)–CaO–SiO\(_2\)–Al\(_2\)O\(_3\)–CaF\(_2\) synthetic slags by Fe–C melts, it was reported that the reduction rate was promoted in the case of slag with CaO/SiO\(_2\) = 1.11. Consequently, the slag with 10 mass%
SiO₂ addition was more effective for increasing the chromium recovery in these runs.

3.4. Effect of Metal Composition

Figure 6 shows the results of the reduction of stainless slag with and without 10 mass% SiO₂ addition by Fe–C, Fe–C–Al and Fe–C–Si melts at 1500°C. It is found that the addition of aluminum and silicon to Fe–C melt had little influence on the recovery of chromium, although the initial reduction rate of chromium slightly increased in runs with 10 mass% SiO₂ addition. The difference between these runs may be attributed to the formation of liquid slag at earlier stage. In these runs, aluminum and silicon in iron melt should be considered to be oxidized dominantly for the reduction of Cr₂O₃ to produce Al₂O₃ and SiO₂ in the early period, because the reducing power of them is superior to that of carbon under the present experimental conditions, which is discussed in Sec. 4.1. As a result, in runs with no SiO₂ addition, when a liquid slag phase was not fully formed at 1500°C, the slag-metal interface was considered to be partly covered with Al₂O₃ and SiO₂ to obstruct the contact of slag and metal from the X-ray diffraction analysis, and then the reduction was not promoted. On the other hand, in runs with 10 mass% SiO₂ addition, when a liquid slag phase was fully formed at 1500°C, the reduction was slightly promoted by the addition of aluminum and silicon to iron melt. Furthermore, it is found that for Fe–C–Al melt, aluminum was also used for the reduction of SiO₂ in slag, as seen from the increase in the silicon content during a run. This means that the addition of aluminum to iron melts is effective for the recovery of not only chromium but also manganese, silicon, titanium from slag.

3.5. Reduced Slag Samples

In order to examine the state of chromium in slag, the X-ray diffraction analysis and the EPMA mapping analysis were made on final slag samples. It was evident that all of Cr₂O₃ in slag were reduced within 1800 s, and hollow patterns characteristic for glassy state were observed for the slags in runs with 10 mass% SiO₂ addition at higher temperature. Therefore, it is considered that the slags after performing this treatment to recover chromium from stainless slag by iron melt can be recycled as a source of CaO in the steelmaking process.

4. Discussion

4.1. Thermodynamic Consideration

The oxidation behavior of carbon, aluminum and silicon in iron melt during runs was thermodynamically investigated using the equilibrium relations² for Reactions (1) and (3), respectively:

\[
\log K_{\text{Al-C}} = \log \frac{a_{\text{AlO}_2} a_{C}^{1.5}}{a_{\text{Al}} a_{\text{CO}}^{1.5}} = \frac{30250}{T} - 13.29
\]

\[
\log K_{\text{Si-C}} = \log \frac{a_{\text{SiO}_2} a_{C}^{2}}{a_{\text{Si}} a_{\text{CO}}^{2}} = \frac{27790}{T} - 15.40
\]

where \( K \) is the equilibrium constant given as a function of the absolute temperature, \( T \); \( a \) is the activity; \( P \) is the partial

Fig. 6. Effect of [Al] and [Si] on the reduction behavior of Cr₂O₃ in slag by Fe–C–Al–Si melts at 1500°C.
pressure. The activities of metal components are referred to the infinite dilution, and the reported values\(^4\) for interaction coefficients were used to calculate the activity coefficients of carbon, aluminum and silicon in metal. The activities of slag components are referred to the reference state based on the regular solution model, and the reported values\(^3\) for interaction energies were used to calculate the activity coefficients of Al\(_2\)O\(_3\) and SiO\(_2\) in slag. The pressure of CO gas is assumed to be equal to the pressure in the furnace, then \(P_C=1\) atm is used to solve Eqs. (2) and (4).

Figure 7 shows the relations between carbon and aluminum, silicon content in iron melt measured during the reduction reaction of stainless slags with and without 10 mass% SiO\(_2\) addition by Fe–C–Al–Si melts at 1500°C, and also shows the equilibrium for Reactions (1) and (3) using the final compositions of slag. In this figure, the region above the line means that the formation of Al\(_2\)O\(_3\) and SiO\(_2\) is stable to occur preferentially, on the other hand, the region below the line means that the formation of CO gas is stable to occur preferentially, according to the thermodynamics. In this study, the compositions of metal during runs were found to be in the Al\(_2\)O\(_3\) and SiO\(_2\) stable regions, it was therefore confirmed that the oxidation of aluminum and silicon in iron melt proceeded dominantly, that is, the reducing power of aluminum and silicon were superior to that of carbon under the present experimental conditions. However, for Fe–C–Si melts, the oxidation of carbon in iron melt proceeded simultaneously during the reduction reactions, so that it is necessary to consider its kinetics, too.

### 4.2. Kinetic Reaction Model

#### 4.2.1. Rate Calculation

The kinetic reaction model\(^5\) proposed previously has been applied as follows, and has been compared to the present experimental results on the recovery of chromium from stainless slag by iron melt.

The following reactions are considered to take place simultaneously at the slag–metal interface by the addition of stainless slags contained Cr\(_2\)O\(_3\) onto Fe–C–Al–Si melts.

\[
(\text{FeO}) = \text{Fe} + \text{O} \quad \text{(5)}
\]

\[
(\text{MoO}_3) = \text{M} + 3\text{O} \quad (\text{M} = \text{Cr, Si, Mn, Ti}) \quad \text{(6)}
\]

\[
\text{M} + x\text{O} = (\text{MoO}_3) \quad (\text{M} = \text{Al, Si}) \quad \text{(7)}
\]

\[
\text{C} + \text{O} = \text{CO}\text{(g)} \quad \text{(8)}
\]

Progress of reactions between two phases should be realized by diffusion of the reactants and the products through a boundary layer from or to the interface where chemical reactions occur. Many investigators\(^6–12\) have reached the conclusions that the reaction of CO formation is controlled by the chemical reaction at the interface, and other reactions are controlled by the mass transport in the slag and/or metal phases. In this simulation, the dissociation reaction of oxides at the interface for silicon and titanium were taken into consideration. The changes of chromium, carbon, aluminum, silicon, manganese, titanium and oxygen contents in the metal, and FeO content in the slag with the reaction time can be written as follows:

\[
\frac{d(\text{FeO})}{dt} = \frac{A}{W_\text{c}} k_\text{f} \rho_\text{c}(\text{FeO} - L_{\text{O}}^* a_{\text{O}}^*) \quad \text{(9)}
\]

\[
\frac{d[M]}{dt} = \frac{A}{W_\text{m}} k_\text{M} \{ (\text{M}) - L_{\text{M}}^* [\text{M}] \} \quad (\text{M} = \text{Cr, Si, Mn, Ti}) \quad \text{(10)}
\]

\[
\frac{d[C]}{dt} = \frac{A}{W_\text{m}} k_\text{C} \left[ f_\text{C}[\text{C}] a_{\text{C}}^* - \frac{P_{\text{CO}}}{K_\text{C}} \right] \quad \text{(11)}
\]

\[
\frac{d[O]}{dt} = \frac{A}{W_\text{m}} k_\text{O} \rho_\text{m} \left[ a_{\text{O}}^* - \frac{[\text{O}]}{\rho} \right] \quad \text{(13)}
\]

where \(t\) is the reaction time, \(s\); \(A\) is the reaction area assumed to be equal to the sectional area of crucible used, \(m^2\); \(W_\text{c}\) and \(W_\text{m}\) is the weight of metal and slag, kg; \(k_\text{f}\) and \(k_\text{M}\) is the mass transport coefficient in metal and slag, \(m^2\) s\(^{-1}\); \(\rho_\text{c}\) and \(\rho_\text{m}\) is the density of metal and slag, kg m\(^{-3}\); \(k_\text{C}\) and \(k_\text{O}\) are the rate constants for each reaction, kg m\(^{-2}\) s\(^{-1}\); \(L\) is the distribution ratio; \(f\) is the activity coefficient of element in metal, the reference state being the infinitely dilute solution; a superscript, * indicates the slag–metal interface; [ ] and ( ) indicate component in metal and slag phase, mass%.

\[
\frac{1}{k_\text{M}} = \frac{1}{k_\text{f}\rho_\text{c}} + \frac{L_{\text{O}}^*}{k_\text{m}\rho_\text{m}} \quad (\text{M} = \text{Cr, Al, Si, Mn}) \quad \text{(14)}
\]

\[
\frac{1}{k_\text{M}} = \frac{1}{k_\text{f}\rho_\text{c}} + \frac{1}{k_{\text{M}}^*} + \frac{L_{\text{O}}^*}{k_\text{m}\rho_\text{m}} \quad (\text{M} = \text{Si, Ti}) \quad \text{(15)}
\]

For simplification, it was assumed that the mass transport coefficients of each element are equal with each other in the metal or in the slag phase.

The interfacial distribution ratio of each element between slag and metal, \(L_{\text{O}}^*\) and \(L_{\text{M}}^*\), can be expressed as a function of the interfacial oxygen activity, \(a_{\text{O}}^*\), and the apparent equilibrium constant, \(B\), as follows:

\[
\frac{1}{k_\text{M}} = \frac{1}{k_\text{f}\rho_\text{c}} + \frac{1}{k_{\text{M}}^*} + \frac{L_{\text{O}}^*}{k_\text{m}\rho_\text{m}} \quad (\text{M} = \text{Si, Ti}) \quad \text{(15)}
\]
Using the parameters presented in Table 4, the concentration changes of each element in the metal and slag during a run were also taken into consideration, due to the slag–metal reaction and the dissolution of crucible material, Al₂O₃, into the slag, as shown in Table 4, and further investigations are necessary to discuss these values in particular for the range of 0.0008 to 0.2 kg m⁻³ s⁻¹ as seen from Table 4, and were smaller than the literature values. The main reason is that a liquid slag phase was formed or not during the reaction. Therefore, these values are strongly dependent on temperature and composition of slag, which indicates that the mass transport in the slag phase is the rate-determining step, or at least partly dominates the overall recovery rate of chromium from stainless slag by iron melt.

The values of \( k_{\text{Cr}} \) and \( k_{\text{M}} \) obtained in this study were as seen from Table 4, and further investigations are necessary to discuss these values in particular for \( k_{\text{M}} \), which can be regarded as the ability of oxygen supply to the metal bath.

The values of \( B_{\text{Fe}} \) and \( B_{\text{M}} \) can be theoretically calculated from the following relations using the values of equilibrium constant \( K_{\text{MO}} \) and activity coefficient of the oxide in slag, \( \gamma_{\text{MO}} \), estimated from the literature values and the initial and final compositions of slag.

\[
B_{\text{Fe}} = \frac{M_{\text{FeO}} \sum (\text{MO})}{K_{\text{FeO}}' M_{\text{MO}}},
\]

\[
B_{\text{M}} = \frac{M_{\text{MO}} \sum (\text{MO})}{K_{\text{MO}}' M_{\text{MO}}},
\]

\[
B_{\text{Al}} = \frac{M_{\text{AlO}} \sum (\text{MO})}{\gamma_{\text{MO}}},
\]

where \( \text{MO} \) indicates oxides in slag.

As seen in Fig. 8, it is evident that the theoretical and the calculated values for \( B_{\text{Fe}} \) and \( B_{\text{M}} \) agree well with each other, although the values of \( B_{\text{Al}} \) deviate significantly for the lack of the slag phase, and this result was practically the same as the previous work. 

### Table 4. The parameters determined by modeling calculation.

| Run No. | \( k_{\text{Cr}} \) | \( k_{\text{M}} \) | \( k_{\text{M}} \times 10^{10} \) | \( \text{FeO} / 10^{0} \) | \( \text{FeO} / 10^{0} \) | \( \text{FeO} / 10^{0} \) | \( \text{FeO} / 10^{0} \) |
|---------|-----------------|-----------------|-----------------|----------------|----------------|----------------|----------------|
| SC-1    | 0.2             | 15              | 1               | 1              | 1              | 6              | 1              |
| SC-2    | 0.02            | 10              | 0.5             | 1              | 1              | 40             | 1              |
| SC-3    | 0.02            | 1              | 50              | 1              | 0.5            | 4              | 0.5            |
| SC-4    | 0.025           | 10              | 0.5             | 1              | 0.5            | 2              | 0.5            |
| SC-5    | 0.007           | 10              | 0.5             | 1              | 1              | 90             | 1              |
| SC-6    | 0.0008          | 10              | 0.01            | 1              | 1              | 90             | 1              |
| SB-7    | 0.0028          | 10              | 0.3             | 1              | 1              | 10             | 1              |
| SC-8    | 0.05            | 10             | 0.5             | 1              | 1              | 2              | 1              |
| SC-9    | 0.08            | 1              | 50              | 1              | 0.2            | 0.4            | 0.2            |
| SC-10   | 0.08            | 5              | 0.5             | 1              | 0.2            | 1.5            | 0.2            |
| SC-11   | 0.015           | 10              | 0.2             | 1              | 1              | 50             | 1              |
| SD-12   | 0.0028          | 10              | 0.45            | 1              | 1              | 8              | 1              |
| SF-13   | 0.0015          | 10              | 0.05            | 1              | 1              | 90             | 1              |

\( k_{\text{FeO}} = 1.4 \text{ kg m}^{-2} \text{ s}^{-1} \) was used in the same way as the previous work. 

4.2.2. Parameters

The values of \( k_{\text{Cr}} \) were in the range of 0.0008 to 0.2 kg m⁻³ s⁻¹ as seen from Table 4, and were smaller than the literature values. The main reason is that a liquid slag phase was formed or not during the reaction. Therefore, these values are strongly dependent on temperature and composition of slag, which indicates that the mass transport in the slag phase is the rate-determining step, or at least partly dominates the overall recovery rate of chromium from stainless slag by iron melt.

The values of \( k_{\text{Cr}} \) and \( k_{\text{M}} \) obtained in this study were as shown in Table 4, and further investigations are necessary to discuss these values in particular for \( k_{\text{M}} \), which can be regarded as the ability of oxygen supply to the metal bath.

The values of \( B_{\text{Fe}} \) and \( B_{\text{M}} \) can be theoretically calculated from the following relations using the values of equilibrium constant \( K_{\text{MO}} \) and activity coefficient of the oxide in slag, \( \gamma_{\text{MO}} \), estimated from the literature values and the initial and final compositions of slag.

\( B_{\text{Fe}} = \frac{M_{\text{FeO}} \sum (\text{MO})}{K_{\text{FeO}}' M_{\text{MO}}}, \)

\( B_{\text{M}} = \frac{M_{\text{MO}} \sum (\text{MO})}{K_{\text{MO}}' M_{\text{MO}}}, \)

\( B_{\text{Al}} = \frac{M_{\text{AlO}} \sum (\text{MO})}{\gamma_{\text{MO}}}, \)
of the thermodynamic data on titanium equilibrium between slag and metal. So it can be said that this reaction model is applicable to the prediction of the kinetic behavior of Cr₂O₃ reduction in stainless slags by Fe–C–Al–Si melts.

As has been noted, since the values of $k_{r_s}$ varied remarkably by various factors, it is difficult to predict the values in the simulation. Here the relationships between the slag property such as liquid phase fraction, viscosity and the mass transport coefficient in slag were examined to obtain useful information for designing the composition of slag. The results are shown in Figs. 10 and 11. The axis of abscissa in these figures is the average values obtained from the computational thermodynamics program¹-six) for calculating equilibrium, and from the equation proposed by Iida ¹-seven) for estimating the viscosities of multicomponent slags, using the initial and final compositions of slag, respectively. It is seen that the values of $k_{r_s}$ increase with increasing liquid phase fraction of slag, and with decreasing viscosity of slag. This tendency seems to be the same as that reported by Miyamoto et al.,² and therefore, it is important for the promotion of reduction reaction of Cr₂O₃ in slag to not only lower the liquidus temperature of slag and also control the composition of slag, although the reduction rate was also affected by the activity of chromium in slag.

4.3. Effective Slag Treatment Technique

Finally, the effective conditions to recover chromium from stainless steelmaking slag used in this study were discussed on the basis of experimental results. Figure 12 shows the relation between initial reduction rate and recovery ratio of chromium for each experiment, and shows the comparison with the results of Cr₂O₃-saturated slags, that is chromium content in slag were 5.58–12.2 mass%. It can be said that higher temperature and addition of Al₂O₃ and SiO₂ to the slag, which leads to promote the formation of liquid slag, or composition of slag with CaO/SiO₂/H₂O is desirable for high chromium recovery from stainless slag. Besides, the reduction reaction for chromium recovery will be promoted by stirring of slag and metal.

5. Conclusions

In order to improve the recycle technique for stainless steelmaking slags, the effect of various factors on the re-
covery rates of chromium from slags by iron melts were investigated in the temperatures range of 1 400 to 1 600°C under an argon atmosphere, and the efficient method for high chromium recovery was discussed.

The recovery rate of chromium was fairly slow at all temperatures, but it was considerably accelerated by the addition of some fluxes, such as Al₂O₃ and SiO₂ to the slag, which promoted the formation of liquid slag at the early stage of the reaction, and the recovery ratio of chromium was also improved. In addition, SiO₂ addition was more effective for increasing the chromium recovery than Al₂O₃ addition due to the effect of CaO/SiO₂ ratio of slag on the reduction rate of Cr₂O₃ in slag. The recovery ratio of chromium decreased by the addition of aluminum and silicon to iron melts, such a decrease was attributed to little formation of liquid slag phase. Higher temperatures were favorable for the reduction reaction in all runs and it remarkably enhanced the recovery rate and ratio of chromium from stainless slags.

The kinetic behavior of reduction of Cr₂O₃ in slag could be well simulated by the previous kinetic reaction model. It was found from the modeling calculation that the transfer rate of chromium from slag to metal was controlled by the mass transport in the slag phase during the entire period of reaction.

Acknowledgements

The authors are grateful to Nippon Steel Corporation for the financial support.

REFERENCES

1) R. Nakao, S. Tanaka and H. Takao: Tetsu-to-Hagané, 80 (1994), 30.
2) K. Miyamoto, K. Kato and T. Yuki: Tetsu-to-Hagané, 88 (2002), 838.
3) K. Taoka, M. Tada, H. Nomura and H. Baba: Tetsu-to-Hagané, 76 (1990), 1863.
4) S. Yokoyama, M. Takeda, K. Ito and M. Kawakami: Tetsu-to-Hagané, 78 (1992), 223.
5) T. Nakasuga, H. Sun, K. Nakashima and K. Mori: ISIJ Int., 41 (2001), 937.
6) T. Nakasuga, H. Sun, K. Nakashima and K. Mori: Proc. of the 2nd Int. Conf. on Processing Materials for Properties, Vol. 86, TMS, Warrendale, PA, (2000), 553.
7) E. Shibata, S. Egawa and T. Nakamura: ISIJ Int., 42 (2002), 869.
8) Recommended Equilibrium Value of Steel-Making, Japan Society for Promotion of Science and Technology 19th Committee on Steelmaking, Tokyo, (1984), 38, 49, 83, 99, 114, 131, 255–262.
9) S. Ban-ya: ISIJ Int., 33 (1993), 2.
10) S. Kitamura, N. Sato and K. Okohara: Trans. Iron Steel Inst. Jpn., 28 (1988), 364.
11) K. Mori, Y. Kawai and Y. Fukami: Trans. Iron Steel Inst. Jpn., 28 (1988), 315.
12) E. Shibata, H. Sun and K. Mori: Tetsu-to-Hagané, 82 (1996), 575.
13) K. Mori, S. Hiiwasa and Y. Kawai: J. Jpn. Inst. Met., 44 (1980), 1282.
14) Handbook of Iron and Steel, 3rd Ed., I, Fundamental Theory of Iron and Steel, ed. by ISIJ, Maruzen, Tokyo, (1981), 15, 19, 164.
15) Y. P. Xiao, L. Holappa and M. A. Reuter: Metall. Mater. Trans. B, 33B (2002), 595.
16) W. Yamada and T. Matsumiya: Nippon Steel Tech. Rep., 342 (1991), 38.
17) T. Iida, H. Sakai, Y. Kita and K. Murakami: High Temp. Mater. Process., 19 (2000), 153.