MORITA, K and SANO, N. Activity of chromium oxide in $CaO-SiO_2$ based slags at 1873 K. *VII International Conference on Molten Slags Fluxes and Salts,* The South African Institute of Mining and Metallurgy, 2004.

Activity of chromium oxide in $CaO-SiO_2$ based slags at 1873 K

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Thermodynamic properties of chromium oxides in molten slags are very important for optimization of stainless steel refining processes as well as reduction processes of chromium ores. The solubility of chromite into molten slags has been found to vary considerably with oxygen partial pressure and slag composition in former studies by the authors. In the present study, activity data and redox equilibria of chromium oxides measured under moderately reducing conditions, $P_{O_2} = 6.95\times10^{-11}$ atm, at 1873 K are summarized. For the $CaO-SiO_2-CrO_X$ system, the activity coefficient of chromium oxide increased with increasing basicity, and the optimized slag composition for stainless steel refining is assessed as that saturated with $CaCr_2O_4$ and Cr_2O_3 using the phase relations determined. On the other hand, the presence of MgO and Al_2O_3 brings about different behaviour of chromium oxide activity and redox equilibiria and the 44 mass per cent CaO-39 mass per cent SiO_2-11 mass per cent Al_2O_3-6 mass per cent MgO slag is recommended to reduce the chromium oxidation loss in the practical stainless steel refining process at 1873 K.

Keywords: chromium, activity, stainless steel, AOD, VOD, oxidation loss, redox, $CaO-SiO_2-Al_2O_3-MgO$ slag

Introduction

Chromium is one of the indispensable elements as a component of high quality steels, and a number of researches have been carried out in order to improve the reduction behaviour and chromium yield in the smelting of molten ferrochromium or crude stainless steel. Among others, the thermodynamic properties of chromium in molten slags are extremely important for effective production of such alloys since the dissolution of chromium ore has been known as the rate determining step in the overall reaction processes. Authors[1–2] have evaluated the solubility of chromite in various silicate slags by the chromium content of the slags equilibrated with $MgCr_2O_4$, a typical compound of undissolved chromite due to the preferential reduction of iron in chromium ore. We have reported that oxygen partial pressure, as well as slag composition, significantly affects its solubility, redox equilibria and the activity of chromium oxide in such slags. In the carbonaceous reduction process, oxygen partial pressure around the slag-metal interface reaches as low as 10^{-16} atm assuming P_{CO}=1 atm at 1873 K, and eventually the pure chromium oxide cannot be thermodynamically stable leaving a small amount of chromium in the molten slags mainly as Cr^{2+} in acidic slags.

On the other hand, slag composition is an important factor for the better operation of decarburization processes of stainless steels, such as VOD and AOD. Since the Gibbs energy of formation for chromium oxide is significantly negative at steelmaking temperatures compared with those for FeO, NiO and CO, chromium in molten steels can be preferentially oxidized and lost in a coexisting slag phase. Despite that it has been tried to lower the partial pressure of CO gas generated by decarburization by either evacuation or dilution with argon gas, the oxidation loss of chromium in molten slags essentially occurs and a large amount of silicon or silicon based alloys must be added for the recovery of chromium from the slags in the final stage of the decarburization process.

In order to optimize the slag composition for stainless steel treatment, precise information is needed on thermodynamic properties of ladle slags, such as chromium oxide activity and redox equilibria of chromium, in the oxygen partial pressure close to that of the practical processes since they are strongly dependent on oxygen partial pressure as reported by the present authors[1–2] and other researchers[3–4]. As shown in Figure 1[2], the solubility of chromite increases considerably with decrease in oxygen partial pressure accompanied by the increase in the Cr^{2+} fraction. (Figure 2[2]) At the same time, phase stability considerably changes and the liquid region is enlarged, as shown in Figure 3. Xiao and Holappa[5–6] measured the activities of chromium oxides in the $CaO-SiO_2-MgO-Al_2O_3-CrO_X$ slags under strongly reducing conditions by the EMF method at 1773–1873 K and introduced a concept of the activity of chromium oxide, a_{CrO_X} defined as Equation [1].

$$a_{CrO_X} = a_{CrO_{1.5}}{}^{\left(X_{CrO_{1.5}}/X_{CrO_X}\right)}\, a_{CrO}{}^{\left(X_{CrO}/X_{CrO_X}\right)} \qquad [1]$$

However, their results might be hardly utilized in the the practical decarburization process because the variation of divalent chromium content due to the difference in oxygen partial pressure will cause a significant discrepancy in thermodynamic properties. Hence, the present authors[7] have focused on such properties of $CaO-SiO_2$ based slags especially under moderately reducing conditions, $P_{O_2}= 6.95\times10^{-11}$ atm at 1873 K. The activity of chromium oxide for this system has been measured in terms of a_{CrO_X} by a chemical equilibration technique. In the present study, further optimization of decarburization slags has been carried out by investigating the effects of MgO and Al_2O_3 as well as summarizing the thermodynamic properties of chromium oxide in $CaO-SiO_2$ based slags.

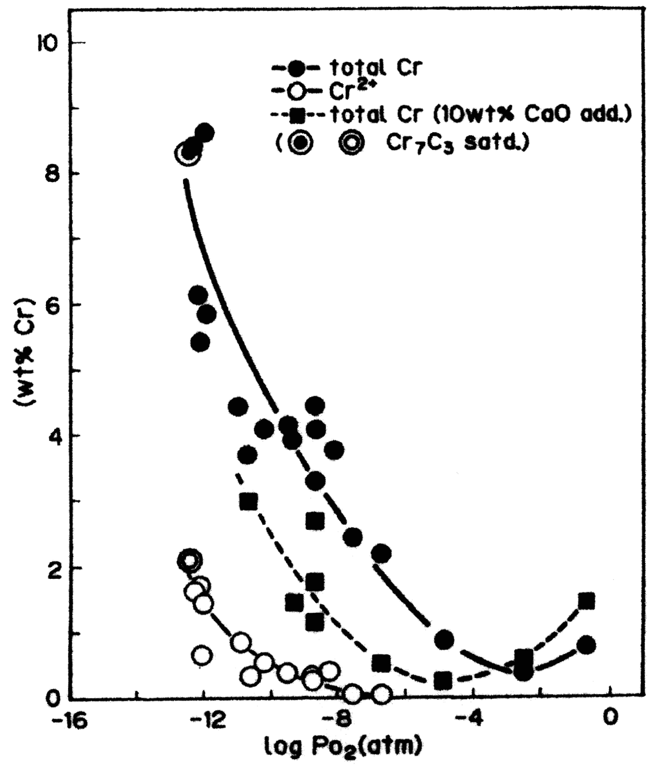

Figure 1. Oxygen partial pressure dependence of the solubility of $MgCr_2O_4$ in $MgO-SiO_2(-CaO)$ $(-CrO_X)$ melts (Mg_2SiO_4 satd.) at 1873 K

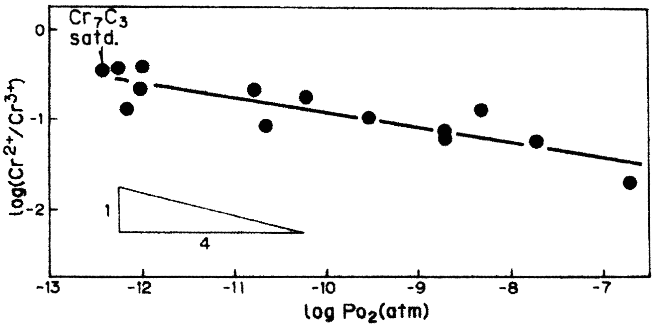

Figure 2. Oxygen partial pressure dependence of Cr^{2+}/Cr^{3+} ratio in $MgO-SiO_2(-CrO_X)$ melts (Mg_2SiO_4 satd.) at 1873 K

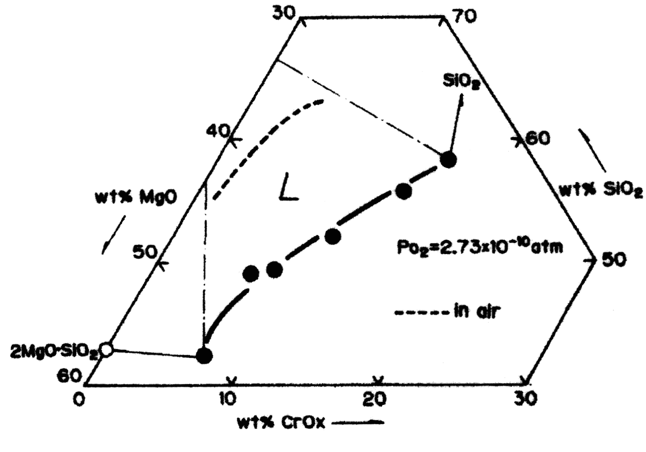

Figure 3. Solubility of $MgCr_2O_4$ in $MgO-SiO_2(-CrO_X)$ melts at 1873 K under a lower oxygen partial pressure

Experimental

Four grammes of $CaO-SiO_2-Al_2O_3-MgO-Cr_2O_3$ slags and 10 g of Cu-Cr alloys were equilibrated in a molybdenum crucible for 20 h using an electric resistance furnace equipped with $MoSi_2$ as a heating element. Slags were prepared by mixing reagent-grade oxides, although CaO was previously calcined from $CaCO_3$. The gas mixture of 50 CO-1 CO_2 was flowed onto the sample at the flow rate of 170 cm^3/min STP and the oxygen partial pressure was controlled to be $P_{O_2} = 6.95\times10^{-11}$ atm at 1873 K in most experiments. Samples were quickly withdrawn from the furnace, quenched by flushing argon gas after the equilibration, then slags and alloys were subjected to chemical analyses. Contents of total Cr, Mg and Al in the slag as well as Cr contents of the alloy were determined by inductively coupled plasma emission spectroscopy, while divalent chromium in the slag was determined by volumetric titration and silicon content by gravimetry.

Activity of chromium oxide was derived from the chromium content of the alloy, the activity coefficient of chromium in the Cu-Cr alloy and the Gibbs energies of formation for CrO and $CrO_{1.5}$ as described below,

$$Cr(s) + 3/4\ O_2(g) = CrO_{1.5}(s) \qquad [2]$$

$$\Delta G^o = -555{,}070 + 123.65\ \mathrm{T(J/mol)}^8 \qquad [3]$$

$$Cr(s) + 1/2\ O_2(g) = CrO(1) \qquad [4]$$

$$\Delta G^o = -334{,}220 + 63.81\ \mathrm{T(J/mol)}^8 \qquad [5]$$

where *s*, *l*, and *g* denote the standard states of pure substances, solid, liquid and gas, respectively. Since chromium contents of the alloys were as low as 0.05–0.30 mass per cent after equilibration, the molten Cu-Cr alloys were considered to conform to dilute solution in the present experiments. Hence, the activity coefficient of chromium in molten copper at infinitely dilute solution, $\gamma^o_{Cr(s)\ in\ Cu} = 11.0$[7], was employed for all the calculations.

Results and discussion

Phase relations and the iso-activity contours of chromium oxide for the $CaO-SiO_2-CrO_X$ system

In our previous work[7] we clarified the phase relations and drew the iso-activity contours of CrO_X for the $CaO-SiO_2-CrO_X$ system at 1873 K as shown in Figure 4. Solubilities of $CrO_{1.5}$ and $CaCr_2O_4$ drastically decrease with CaO content of the slag, and the iso-activity contours demonstrate a similar shape to both of the solubility curves. This figure shows that the solubility of chromium oxide is so sensitive to the slag composition and the 10 mass per cent decrease in CaO content could make the chromium oxidation loss double. In order to minimize such losses, highly basic slags, e.g. 60 mass per cent CaO-40 mass per cent SiO_2 ($X_{CaO}/X_{SiO_2} = 1.61$), could be recommended for the practical process. However, stable compound $CaCr_2O_4$ can be easily formed when CaO activity exceeds 0.024 according to its Gibbs energy of formation[9] even with lower chromium oxide activity. Furthermore, the oxidation reaction would not stop until the activity of $CaCr_2O_4$ becomes lower than unity in such cases. From the standpoint of avoiding solid phase precipitation, as seen by the values of a_{CrO_X} on the $CaCr_2O_4$ saturation curve, lower CaO content is considered to be favorable. Hence, in our previous work, the slag doubly saturated with $CrO_{1.5}$ and

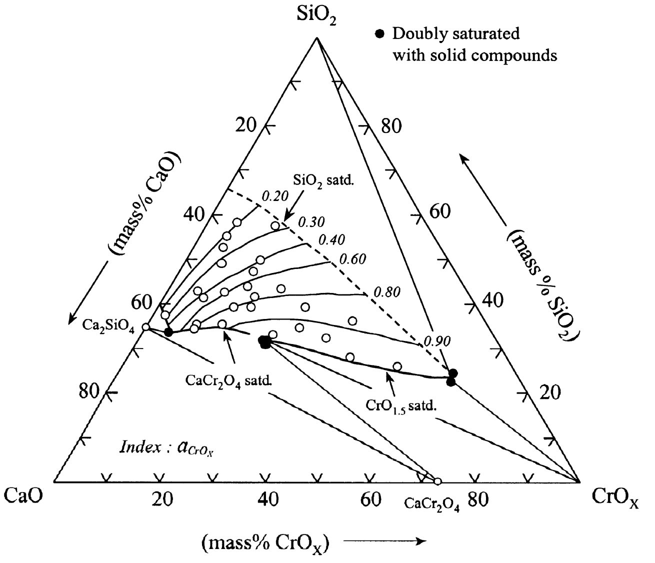

Figure 4. Iso-activity contours of CrO_X and phase relations for the $CaO-SiO_2-CrO_X$ system at 1873 K with $P_{O_2} = 6.95 \times 10^{-11}$ atm

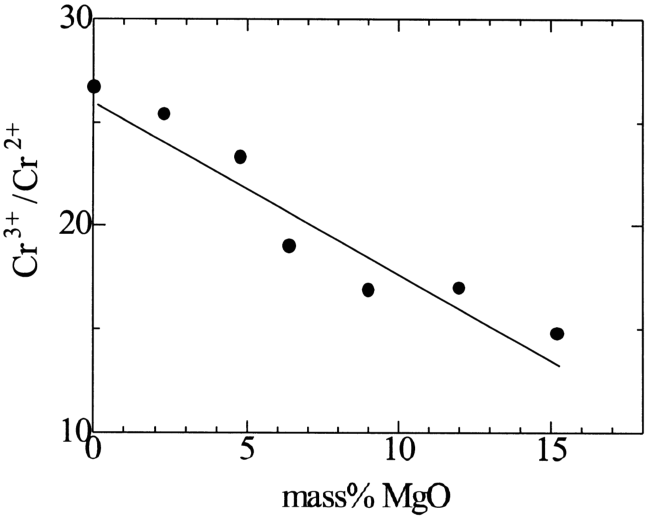

Figure 5. Effect of MgO addition on the ratio of Cr^{3+}/Cr^{2+} for the 41 mass per cent CaO-41 mass per cent SiO_2-10 mass per cent Al_2O_3-8 mass per cent CrO_X slags at 1873 K with $P_{O_2} = 6.95 \times 10^{-11}$ atm

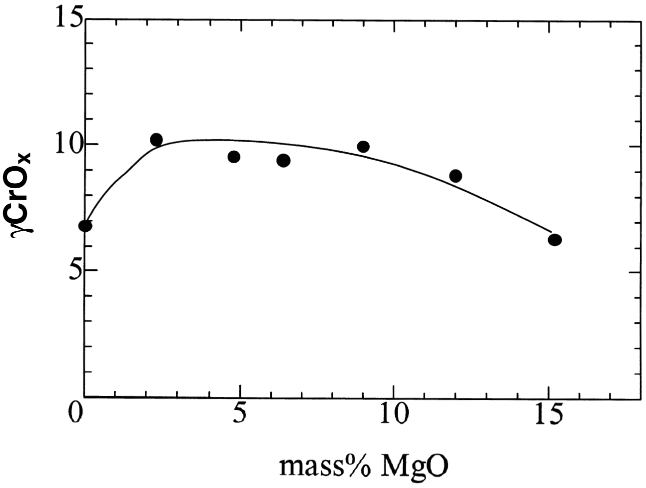

Figure 6. Effect of MgO addition on the activity coefficient of CrO_X for the 41 mass per cent CaO-41 mass per cent SiO_2-10 mass per cent Al_2O_3-8 mass per cent CrO_X slags at 1873 K with $P_{O_2} = 6.95 \times 10^{-11}$ atm

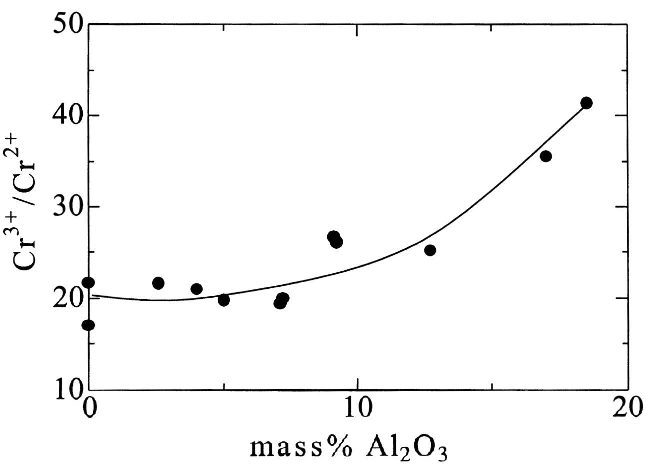

Figure 7. Effect of Al_2O_3 addition on the ratio of Cr^{3+}/Cr^{2+} for the 43 mass per cent CaO-43 mass per cent SiO_2-5 mass per cent MgO-9 mass per cent CrO_X slags at 1873 K with $P_{O_2} = 6.95 \times 10^{-11}$ atm

$CaCr_2O_4$ was recommended for low oxidation loss of chromium and the prevention of $CaCr_2O_4$ precipitation during decarburization of stainless steel, namely $X_{CaO}/X_{SiO_2} = 1.47$ at 1873 K. Then, we focused on the composition dependency of the slag.

Effect of MgO and Al_2O_3 content on the activity of chromium oxide

Since MgO is unavoidably dissolved from refractory materials in the practical decarburization slags and the addition of Al_2O_3 may depress the liquidus temperature of the slag, the effects of MgO and Al_2O_3 on the chromium oxide activities were determined.

Regarding the effect of MgO addition to the slag, 41 mass per cent CaO-41 mass per cent SiO_2-10 mass per cent Al_2O_3-8 mass per cent CrO_X was selected as a standard composition. Figure 5 shows the change in the Cr^{3+}/Cr^{2+} ratio with MgO content of the slag. The ratio shows continuous decrease due to the change in the activity coefficients of both CrO and $CrO_{1.5}$. Consequently, the activity coefficient of CrO_X once increased with 2.5 mass per cent MgO addition and then levelled off up to 10 mass per cent MgO as shown in Figure 6. The reason for an apparent decrease afterwards is considered to be the precipitation of $Mg(Cr,Al)_2O_4$, which was identified by X-ray diffraction (XRD). From the view point of lowering chromium loss in the process, slag with 2.5–10 mass per cent MgO is favourable.

As for the effect of Al_2O_3 addition to the slag, 43 mass per cent CaO-43 mass per cent SiO_2-5 mass per cent MgO-9 mass per cent CrO_X was selected as a standard slag composition. Figure 7 shows the change in the Cr^{3+}/Cr^{2+} ratio with Al_2O_3 content of the slag. The ratio remains almost constant up to 7 mass per cent Al_2O_3, then gradually increases also due to the change in the activity coefficients of both CrO and $CrO_{1.5}$. On the other hand, the activity coefficient of CrO_X very slightly decreases with Al_2O_3 content as shown in Figure 8. Contrary to the MgO addition, precipitation of $Mg(Cr,Al)_2O_4$ was not observed and all the slag samples were characterized as glassy state by XRD. Although the addition of Al_2O_3 was reported to

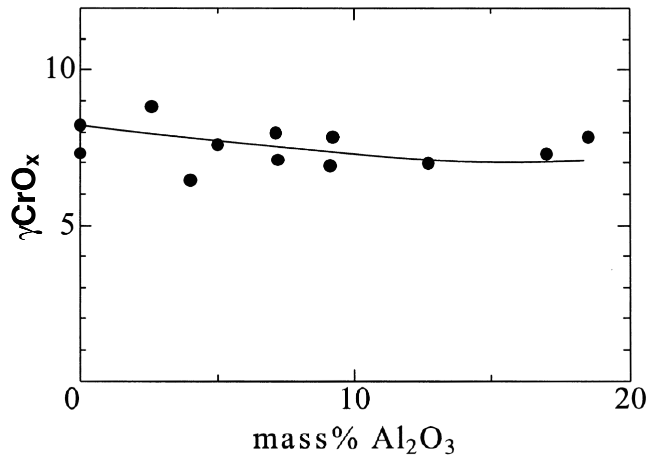

Figure 8. Effect of Al_2O_3 addition on the activity coefficient of CrO_X for the 43 mass per cent CaO-43 mass per cent SiO_2-5 mass per cent MgO-9 mass per cent CrO_X slags at 1873 K with P_{O_2} = 6.95×10^{-11} atm

lower the solubility of $Mg(Cr,Al)_2O_4$ in the authors' previous work, Al_2O_3 may work as an appropriate additive in the present slag composition for lowering liquidus temperature and viscosity.

Effect of basicity on the activity of chromium oxide in the slag

The effect of basicity on the activity of chromium oxide in the $CaO-SiO_2-CrO_X$ slag system has been investigated at three discreet levels of chromium content. Figures 9 and 10 show the effects of X_{CaO}/X_{SiO_2} on the activity coefficient of $CrO_{1.5}$, and that of CrO, respectively. They show that an increase in basicity of the present slags brings about increases in the activity coefficients of $CrO_{1.5}$ and CrO. Therefore, the ratio of Cr^{3+}/Cr^{2+} significantly increases with basicity as shown in Figure 11.

In the present study, the effect of X_{CaO}/X_{SiO_2} has been investigated for the slag with 10 mass per cent Al_2O_3-5 mass per cent MgO-10 mass per cent CrO_X. The changes in the activity coefficients of $CrO_{1.5}$ and CrO with X_{CaO}/XS_{iO_2} are demonstrated in Figure 12. Both activity coefficients show considerable increases up to X_{CaO}/XS_{iO2} = 1.1, similar to the MgO and Al_2O_3 free system. However, the precipitation of $Mg(Cr,Al)_2O_4$ was observed when X_{CaO}/X_{SiO_2} = 1.3, which lowers both apparent activity coefficients, although they showed continuous increase up to X_{CaO}/X_{SiO_2} = 1.5 for the $CaO-SiO_2-CrO_X$ slag system. These facts suggest that higher basicity of the slag is considered to reduce the chromium oxidation loss during the practical decarburization process of stainless steel production as long as the chromium in an oxide phase exists as molten state. However, the optimal value of X_{CaO}/X_{SiO_2} for the present slag composition is likely to be 1.1, in spite of 1.47 for the $CaO-SiO_2-CrO_X$ ternary slag system. In order to minimize the chromium oxidation loss in the stainless steel refining process at 1873 K, 44 mass per cent CaO-39 mass per cent SiO_2-11 mass per cent Al_2O_3-6 mass per cent MgO slag is considered to be suitable according to the present results.

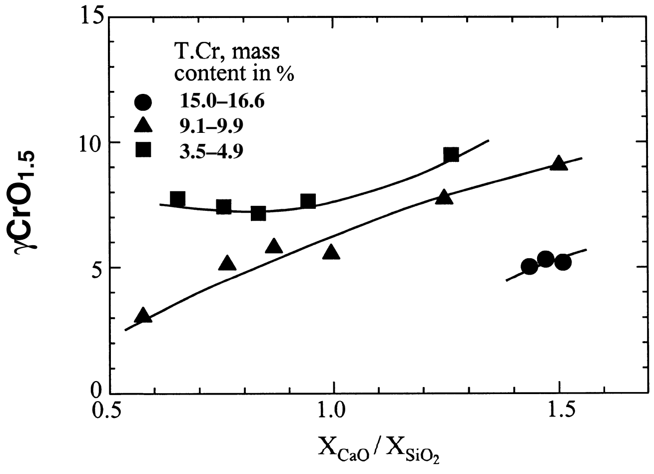

Figure 9. Effect of X_{CaO}/X_{SiO_2} on the activity coefficient of $CrO_{1.5}$ for the $CaO-SiO_2-CrO_X$ slags at 1873 K with P_{O_2} = 6.95×10^{-11} atm

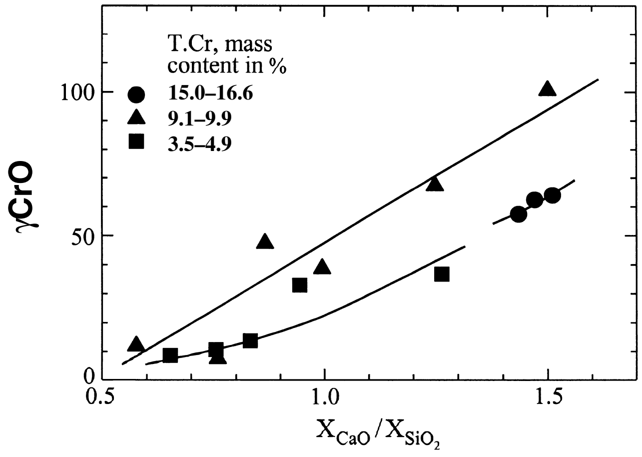

Figure 10. Effect of X_{CaO}/X_{SiO_2} on the activity coefficient of CrO for the $CaO-SiO_2-CrO_X$ slags at 1873 K with P_{O_2} = 6.95×10^{-11} atm

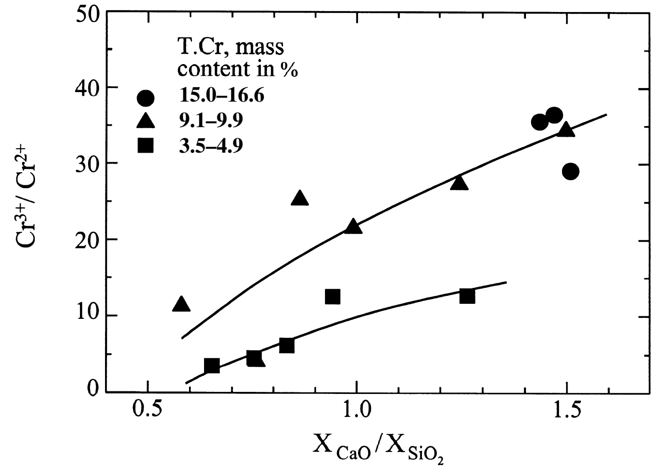

Figure 11. Effect of X_{CaO}/X_{SiO_2} on the ratio of Cr^{3+}/Cr^{2+} for the $CaO-SiO_2-CrO_X$ slags at 1873 K with P_{O_2} = 6.95×10^{-11} atm

Conclusions

Under moderately reducing conditions, thermodynamic properties of chromium oxides in the $CaO-SiO_2-Al_2O_3-MgO-CrO_X$ system have been investigated by equilibrating the slags with molten Cu-Cr alloys at 1873 K and activity data and redox equilibria of chromium oxides measured in the reducing conditions at 1873 K are summarized. For the $CaO-SiO_2-CrO_X$ system, the activity coefficient of

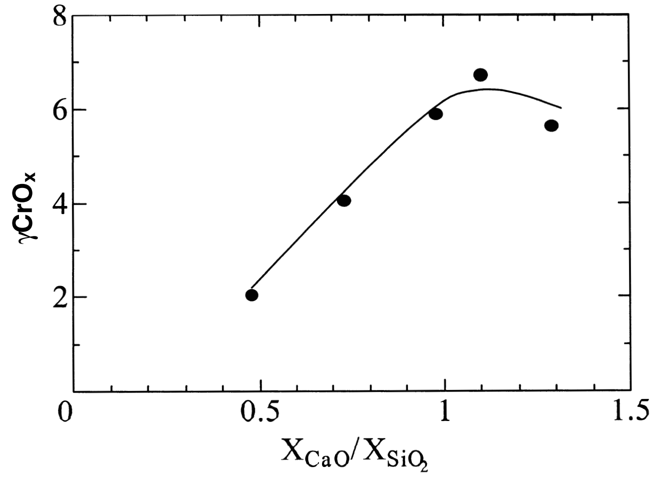

Figure 12. Effect of X_{CaO}/X_{SiO_2} on the activity coefficient of CrO_X for the CaO-SiO_2-10 mass per cent Al_2O_3-5 mass per cent MgO-10 mass per cent CrO_X slags at 1873 K with $P_{O_2} = 6.95 \times 10^{-11}$ atm

chromium oxide increased with increasing basicity and the optimized slag composition for stainless steel refining was assessed as that saturated with $CaCr_2O_4$ and Cr_2O_3 using the phase relations determined under moderately reducing conditions, $P_{O_2} = 6.95 \times 10^{-11}$ atm. For the CaO-SiO_2-Al_2O_3-MgO-CrO_X system, when MgO was added to the 41 mass per cent CaO-41 mass per cent SiO_2-10 mass per cent Al_2O_3-8 mass per cent CrO_X slag, the activity coefficient of CrO_X once increased with 2.5 mass per cent MgO addition and then levelled off up to 10 mass per cent MgO. When Al_2O_3 was added to the 43 mass per cent CaO-43 mass per cent SiO_2-5 mass per cent MgO-9 mass per cent CrO_X slag, the activity coefficient of CrO_X showed a very slight decrease with an increase in Al_2O_3 content. From these results with basicity dependence, 44 mass per cent CaO-39 mass per cent SiO_2-11 mass per cent Al_2O_3-6 mass per cent MgO slag is considered to be adequate for minimizing the chromium oxidation loss in the practical stainless steel refining process at 1873 K.

Acknowledgement

Authors are grateful to Mr K. Tsukiashi and Mr M. Kimura for their contribution to the experiment and chemical analysis.

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