Activities in CaO-SiO_2-CrO_x Slag System at 1600 °C

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ABSTRACT

The activities of CaO and SiO_2 in the quasi-ternary system CaO-SiO_2-CrO_x were calculated. The calculation was based on the measured activities of CrO and $CrO_{1.5}$ and the activity data of the CaO-SiO_2 binary system at 1600°C by applying the Gibbs-Duhem equation. The results were presented as iso-activity diagrams for CaO and SiO_2. The activity of CaO is quite low in the liquid area of the slag. The activity of SiO_2 changes from unity at silica saturation to low values at calcium silicate, calcium chromite, or eskolaite (Cr_2O_3) saturation. The activities of CaO and SiO_2 were qualitatively compared to the activities in the CaO-SiO_2-FeO_x slag system, respectively. The results showed great similarity between these two slag systems.

1. INTRODUCTION

Thermodynamic properties of slags play essential role in the steelmaking process. Slags in the AOD process for stainless steel production consist of the following major oxide components: CaO, SiO_2, CrO and $CrO_{1.5}$ together with some minor proportions of other oxides. The activities of CrO and $CrO_{1.5}$ have been experimentally determined in the liquidus area of CaO-SiO_2-CrO-$CrO_{1.5}$ at 1600 °C by the electromotive force method by the present authors[1]. The equilibrium was achieved between the slag and the Cr-saturated Cr-Ag alloy. The fraction of Cr^{2+} and Cr^{3+} in the slags was analyzed by wet-chemical method. The iso-activity contours of CrO and $CrO_{1.5}$ were obtained. Pure liquid and pure solid oxide were used as the standard state of CrO and $CrO_{1.5}$, respectively. Based on the previous work, the activities of CaO and SiO_2 were calculated over a wide range of liquidus slag area in the system CaO-SiO_2-CrO-$CrO_{1.5}$ at 1600 °C by Gibbs-Duhem equation. The results were compared with the corresponding data of iron oxides containing system for better understanding the thermodynamic behavior of AOD slags.

2. CALCULATION METHOD

The Gibbs-Duhem equation is well known for deriving the partial molar properties of other components from the known partial molar property of one component in multi-component systems. The effort for developing a convenient method to mathematically solve the equation has been made for several decades. The traditional methods[2-10] can not avoid the strenuous graphical integration and differentiation. An analytical solution of the Gibbs-Duhem equation for ternary system has also been developed[11-14]. The solution has been widely used in calculating partial molar properties of the other two components and the corresponding integral properties from the known partial molar property of one component in ternary systems. Nevertheless, the properties of all three pure components and the binary sub-systems should be taken as boundary conditions in order to keep thermodynamic consistency.

In the present study, the quarternary system is simplified to a quasi-ternary slag system in order to obtain the activities of CaO and SiO_2 in the CaO-SiO_2-CrO-$CrO_{1.5}$ slag system. The calculation was based on the hypothetical component, CrO_x, which was obtained by considering the total chromium in the slag consisting of CrO and $CrO_{1.5}$. The first step is to establish the curves of the excess Gibbs energy of mixing for the CaO-SiO_2 binary system and the activity surface of CrO_x for the quasi-ternary system from the experimental results and the phase diagram; then to integrate along constant slag basicity values, and to differentiate along the iso-activity curves of CrO_x with computer program to obtain the activity coefficients for CaO and SiO_2.

2.1 Simplification of quarternary to quasi-ternary system

In the CaO-SiO_2-CrO-$CrO_{1.5}$ quarternary system, the Gibbs-Duhem equation can be written as:

$$N_{CaO} \cdot d\mu_{CaO} + N_{SiO_2} \cdot d\mu_{SiO_2} + N_{CrO} \cdot d\mu_{CrO} + N_{CrO_{1.5}} \cdot d\mu_{CrO_{1.5}} = 0 \tag{1}$$

$$N_{CaO} + N_{SiO_2} + N_{CrO} + N_{CrO_{1.5}} = 1 \tag{2}$$

In the CaO-SiO_2-CrO_x quasi-ternary system, the Gibbs-Duhem equation can be constructed as:

$$N_{CaO} \cdot d\mu_{CaO} + N_{SiO_2} \cdot d\mu_{SiO_2} + N_{CrO_x} \cdot d\mu_{CrO_x} = 0 \tag{3}$$

$$N_{CaO} + N_{SiO_2} + N_{CrO_x} = 1 \tag{4}$$

where, N_i and μ_i represent mole fractions and chemical potentials of the component i in the system, respectively.

By comparing Eq. 1 to Eq. 3 and Eq. 2 to Eq. 4, the following relationship can be obtained:

$$N_{CrO_x} \cdot d\mu_{CrO_x} = N_{CrO} \cdot d\mu_{CrO} + N_{CrO_{1.5}} \cdot d\mu_{CrO_{1.5}} \tag{5}$$

$$N_{CrO_x} = N_{CrO} + N_{CrO_{1.5}} \tag{6}$$

Define $\beta = \frac{N_{CrO}}{N_{CrO_{1.5}}}$, then,

$$d\mu_{CrO_x} = \frac{\beta \cdot d\mu_{CrO} + d\mu_{CrO_{1.5}}}{1+\beta} \tag{7}$$

For the chemical potentials, it can be written as:

$$\mu_{CrO} = \mu^{\circ}_{CrO} + RT\ln a_{CrO} \tag{8}$$

$$\mu_{CrO_{1.5}} = \mu^{\circ}_{CrO_{1.5}} + RT\ln a_{CrO_{1.5}} \tag{9}$$

Accordingly, the following relation is valid:

$$\mu_{CrO_x} = \frac{\beta \cdot \mu^{\circ}_{CrO} + \mu^{\circ}_{CrO_{1.5}}}{1+\beta} + RT\ln(a_{CrO}{}^{(\frac{\beta}{1+\beta})} \cdot a_{CrO_{1.5}}{}^{(\frac{1}{1+\beta})}) \tag{10}$$

In general, the chemical potential of CrO_x can be written as:

$$\mu_{CrO_x} = \mu^{\circ}_{CrO_x} + RT\ln a_{CrO_x} \tag{11}$$

Here, the standard state for the activity of CrO_x can be defined based on the following equation:

$$\mu^{\circ}_{CrO_x} = \frac{\beta \cdot \mu^{\circ}_{CrO} + \mu^{\circ}_{CrO_{1.5}}}{1+\beta} \tag{12}$$

Then, the activity of CrO_x can be derived as follows:

$$a_{CrO_x} = a_{CrO}{}^{(\frac{\beta}{1+\beta})} \cdot a_{CrO_{1.5}}{}^{(\frac{1}{1+\beta})} \tag{13}$$

In order to maintain thermodynamic consistency, the β value should be constant on the single iso-activity line, so that the activity has the same standard state on the iso-activity line. However, the standard state for the activity of CrO_x at different activity values may be different, because β is a variable value depending on oxygen partial pressure. Fig. 1 shows the relationships among $\log P_{O_2}$ and the β values as well as the activities of CrO_x in the slag system of CaO-SiO_2-CrO-$CrO_{1.5}$ in equilibrium with metallic chromium at 1600 °C. The original experimental data were presented earlier by the authors[1]. From this figure, it can be seen that at the same activity of CrO_x, the β value almost keeps constant, but with increasing activity of CrO_x, the β value will decrease. According to the experimental data of the activities of CrO and $CrO_{1.5}$ in the CaO-SiO_2-CrO_x slag system, the iso-activity lines for CrO_x in the quasi-ternary system were constructed from Eq. 13 as shown in Fig. 2. The lines in the liquidus area in Fig.2 are based on the activity data for CrO and $CrO_{1.5}$ measured in the experimental work[1]. The tie lines are drawn according to the phase diagram[15]. The activity of the component should be constant on the tie lines in the two-phase areas.

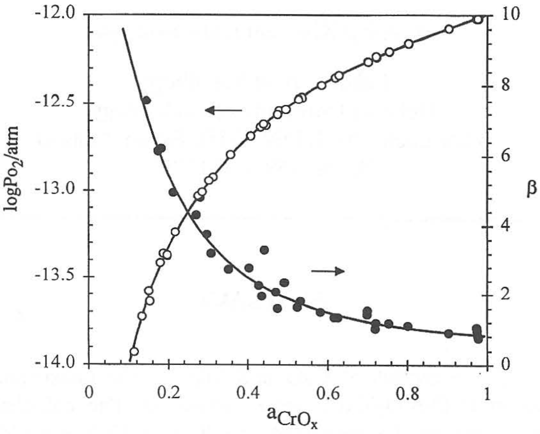

Fig. 1 Relationships of oxygen partial pressure with β value and CrO_x activity in the CaO-SiO_2-CrO_x slag system in equilibrium with metallic chromium at 1600 °C, standard state of CrO_x defined by Eq. 12.

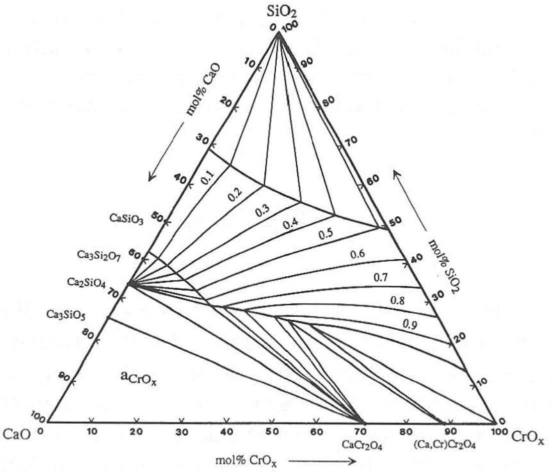

Fig. 2 Iso-activity diagram of CrO_x in the CaO-SiO_2-CrO_x slag system at 1600 °C in equilibrium with metallic chromium, standard state defined by Eq. 12.

2.2 Derivation of partial molar properties in CaO-SiO_2-CrO_x system

When the activity of one component of a ternary system is known, the activity of the other two can be calculated with the ternary Gibbs-Duhem equation. Based on Wang's method[10], by quoting the excess function, the thermodynamic relationships and parameter definitions are listed as follows:

$$G^E = N_{CrO_x}\mu^E_{CrO_x} + N_{CaO}\mu^E_{CaO} + N_{SiO_2}\mu^E_{SiO_2} \qquad (14)$$

$$N_{CaO}\cdot d\mu^E_{CaO} + N_{SiO_2}\cdot d\mu^E_{SiO_2} + N_{CrO_x}\cdot d\mu^E_{CrO_x} = 0 \qquad (15)$$

$$y \equiv \frac{N_{SiO_2}}{N_{CaO} + N_{SiO_2}} \qquad (16)$$

$$\Theta^E \equiv \frac{G^E - N_{CrO_x}\mu^E_{CrO_x}}{1 - N_{CrO_x}} \qquad (17)$$

$$\alpha = \frac{\mu^E_{CrO_x}}{(1 - N_{CrO_x})^2} \qquad (18)$$

where, G^E is the excess molar Gibbs energy, y, Θ^E, and α are the defined parameters.

According to Eqs. 14, 15 and 16, Θ^E in Eq. 17 can be re-written as:

$$\Theta^E = (1-y)\mu^E_{CaO} + y\mu^E_{SiO_2} \qquad (19)$$

Dividing Eq. 19 by y, differentiating it, and comparing with the Gibbs-Duhem Eq. 15, it follows:

$$d\frac{\Theta^E}{y} = \mu^E_{CaO}d(\frac{1}{y}) - \frac{N_{CrO_x}}{y(1-N_{CrO_x})}d\mu^E_{CrO_x} \qquad (20)$$

Θ^E can be derived by integrating the above equation at a constant y value, by combining Eq. 18 and integrating it from $N_{CrO_x} = 0$, thus:

$$\Theta^E = (G^E)_{N_{CrO_x}=0} - N_{CrO_x}(1-N_{CrO_x})\alpha + \int_0^{N_{CrO_x}} \alpha dN_{CrO_x} \qquad (21)$$

where, $(G^E)_{N_{CrO_x}=0}$ can be derived from the activities in the CaO-SiO$_2$ binary system, shown in Fig. 3[16]. Based on thermodynamic principles, excess chemical potential of CrO$_x$ can be expressed as:

$$\mu^E_{CrO_x} = \mu_{CrO_x} - \mu^{\circ}_{CrO_x} - RT\ln N_{CrO_x} \qquad (22)$$

Adding the item of $d(\frac{RT\ln(1-N_{CrO_x})}{y})$ to both sides of the Eq. 20, and combining Eq. 22, it then yields:

$$d\frac{\Theta^E + RT\ln(1-N_{CrO_x})}{y} = (\mu^E_{CaO} + RT\ln(1-N_{CrO_x}))d(\frac{1}{y}) - \frac{N_{CrO_x}}{y(1-N_{CrO_x})}d\mu_{CrO_x} \qquad (23)$$

Therefore,

$$\mu^E_{CaO} + RT\ln(1-N_{CrO_x}) = \left(\frac{\partial((\Theta^E + RT\ln(1-N_{CrO_x}))/y)}{\partial(1/y)}\right)_{\mu_{CrO_x}} \qquad (24)$$

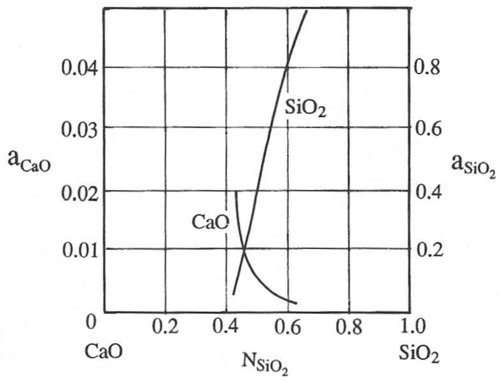

Fig. 3 Activities of CaO and SiO$_2$ for the CaO-SiO$_2$ binary system at 1600 °C, standard states - pure solid CaO and SiO$_2$[16].

In analogy to Eq. 24, the excess chemical potential of SiO$_2$ can be expressed as follows:

$$\mu^E_{SiO_2} + RT\ln(1-N_{CrO_x}) = \left(\frac{\partial((\Theta^E + RT\ln(1-N_{CrO_x}))/(1-y))}{\partial(1/(1-y))}\right)_{\mu_{CrO_x}} \qquad (25)$$

Consequently,

$$\mu^E_{CaO} = RT\ln\gamma_{CaO} \qquad (26)$$

$$\mu^E_{SiO_2} = RT\ln\gamma_{SiO_2} \qquad (27)$$

and,

$$a_{CaO} = \gamma_{CaO}\cdot N_{CaO} \qquad (28)$$

$$a_{SiO_2} = \gamma_{SiO_2}\cdot N_{SiO_2} \qquad (29)$$

In brief, activities of CrO$_x$ should be first derived from the activities of CrO and CrO$_{1.5}$ by Eq. 13, and α values can be calculated with Eq. 18. Then α-N_{CrO_x} functions are regressed into polynomials at constant y values, and adopted into Eq. 21 to make the integration, so that Θ^E values are acquired. In succession, by using Eq. 24 and Eq. 25, the excess chemical potentials of CaO and SiO$_2$ are calculated along the iso-activity lines of CrO$_x$ by application of logarithmic regressions and then by differentiation.

3. CALCULATION RESULTS

By adopting the Gibbs-Duhem equation and knowledge of phase diagram, the activity coefficients and activities of CaO and SiO_2 have been obtained. The results are shown in Figs. 4 to 7.

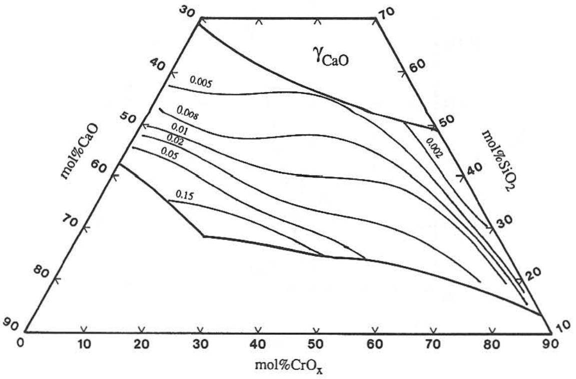

Fig. 4 Activity coefficients of CaO derived from activities of chromium oxides in the $CaO-SiO_2-CrO_x$ system at 1600 °C in equilibrium with metallic chromium, standard state - pure solid CaO.

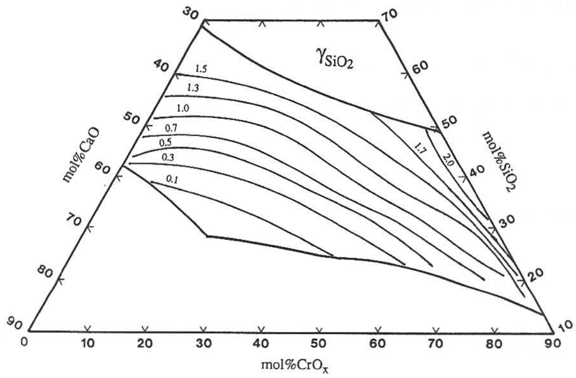

Fig. 5 Activity coefficients of SiO_2 derived from activities of chromium oxides in the $CaO-SiO_2-CrO_x$ system at 1600 °C in equilibrium with metallic chromium, standard state - pure solid SiO_2.

The standard states for activities of CaO and SiO_2 are pure solid oxides. From all these results, the effect of chromium oxide on the activity of CaO is not substantial. Increasing chromium oxide appears moderately decrease the activity of SiO_2. This is in accordance with the weakly basic or amphoteric character of chromium oxides.

The activity of CaO in the $CaO-SiO_2-CrO_x$ slag system has a strong negative deviation from the ideal solution. However, SiO_2 shows substantial positive deviation from ideal solution at higher SiO_2 contents. At lower SiO_2 contents, the activity of SiO_2 has a significant drop, so that SiO_2 has a negative deviation from ideal. In silica-rich melts, silica networks exist. Basic calcium oxide is bonded in the silica network with its oxygen ions, which phenomenon then results in low activity of CaO in the slag. In addition, the tendency to form compounds such as $CaO \cdot SiO_2$, $3CaO \cdot 2SiO_2$, $2CaO \cdot SiO_2$ etc., appears as lowered activities of both CaO and SiO_2 in slags. Herewith, both CaO and SiO_2 have negative deviations from ideal behavior at a slag basicity higher than unity in mole ratio.

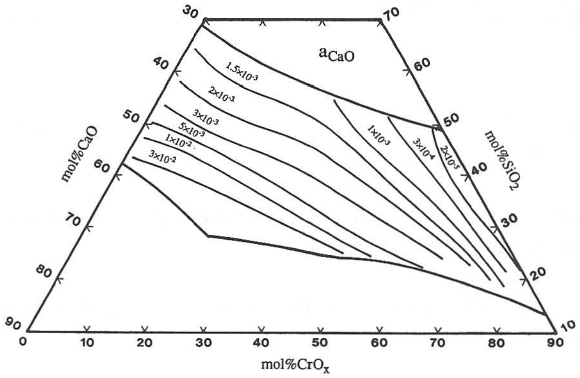

Fig. 6 Iso-activity contours for CaO derived from activities of chromium oxides in the $CaO-SiO_2-CrO_x$ system at 1600 °C in equilibrium with metallic chromium, standard state - pure solid CaO.

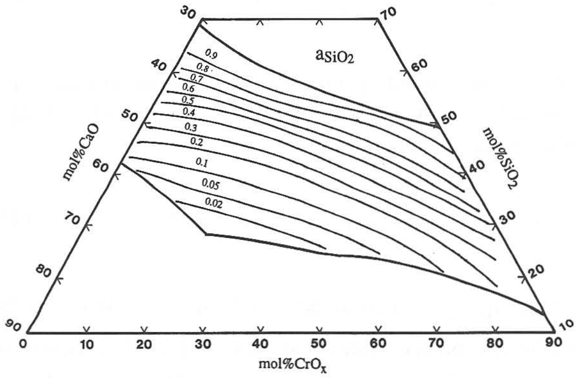

Fig. 7 Iso-activity contours for SiO_2 derived from activities of chromium oxides in the $CaO-SiO_2-CrO_x$ system at 1600 °C in equilibrium with metallic chromium, standard state - pure solid SiO_2.

4. COMPARISON WITH THE ACTIVITIES IN IRON OXIDE SYSTEM

The most commonly studied ternary slag systems containing CaO and SiO_2 include $CaO-SiO_2-FeO_x$, $CaO-SiO_2-MnO$, and $CaO-SiO_2-Al_2O_3$ systems. The activities of CaO and SiO_2 can either be measured by experiments or calculated with the Gibbs-Duhem equation under the condition that the activity of the third component is known. However, the activities of SiO_2 and CaO in the CaO-SiO_2-CrO_x slag system have not been found in the literature so far. A direct comparison of this slag system is not possible. However, the calculated results with application of the Gibbs-Duhem equation based on the measured activity values of CrO and $CrO_{1.5}$ can be qualitatively compared to other similar slag systems such as the system of CaO-SiO_2-FeO_x, so that the behavior of CaO and SiO_2 in different slag systems can be further examined.

CaO-SiO_2-FeO_x slag system is of central importance in steel refining processes. According to the literature, the CaO-SiO_2-FeO_x slag system has been investigated extensively due to the significance in the oxidizing capacity of the slag represented by the activity of "FeO" in slags. The activity values of FeO were determined from the equilibrium between the slag and the liquid iron, and the activities of lime and silica were obtained by integrating the Gibbs-Duhem equation. This slag system has much resemblance to the present CaO-SiO_2-CrO_x slag system due to the multi-valence nature of iron and chromium. Figs. 8 and 9 show the comparison of iso-activity contours of CaO and SiO_2 in both CaO-SiO_2-FeO_x[17] and CaO-SiO_2-CrO_x quasi-ternary systems calculated with Gibbs-Duhem equation at 1600 °C.

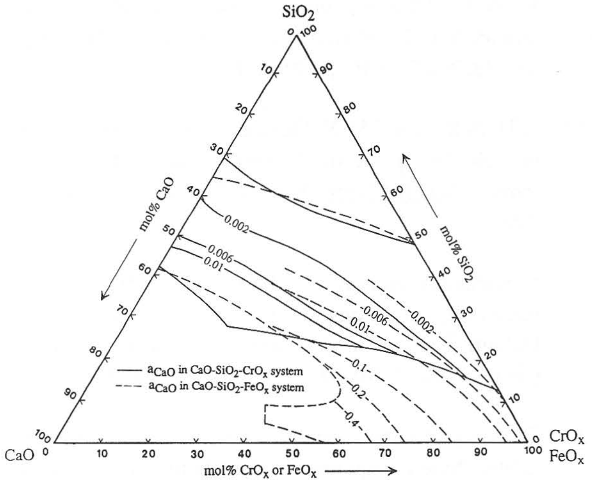

Fig. 8 Comparison of iso-activity contours of CaO in CaO-SiO_2-FeO_x and CaO-SiO_2-CrO_x slag systems at 1600 °C, standard state - pure solid CaO.

From these comparisons, one can see the similarity of the activities of CaO and SiO_2 in the two slag systems, especially for the activities of silica. The effect of FeO_x or CrO_x addition on the activities of both lime and silica is quite small. At the equivalent slag composition, the activity of CaO in the CaO-SiO_2-CrO_x system is lower than that in the CaO-SiO_2-FeO_x system. The activity of silica has quite similar behavior in both slag systems at lower slag basicity, while at higher slag basicity the activity of silica in CaO-SiO_2-CrO_x system is slightly lower than that in CaO-SiO_2-FeO_x system.

Owing to the more basic character of FeO than that of CrO, the increase of activity of calcium oxide by increasing iron oxides is more significant than by increasing chromium oxides. The different behavior is more evident in high FeO_x or CrO_x regions. The iso-activity contours for FeO_x in the slag system have more or less resemblance to that for CrO_x in the corresponding slag system, shown in Fig. 10.

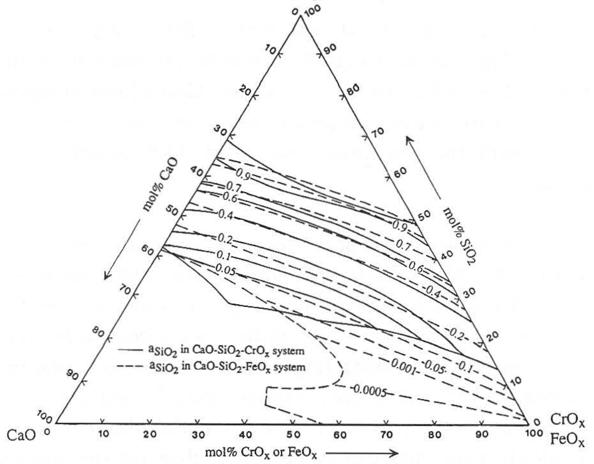

Fig. 9 Comparison of iso-activity contours of SiO_2 in CaO-SiO_2-FeO_x and CaO-SiO_2-CrO_x slag systems at 1600 °C, standard state - pure solid SiO_2.

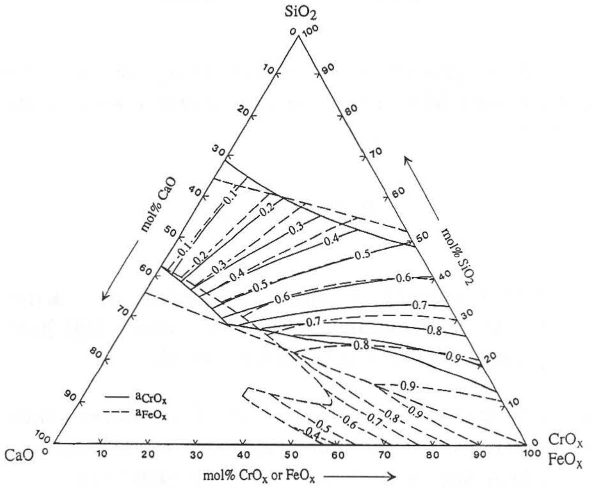

Fig. 10 Comparison of iso-activity contours of FeO_x and CrO_x in CaO-SiO_2-FeO_x and CaO-SiO_2-CrO_x slags at 1600 °C, standard state of FeO_x is pure FeO_x in equilibrium with metallic iron, and that of CrO_x is defined by Eq. 12.

Even though similar results or behavior have been observed, when introducing CrO_x, respectively FeO_x into CaO-SiO_2 slags, the comparison should be only qualitative. The great thermodynamic and physical difference in the FeO_x and CrO_x bearing slags must be recognized. This means, a.o., the different relative basicities of oxides FeO/CrO and $FeO_{1.5}/CrO_{1.5}$, respectively, the different fraction of the corresponding two- and three-valent oxides in the slags depending on the ambient equilibrium Po_2, the interaction of these oxides with the base slag components CaO and SiO_2, as well as the phase diagram, i.e., the liquidus area at the examined temperature.

5. SUMMARY

The activities of CaO and SiO_2 in the CaO-SiO_2-CrO-$CrO_{1.5}$ slag system in equilibrium with metallic chromium were calculated at 1600 °C with the Gibbs-Duhem equation. The iso-activity diagrams were obtained, and compared with the respective ones in CaO-SiO_2-FeO_x slag system.

The knowledge of activities of chromium oxides, lime and silica settles a basis for understanding reduction processes of chromium containing slags in AOD process for stainless steel production. According to the present investigation results, increasing slag basicity can promote the reduction of chromium from slag to metal. In addition, it is expected that the present results will enrich the thermodynamic database and supply necessary data for the studies on the slag systems.

ACKNOWLEDGEMENT

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