INFACON 7, Trondheim, Norway, June 1995
Eds.: Tuset, Tveit and Page
Publishers: FFF, Trondheim, Norway

THERMODYNAMICS OF SLAGS CONTAINING CHROMIUM OXIDES

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ABSTRACT

Thermodynamic properties of chromium containing slags play a very important role in both ferrochromium and stainless steelmaking processes. In the present study, the activities of chromium oxides in a quasi-binary SiO_2-CrO_x system in equilibrium with solid metallic chromium at 1600 °C were measured by the electromotive force (EMF) method, and the oxidation state of chromium in the slags was investigated by chemical analysis. The standard states of CrO and $CrO_{1.5}$ were the pure liquid and pure solid oxide, respectively. With increasing total chromium oxide content, the activities of CrO and $CrO_{1.5}$ increase, and the divalent chromium fraction decrease slightly.

The thermodynamic data on slags containing CaO, SiO_2, MgO, Al_2O_3, CrO and Cr_2O_3 components were assessed based on the regular solution model to mathematically describe the activities of chromium oxides in different chromium containing slags. A group of model parameters were obtained. The calculated activities of chromium oxides were quite comparable to those experimentally measured.

INTRODUCTION

The increasing demand for ferrochromium and stainless steel in the world has brought a great challenge to develop the production technology. As an essential goal, higher chromium yield throughout the process is strongly desirable. High chromium recovery will be beneficial in saving raw materials and energy as well as in reducing chromium pollution from chromium containing slags and wastes. From a thermodynamic standpoint, the reactions between slag and metal control the chromium recovery in the process. In order to evaluate the equilibrium distribution, to promote thermodynamic process modeling, and further to optimize the process for a higher recovery of chromium from the minerals, thermodynamic activities of chromium oxides in slags are required. In an earlier work by the authors[1,2], activities of chromium oxides were measured in several multi-component slag systems. However, the activities in the quasi-binary system SiO_2-CrO_x are not known though they are of great value especially for the theoretical evaluation and the slag modeling work. In this work, the activities of chromium oxides in SiO_2-CrO_x slags were

measured with EMF method at 1600 °C in equilibrium with metallic chromium, and the oxidation state of chromium in the slags was investigated based on chemical analysis. In addition, the mathematical formulas based on the Regular Solution Model have been applied to evaluate the activities of chromium oxides in different slags. The calculated results have been compared to the experimental data.

ACTIVITY MEASUREMENT IN SiO_2-CrO_x SYSTEM

Experimental System

The experimental system consisted of high temperature furnace, oxygen probe, argon purification line, as well as emf measuring and recording instruments. The details of the experimental apparatus and procedure were reported in the previous publications[1,2]. A chromium crucible, 28 mm i.d., 32 mm o.d. and 50 mm h, was charged with about 30 g of the slag and 16 g of Cr-Ag alloy, and heated to 1600 °C for equilibrium measurement in a $LaCrO_3$ resistance furnace. The use of Cr-Ag alloy can improve the electrical contact to the outer surface of the zirconia probe and make the equlibrium easier to reach.

The isostatically-pressed zirconia solid electrolyte crucibles were supplied by Nippon Kagaku Togyo Co. Ltd. These crucibles had dimensions of 5 mm i.d., 8 mm o.d. and 50 mm h. The solid electrolyte oxygen probe, Mo/Cr+Cr_2O_3/ZrO_2(MgO), consisted of a 9 mol% MgO stabilized zirconia crucible as an oxygen conductive electrolyte, and a mixture of 4 parts Cr and 1 part Cr_2O_3 by weight as a reference electrode. The probe was sealed with Al_2O_3 cement. A molybdenum wire of 0.5 mm in diameter was used as an electrical lead. Electrical contact to the outer surface of the zirconia probe was accomplished by a Cr-Ag alloy equilibrated with the slag, and a ZrO_2-Mo cermet rod welded to a Mo wire in order to reduce the reaction between the electrical lead and the slag/alloy melt.

The reaction system was protected by purified argon gas with a flow rate of 6 l/h. The purification train for argon consisted of KOH for removing CO_2, silica gel and phosphorus pentoxide for removing moisture, and sponge titanium chips kept at 850 °C in a resistance furnace for reducing oxygen partial pressure. In addition, the lower part of the measuring furnace was filled with sponge titanium in order to further lower the oxygen partial pressure in the argon atmosphere. The temperature of the system was controlled and measured by two PtRh30-PtRh6 thermocouples, respectively. The measuring thermocouple was calibrated referring to the melting points of copper, nickel and palladium. The overall error in the measurement and control of the temperature was estimated to be less than ± 4 K. The emf values were recorded with an accuracy of 0.017 mV.

Experimental Principles

The general galvanic cell in the present experiment was constructed as follows:

$$(+)\ Mo,(Cr+Cr_2O_3)\|ZrO_2(9MgO)\|(SiO_2\text{-}CrO_x),(Cr\text{-}Ag),(ZrO_2\text{-}Mo),Mo\ (-)$$

Considering the influence of electronic conduction in the electrolyte at high temperatures, the open-circuit electromotive force of the cell is given as follows according to the Nernst equation:

$$E = \frac{RT}{F} \ln \frac{Po_2(ref.)^{1/4} + Pe^{1/4}}{Po_2(slag)^{1/4} + Pe^{1/4}} \quad (1)$$

where, E, the electromotive force measured, V;

R, gas constant, 8.314 J/K·mole;

F, Faraday constant, 96500 J/V·mole;

T, temperature, K;

Po_2(slag), the oxygen partial pressure referring to the slag system to be measured, atm;

Po_2(ref.), the oxygen partial pressure referring to the Cr/Cr_2O_3 reference electrode, atm:

$\log Po_2(ref.) = 8.613 - 3.87 \times 10^4 / T$ [3]

Pe, the characteristic oxygen partial pressure at which the ionic and n-type electronic conductivities are equal[4], atm: $\log Pe = 20.40 - 6.45 \times 10^4 / T$ [5]

In the investigated slag system, chromium exists in both 2- and 3-valent oxidation states which can be marked as CrO and $CrO_{1.5}$, respectively. The equilibrium relations of chromium in the measuring system can be represented as follows:

$$Cr_{(s)} + \frac{1}{2}O_2 = CrO_{(slag)} \quad (2)$$

$$\Delta G_1^o = -RT \ln \frac{a_{CrO}}{a_{Cr} \cdot Po_2^{1/2}} \quad (3)$$

When pure liquid CrO and pure solid Cr are chosen as the standard states of activities of CrO and Cr respectively, the standard Gibbs energy of formation for liquid CrO is given by:

$$\Delta G_1^o = -79880 + 15.25 \text{ (cal)} [6] \quad (4)$$

ΔG_1^o was given only in the temperature range of 1665 - 1750 °C[6]. Since these were the only data available, they were adopted and extrapolated to the present experimental temperatures.

For $CrO_{1.5}$ in the slag, the equilibrium can be written as:

$$Cr_{(s)} + \frac{3}{4}O_2 = CrO_{1.5(slag)} \quad (5)$$

$$\Delta G_2^o = -RT \ln \frac{a_{CrO_{1.5}}}{a_{Cr} \cdot Po_2^{3/4}} \quad (6)$$

The standard Gibbs energy of formation for solid Cr_2O_3 was taken from the same literature as the oxygen partial pressure in the reference electrode in Eq. 1[3]. Since,

$$\Delta G_{CrO_{1.5}}^o = \frac{1}{2} \Delta G_{Cr_2O_3}^o \quad (7)$$

it follows, accordingly:

$$\Delta G_2^o = -132665 + 29.55T \text{ (cal)} \quad (8)$$

where a pure solid was chosen as the standard state for both Cr and $CrO_{1.5}$.

Since the melt was saturated with Cr crucible, the activity of chromium (a_{Cr}) was unity under the present experimental condition. According to Eq. 1, if the electromotive force is measured, the oxygen partial pressure Po_2 in the slag system can be calculated. Consequently, the activities of CrO and $CrO_{1.5}$ in the slags can be derived based on Eq. 2 through Eq. 8.

Slag samples were carefully removed from the Al_2O_3 sampling tubes, ground under protecting alcohol media, screened to -170 mesh, and stored in a vacuum container for slag analysis. The divalent chromium in the slags was analyzed by wet-chemical analysis[2]. The total chromium was determined both by the X-ray spectrometer and by the wet-chemical analysis, and the slag component SiO_2 was determined by the X-ray spectrometer.

Experimental Results and Discussion

In analogy with iron oxide containing slags, the chromium oxide slags have the same problem of varying oxidation state of chromium or non-stoichiometry of CrO_x in slags depending on temperature, slag basicity and even total chromium oxides content in the system equilibrated with metallic chromium[2]. In order to investigate the thermodynamic activities of chromium oxides in different slag systems, it is necessary to simultaneously clarify the oxidation state of chromium in the slag system. When $CrO_{1.5}$ is mixed with other slag-forming oxide components at high temperatures in contact with metallic chromium, the following equilibrium of chromium oxides can be expected in the slag-metal reaction system under the present experimental conditions:

$$2(CrO_{1.5}) + Cr = 3(CrO) \quad (9)$$

$$\Delta G_3^o = 25690 - 13.36T \text{ (cal)} \quad (10)$$

Chromium is therefore distributed in the slag as both divalent and trivalent states in different fractions, depending on the experimental conditions. In the present experimental conditions, the activity of metallic chromium is unity, at 1873K, the activities of chromium oxides have the relation of $a_{CrO} = 0.94 a_{CrO_{1.5}}^{2/3}$. For the calculation of slag composition, the total content of chromium oxides was expressed with CrO_x and calculated with the following formula:

$$\text{mol\%}CrO_x = \text{mol\%}CrO + \text{mol\%}CrO_{1.5} \quad (11)$$

The experimental results of the activities of CrO and $CrO_{1.5}$ and the oxidation state of chromium in slags in the SiO_2-CrO_x slag system are listed in TABLE 1, and the data are plotted in FIG.1 and FIG.2, respectively. The activities of SiO_2 were calculated by the Gibbs Duhem equation. The calculation method was described in the previous paper[2]. From these results, the activities of CrO and $CrO_{1.5}$ increase with increasing concentration of total chromium oxides, but the divalent chromium fraction decreases slightly. The explanation could be that the higher chromium oxide content will raise the system's oxygen partial pressure and may also slightly increase the slag

basicity. These conclusions are in agreement with the previous one[2]. The higher the slag basicity, the lower the divalent chromium fraction, and the higher the activities of chromium oxides.

TABLE 1. Experimental results in SiO_2-CrO_x system at 1873K in equilibrium with Cr.

mol%CrO	mol%$CrO_{1.5}$	mol%SiO_2	a_{CrO}	$a_{CrO1.5}$	a_{SiO2}	Cr^{2+}/T_{Cr}	$LogPo_2$
14.16	67.54	18.30	0.91	0.95	0.12	0.17	-12.06
8.55	75.93	15.52	0.94	1.00	0.06	0.10	-12.03
19.48	59.32	21.20	0.80	0.79	0.19	0.25	-12.17
11.99	61.31	26.70	0.72	0.67	0.37	0.16	-12.26
18.88	54.59	26.53	0.66	0.59	0.36	0.26	-12.33
19.46	45.01	35.53	0.54	0.43	0.66	0.30	-12.51
10.48	50.82	38.70	0.55	0.44	0.75	0.17	-12.50
13.16	63.37	23.47	0.77	0.74	0.26	0.17	-12.20
13.35	57.48	29.17	0.62	0.53	0.46	0.19	-12.39
7.23	55.74	37.03	0.60	0.51	0.70	0.11	-12.42
13.10	47.40	39.50	0.55	0.44	0.77	0.22	-12.50

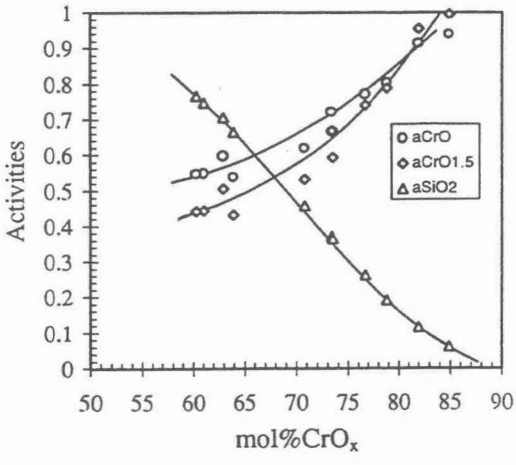

FIG.1 Activities of $CrO_{1.5}$, CrO and SiO_2 in the SiO_2-CrO_x quasi-binary system at 1873 K in equilibrium with metallic chromium; standard state - pure solid $CrO_{1.5}$ and pure liquid CrO

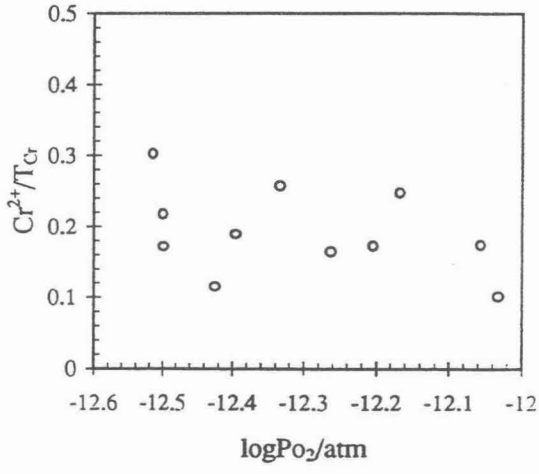

FIG.2 Divalent chromium fraction in the SiO_2-CrO_x quasi-binary system with oxygen partial pressure at 1873 K in equilibrium with metallic chromium

MATHEMATICAL EXPRESSION OF CHROMIUM OXIDES ACTIVITIES BASED ON REGULAR SOLUTION MODEL

Introduction to Regular Solution Model

The original regular solution model was proposed in 1961 by Lumsden[7]. In the melts with regular solution behavior, the molecular/ionic species such as SiO_2 or SiO_4^{4-} were taken as "dissociated" ionic species consisting of Si^{4+} cations and O^{2-} anions. It was assumed that the

cations are almost randomly distributed among a three dimensional matrix of oxygen anions (O^{2-}). The mixing energy of the system can be expressed in terms of the binary interaction energies between cations and the mole fractions of the cations. Due to the fact that there is not any restriction for choosing the standard state of the activity, in order to calculate the activities of species, the hypothetical pure liquid oxides with regular nature was taken as the standard states of chromium oxides. The conversion energy from this hypothetical regular solution standard state (R.S.) to the conventional standard states(pure solid or liquid) is necessary[8]. The general relations expressing the excess Gibbs energy of the multi-component solutions based on regular solution model are listed as follows:

$$RT\ln(\gamma_i)_{(R.S.)} = \sum_j \alpha_{ij} X_j^{\,2} + \sum_j \sum_k (\alpha_{ij} + \alpha_{ik} - \alpha_{jk}) X_j X_k \tag{12}$$

$$RT\ln(\gamma_i)_{(s/liq.)} = RT\ln(\gamma_i)_{(R.S.)} + \Delta G_{conv.} \tag{13}$$

here, $i \neq j$ or k, $\alpha_{ij} = \alpha_{ji}$, $\alpha_{ii} = \alpha_{jj} = \alpha_{kk} = 0$, and $\Delta G_{conv.}$ is the conversion factor associated with the change in the standard states. These parameters can be assessed by the experimental data.

Constraint of the Assessment: Equilibrium Relations of Cr^{2+} and Cr^{3+} in Slags

The distribution of divalent and trivalent chromium in the slags equilibrated with metallic chromium is very important in order to clarify the activities of chromium oxides in slags. The quantitative relation between the oxidation state of chromium and their activity coefficient can be derived from the thermodynamic relationship. By combining reactions (2) and (5), the distributions of divalent chromium and trivalent chromium can be obtained as follows:

$$CrO_{1.5}(s) = CrO(liq.) + \frac{1}{4}O_2 \tag{14}$$

$$\Delta G_4^o = -RT\ln\frac{a_{CrO}\cdot Po_2^{\,1/4}}{a_{CrO_{1.5}}} = 52785 - 14.31T\ (\text{cal}) \tag{15}$$

The divalent-trivalent chromium ratio, a constraint in the assessment, can be expressed as:

$$\ln\left(\frac{X_{CrO_{1.5}}}{X_{CrO}}\right) = \ln\left(\frac{\gamma_{CrO}}{\gamma_{CrO_{1.5}}}\right) + \frac{1}{4}\ln P_{O_2} + 26565/T - 7.199 \tag{16}$$

Assessment of the Model Parameters

The applicability of Regular Solution Model in various slag systems has been investigated for over thirty years by many researchers[9-18]. The investigated slag systems with respect to the Regular Solution Model contain the following components: Al_2O_3, CaO, CoO, Cu_2O, FeO, Fe_2O_3, MgO, MnO, NiO, P_2O_5, PbO, SiO_2, TiO_2 and ZnO. However, for the slags containing chromium oxides, there is not yet any publication found to describe the thermodynamic properties with the

regular solution model. In the present assessment work, multiple linear regression analysis has been used as a quick and convenient method for determining the model parameters. The assessment was processed from binary $CaO-SiO_2$ system to multi-component systems step by step. The experimental data in $CaO-SiO_2$ system were taken from the literature[19-22]. The activity data for chromium oxides were based on the experimental data obtained in both the present work and the authors' previous work[1,2] over $CrO-CrO_{1.5}-SiO_2$, $CrO-CrO_{1.5}-CaO-SiO_2$, $CrO-CrO_{1.5}-CaO-SiO_2-MgO$, $CrO-CrO_{1.5}-CaO-SiO_2-AlO_{1.5}$, and $CrO-CrO_{1.5}-CaO-SiO_2-MgO-AlO_{1.5}$ systems. A group of interaction energy parameters were optimized mathematically, and are given in TABLE 2. Due to lacking of thermodynamic data of chromium oxides complex, the physical significance of the model parameters can not be discussed in the present stage.

TABLE 2. Optimized interaction energy parameters, α_{ij}(J), between cations in $CrO-CrO_{1.5}-CaO-SiO_2-MgO-AlO_{1.5}$ slags. The data with star (*) were published by S. Ban-ya[23].

i\j	Cr^{2+}	Cr^{3+}	Ca^{2+}	Si^{4+}	Mg^{2+}	Al^{3+}
Cr^{2+}	---	32710	-6140	-60540	5520	-30285
Cr^{3+}	32710	---	44235	-48975	28085	-46210
Ca^{2+}	-6140	44235	---	-139100	-100420*	-154810*
Si^{4+}	-60540	-48975	-139100	---	-66940*	-127610*
Mg^{2+}	5520	28085	-100420*	-66940*	---	-71130*
Al^{3+}	-30285	-46210	-154810*	-127610*	-71130*	---

Because the chromium containing slags are not strictly regular solutions, the conversion energies for changing the standard state of activity coefficients from the hypothetical regular solution to the traditional pure solid or pure liquid were also optimized simultaneously by the experimental data. The obtained conversion Gibbs energies for CrO and $CrO_{1.5}$ were recorded in TABLE 3.

TABLE 3. Conversion Gibbs energy of CrO and $CrO_{1.5}$ in slags from the hypothetical pure liquid with the regular solution nature to the traditional pure solid or liquid standard state.

Reactions	Gibbs energy change (J)
CrO (liq.) = CrO (R.S.)	$\Delta G°$=77150-33.5T (J)
$CrO_{1.5}$ (s) = $CrO_{1.5}$ (R.S.)	$\Delta G°$=74967-37.5T (J)
$CrO_{1.5}$ (liq.) = $CrO_{1.5}$ (R.S.)	$\Delta G°$=10152-12.6T (J)
$CrO_{1.5}$ (s) = $CrO_{1.5}$ (liq.)	$\Delta G°$=64815-24.9T (J)

Activity of Silica in Lime-silica Binary System

Based on the activity data by Sharma and Richardson et al.[19-22], the activities of SiO_2 in $CaO-SiO_2$ binary system have been evaluated by the quadratic mathematical formula based on the regular solution model. The interaction energy parameters for CaO and SiO_2 were approximately derived, and the conversion Gibbs energy of silica from pure solid to hypothetical liquid with regular nature was also obtained: $SiO_2(s)=SiO_2(R.S.)$, $\Delta G°_{conv.}$=51346-13.88T (J). The calculated results based on the regular solution model and the experimental results are shown in Fig. 3. From these results, we can see that the data at 1823K show very good agreement with the calculated results based on the regular solution model. At 1773K, the agreement is also acceptable, but the

calculated curve is obviously deviating from the experimental data in the middle range of the concentration at 1873K.

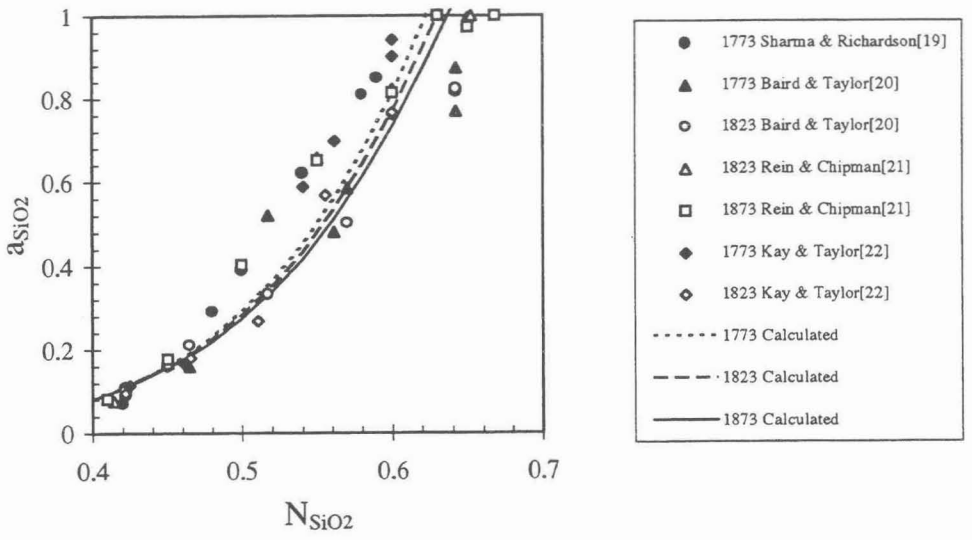

FIG.3 Comparison between measured and calculated activity in $CaO\text{-}SiO_2$ binary system

Activities of Chromium Oxides in Various Slags

The comparison between calculated activities and those experimentally measured in SiO_2-CrO-$CrO_{1.5}$, CaO-SiO_2-CrO-$CrO_{1.5}$, CaO-SiO_2-CrO-$CrO_{1.5}$-MgO, CaO-SiO_2-CrO-$CrO_{1.5}$-$AlO_{1.5}$ and CaO-SiO_2-CrO-$CrO_{1.5}$-MgO-$AlO_{1.5}$ systems are shown in FIG. 4.

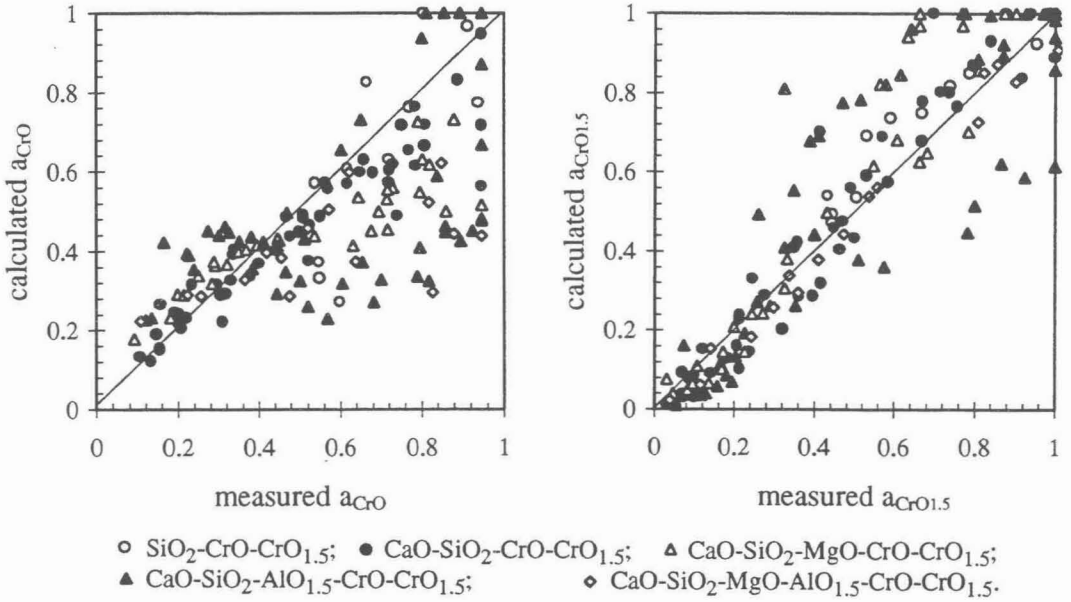

FIG.4 Calculated Activities of CrO and $CrO_{1.5}$ and Measured Values in Various Slag Systems Equilibrated with Metallic Chromium at 1873K.

As a combination result, this figure expresses the assessed activities of chromium oxides in all the related slag systems. The system containing Al_2O_3 had a bigger deviation from the regular solution behavior. Considering the existence of certain degree of scatter in the experimental data, the results give an acceptable fitness.

As a further illustration, the iso-activity lines of CrO and $CrO_{1.5}$ in the $CaO\text{-}SiO_2\text{-}CrO_x$ quasi-ternary system at equilibrium with pure metallic chromium as calculated by the model are compared with the experimentally measured data in FIG.5 and FIG.6, respectively. The dashed lines in the figures are the isothermal liquidus section of the slag system in contact with metallic chromium at 1873K[24]. The results show that the mathematical formalism based on the regular solution model can describe the $CaO\text{-}SiO_2\text{-}CrO_x$ slag system reasonably well in the liquidus area under the present experimental conditions.

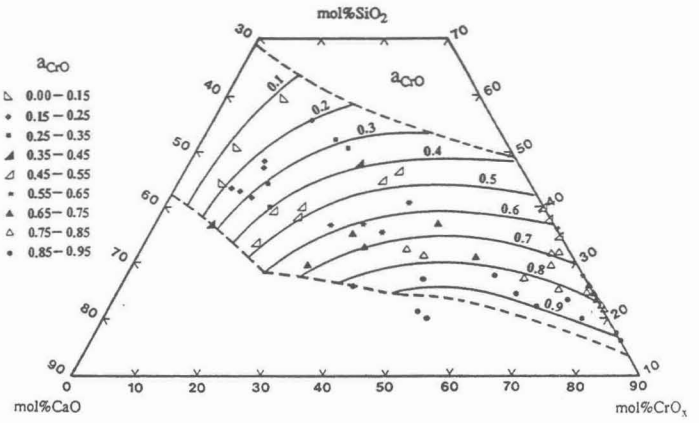

FIG.5 Comparison of calculated iso-activity curves (solid lines) for CrO to the experimental data[2] in $CaO\text{-}SiO_2\text{-}CrO\text{-}CrO_{1.5}$ slags in equilibrium with Cr at 1873K

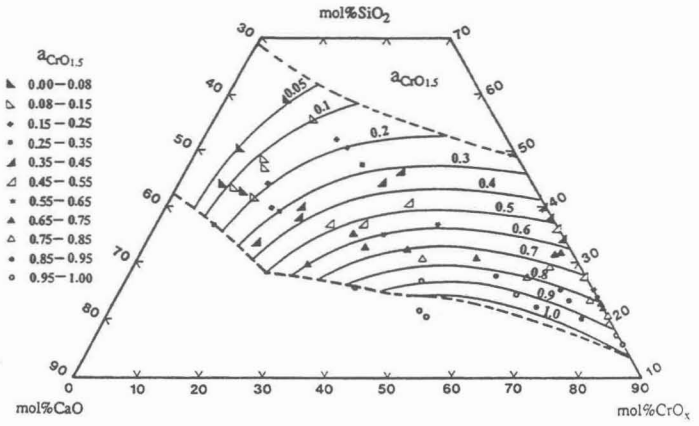

FIG.6 Comparison of calculated iso-activity curves (solid lines) for $CrO_{1.5}$ to the experimental data[2] in $CaO\text{-}SiO_2\text{-}CrO\text{-}CrO_{1.5}$ slags in equilibrium with Cr at 1873K

SUMMARY

The activities of CrO and $CrO_{1.5}$ in $SiO_2\text{-}CrO_x$ quasi-binary slags were measured by means of solid electrolyte oxygen probes at 1600°C in equilibrium with metallic chromium. Oxidation states of chromium in the slag phase were also determined by a wet-chemical analyzing method. The activity of SiO_2 was calculated by the Gibbs-Duhem equation. The results indicate that increasing the concentration of chromium oxides in the $SiO_2\text{-}CrO_x$ slag system, the activities of chromium oxides will increase, the activity of SiO_2 will decrease, and the divalent chromium fraction will be slightly lowered.

The validity of the regular slag model in chromium oxides containing slags has been investigated by applying the present experimental results. The following slag components have been considered: CrO, $CrO_{1.5}$, CaO, SiO_2, MgO, $AlO_{1.5}$. It was shown that the slags containing chromium oxides under the present experimental conditions can be approximately described by mathematical quadratic formalism based on the regular slag model.

REFERENCES

[1] Y. Xiao and L. Holappa, Determination of activities in slags containing chromium oxides. ISIJ Int., 1993, vol.33, p.66.

[2] Y. Xiao, Thermodynamic study on CrO_x containing slags, Dr. Tech. Thesis, Acta Polytechnica Scandinavica, Ch 210, Helsinki, 1993.

[3] E.T. Turkdogan, Physical Chemistry of High Temperature Technology, Academic Press, London, 1980, p.10.

[4] H. Schmalzried, Über Zirkondioxyd als Elektrolyt für elektrochemische Untersuchungen bei höheren Temperaturen. Zeitschrift für Elektrochemie, 1962, vol.66, p.572.

[5] M. Iwase, E. Ichise, M. Takeuchi, and T. Yamasaki, Measurements of the parameter, Pe, for the determinations of mixed ionic and N-type electronic conduction in commercial zirconia electrolytes. Trans. Jpn. Inst. Met., 1984, vol.25, p.43.

[6] N.Y. Toker, Equilibrium phase relations and thermodynamics for the systems chromium-oxygen and iron-chromium-oxygen in the temperature range from 1500 °C to 1825 °C. Ph.D thesis, The Pennsylvania State University, 1978.

[7] J. Lumsden, Physical Chemistry of Process Metallurgy; Part 1, edt. G.R. St Pierre, AIME, Interscience, New York, 1961, p.165.

[8] L.S. Darken, Thermodynamics of binary metallic solutions. Trans. Metall. Soc. AIME, 1967, vol.239, p.80.

[9] M. Fujita and S. Maruhashi, Equilibrium between FeO-MnO-SiO_2 slags and molten iron. Tetsu-to-Hagane, 1970, vol.56, p.830.

[10] I.C. Smith and H.B. Bell, Solubility of copper in silica-saturated iron silicate slag. Trans. IMM, Sect. C, 1971, vol.80, p.55.

[11] R. Altman and H.H. Kellogg, Thermodynamics of FeO-MnO-TiO_2 melts saturated with iron at 1475 °C. Trans. IMM, Sect. C, 1972, vol.81, p.163.

[12] E. Martin, I. Abdelkarim, I.D. Sommerville and H.B. Bell, Metal-Slag-Gas Reactions and Processes, Electrochem. Soc., Toronto, 1975, p.1.

[13] S. Ban-ya, A. Chiba and A. Hikosaka, Thermodynamics of Fe_tO-M_xO_y (M_xO_y = CaO, SiO_2, TiO_2 and Al_2O_3) binary melts saturated with solid iron. Australia-Japan Extractive Metallurgy Symposium, Austr. IMM, Sydney, 16-18 July, 1980, p.457.

[14] R.M. Grant, The derivation of thermodynamic properties of slags from slag fuming plant data. ibid., p.75.

[15] J. Shim and S. Ban-ya, The solubility of magnesia and ferric-ferrous equilibrium in liquid Fe_tO-SiO_2-CaO-MgO slags. Tetsu-to-Hagane, 1981, vol.67, p.1735.

[16] S. Ban-ya and M. Hino, Calculation of activities of the constituents in Fe_tO-(CaO+MgO)-(SiO_2+ P_2O_5) slags by regular solution model. Tetsu-to-Hagane, 1987, vol.73, p.476.

[17] R. Nagabayashi, M. Hino and S. Ban-ya, Mathematical expression of phosphorus distribution in steelmaking process by quadratic formalism. ISIJ Int., 1989, vol.29, p.140.

[18] S. Ban-ya, Y. Iguchi and H. Honda, Proceedings of International Symposium on the Physical Chemistry of Iron and Steelmaking, Can. IMM, Toronto, 1982, p.39.

[19] R.A. Sharma and F.D. Richardson, The solubility of calcium sulphide and activities in lime-silica melts. J. of the Iron and Steel Inst., 1962, vol. 200, p.373.

[20] J.D. Baird and J. Taylor, Reaction between silica and carbon and the activity of silica in slag solution. Trans. of the Faraday Soc., 1958, vol.54, p.526.

[21] R.H. Rein and J. Chipman, Activities in the liquid solution SiO_2-CaO-MgO-Al_2O_3 at 1600 °C. Trans. of the Metall. Soc. of AIME, vol.233, 1965, p.415.

[22] D.A.R. Kay and J. Taylor, Activities of silica in the lime+alumina+silica system. Trans. Faraday Soc., 1960, vol.56, p.1372.

[23] S. Ban-ya, Mathematical expression of slag-metal reactions in steelmaking process by quadratic formalism based on the regular solution model. ISIJ Int., 1993, vol.33, p.2.

[24] J.P.R. de Villiers and A. Muan, Liquidus-solidus phase relations in the system CaO-CrO-Cr_2O_3 -SiO_2. J. Am. Ceram. Soc., 1992, vol.75, p.1333.