Thermodynamics of NiO, CrO and $CrO_{1.5}$ in $CaO\text{-}SiO_2\text{-}CaF_2$ Slag.

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INTRODUCTION

$CaO\text{-}SiO_2\text{-}CaF_2$ slag has been used as a refining agent in the hot-metal treatment process because of its high dephosphorizing and desulfurizing ability. This system is interesting for as a slag chemistry study because it has a wide liquidus region at relatively low temperatures and experiments can be carried out in a wide basicity region. Therefore, it is important to determine the thermodynamic properties of transient metal oxides in this slag system and to compare them . Since studies on the behavior of nickel oxide [1-4] and chromium oxides [5-9] in iron and steelmaking slag is quite limited, the activity coefficients of NiO, CrO and $CrO_{1.5}$ were measured by chemical equilibration technique.

EXPERIMENTAL

A. Measurement of NiO Activity

The schematic drawing of the experimental set up is shown in Figure 1. The $CaO\text{-}SiO_2\text{-}CaF_2$ slag made from chemical reagents was equilibrated with nickel crucible (i.d.=37mm, h=38mm) under selected oxygen pressures. In several experiments NiO was added to the slag to approach equilibrium from the opposite direction. The PO_2 of the system was controlled by a mixture of CO and CO_2. Experimental temperatures were from 1523K to 1673K.

After equilibrium was attained (more than 8 hours), the crucible was quenched in water. The slag sample was crushed, ground to powder and analyzed. Nickel concentration in slag was determined by ICP. Calcium and silicon were analyzed by fluorescent X-rays (glass bead method) and an ionic electrode method was used for fluorine analysis.

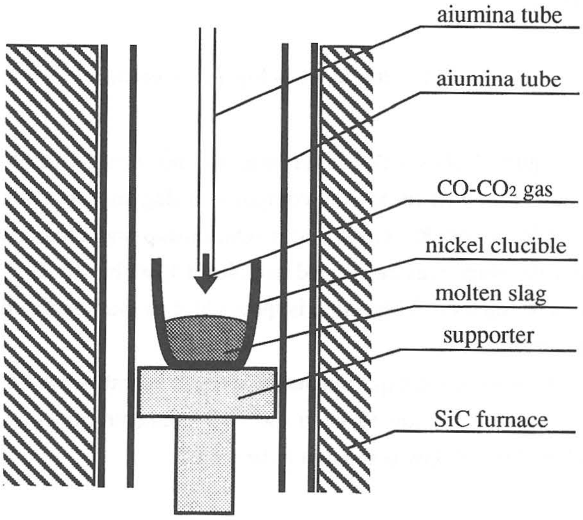


Fig.1. Schematic drawing of experimental set up.

B. Measurement of CrO and $CrO_{1.5}$ Activity Coefficients

The $CaO\text{-}SiO_2\text{-}CaF_2\text{-}Cr_2O_3$ slag made from chemical reagents was equilibrated with liquid silver in an iron crucible (i.d.=24mm, h=100mm) under a CO-CO_2 mixture gas flow for 12 hours. The equilibrium distribution ratio of chromium between slag and metal was obtained by analyzing chromium contents in slag and metal after the equilibration experiment. Since there exist two different species of chromium oxide in a slag CrO (Cr^{2+}) and $CrO_{1.5}$ (Cr^{3+}), the ratio of (XCr^{3+} / XCr^{2+}) was determined by conducting another experiment.

Ten grams of slag containing 0.8wt pct-Cr_2O_3 was kept in a pure nickel crucible and equilibrated with CO-CO_2 mixed gas. After the equilibration (8 hours), divalent chromium (Cr^{2+}) in the slag was determined by the titration method and the trivalent chromium (Cr^{3+}) was calculated by subtracting $\%Cr^{2+}$ from %T.Cr.

RESULTS AND DISCUSSION

A. Dependency of NiO Concentration on PO_2

The equilibrium reaction is equation (1) and its standard Gibbs free energy is given in equation (2):

$$Ni\,(s) + \frac{1}{2}\,O_2\,(g) = NiO\,(s) \qquad (1)$$

$$\Delta G^0 = -234357 + 85.23\,T \qquad (J/mol) \qquad [10] \qquad (2)$$

If Henry's law can be assumed for NiO, equation (3) is derived by modifying the equilibrium constant of reaction (1), K_1,

$$\log(X_{NiO}) = \log K_1 + \frac{1}{2}\log P_{O_2} + const. \qquad (3)$$

Figure 2 shows the equilibrium concentration (mole fraction) of NiO for a fixed composition slag as a function of PO2 at 1623K. Good linear relationship was obtained and the slope was calculated as 0.469 ± 0.04 by the least squares method. This value is quite close to that predicted by equation (3).

In most of the experiments the oxygen potential was set as 6.97×10^{-10} atm to keep the NiO concentration low, where Henry's law is thought to be valid.

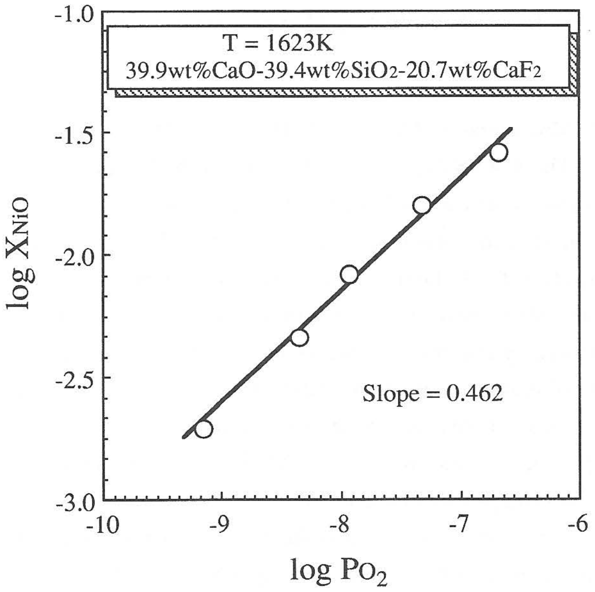


Fig.2. Dependency of an equilibrium NiO concentration on the partial pressure of oxygen at 1623K.

B. Composition Dependency of the Activity Coefficient of NiO

The activity coefficient of NiO, γNiO, was calculated from equation (4) using available thermochemical data.

$$\gamma_{NiO} = \frac{K_1\, a_{Ni}\, P_{O_2}^{1/2}}{X_{NiO}} \qquad (4)$$

Since a pure nickel crucible was used, the activity of nickel, a_{Ni}, is unity. The mole fraction of NiO, XNiO, was experimentally measured and PO2 is calculated from the mixing ratio of CO/CO2. Then γNiO could be obtained, where pure solid NiO was taken as a standard state.

Figure 3 shows the change of the activity coefficient of NiO with slag basicity at 1623K. γNiO seems to decrease as melt basicity increases, but to increase after the basicity becomes higher than about 2.0. This suggests an amphoteric behavior of CrO in this slag system. If the ionic reactions (5) and (6) are assumed, all the experimental results are explained consistently:

$$Ni + \frac{1}{2}O_2 = Ni^{2+} + O^{2-} \qquad (CaO/SiO2<2.0) \qquad (5)$$

$$Ni + \frac{1}{2}O_2 + O^{2-} = NiO_2^{2-} \qquad (CaO/SiO2>2.0) \qquad (6)$$

Figure 4 shows the effect of CaF2 concentration on the activity coefficient of NiO at 1623K. If CaO/SiO2 is fixed, γNiO seems to take a maximum with CaF2 concentration and the peak shifts to higher CaF2 concentration as the basicity increases.

The contour of the iso-activity coefficient of NiO is drawn in the CaO-SiO2-CaF2 ternary phase diagram in Figure 5. γNiO is approximately the only function of slag basicity and its peak is in the vicinity of CaO/SiO2=2.0.

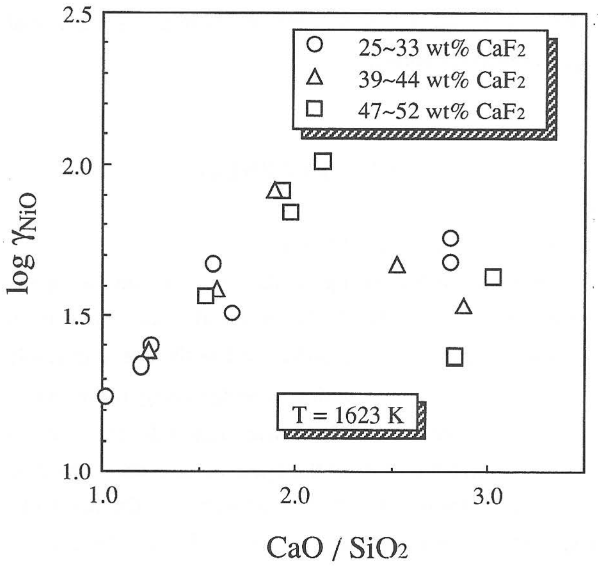


Fig.3. Effect of CaO/SiO2 on the activity coefficient of NiO.

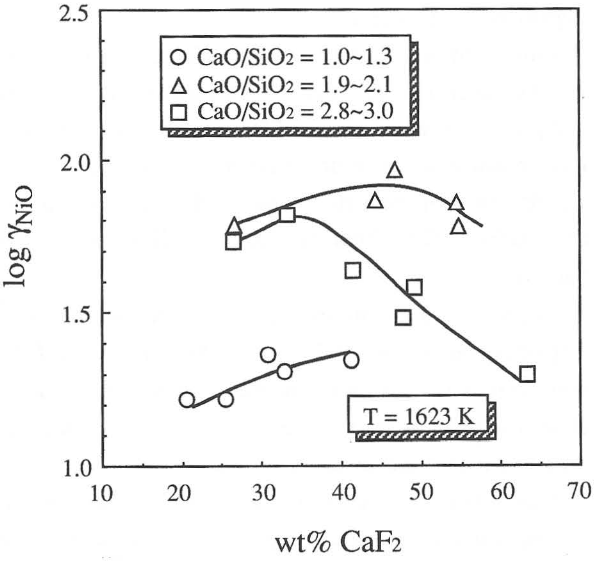


Fig.4. Effect of CaF2 concentration on the activity coefficient of NiO.

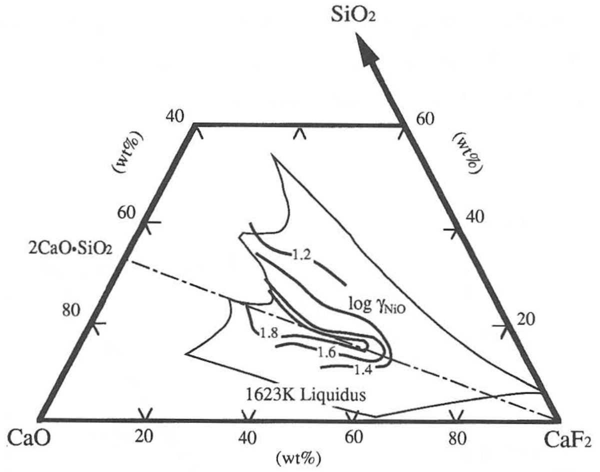


Fig.5. Contour of the iso-activity coefficient of NiO at 1623K for the CaO-SiO2-CaF2 ternary system.

C. Temperature Dependency of the Activity Coefficient of NiO

Figure 6 shows the temperature dependency of the activity coefficient of NiO. The logarithm of γ_{NiO} increases with the increase in 1/T. The enthalpy of dissolution of solid NiO into the slag (32.5CaO-26.1SiO2-41.4CaF2) is calculated as 257 (kJ/mol), which means that the reaction is very endothermic.

Figure 7 shows the comparison of present data with other slag systems. The data in four different systems were measured by E.B.Pretorius et al. [4]. The activity coefficients are plotted against NBO/Si, the slag basicity index proposed by Eugene, which is defined in equation (7):

$$NBO = \frac{2N_O - 4N_{Si}}{N_{Si}} \qquad (7)$$

where NSi is the number of silicon cations and NO is that of oxygen in a slag.

They seem to increase to NBO/Si and achieve maximum around NBO/Si = 4.0, which corresponds to the 2CaO-SiO2 composition, then they changes to decrease.

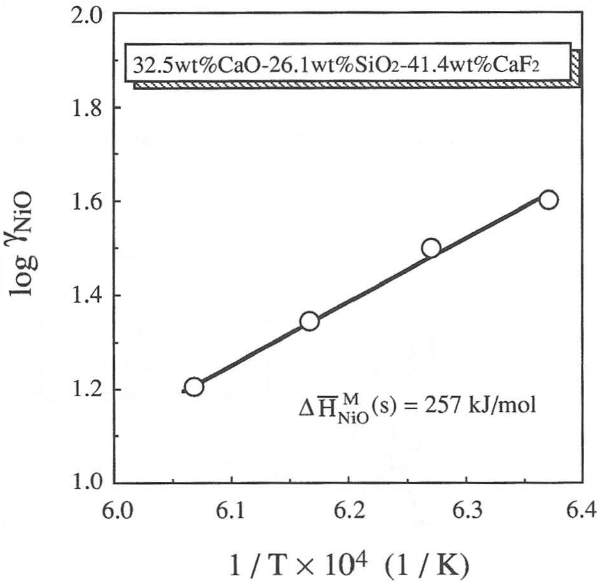


Fig.6. Temperature dependency of the activity coefficient of NiO.

D. Composition Dependency of the Activity Coefficient s of CrO and CrO1.5

The calculated γCrO and γCrO1.5 are plotted in Figure 8 as a function of the melt basicity. γCrO is found to decrease as melt basicity increases, but to increase after a basicity is higher than about 2.0, which proposes an amphoteric behavior of CrO in this slag system. It is the same behavior as NiO in this study. γCrO1.5 in contrast, monotonously decreases to maintain same tense with increasing basicity, which suggests the acidic behavior of CrO1.5 over the entire range of the composition measured in this study.

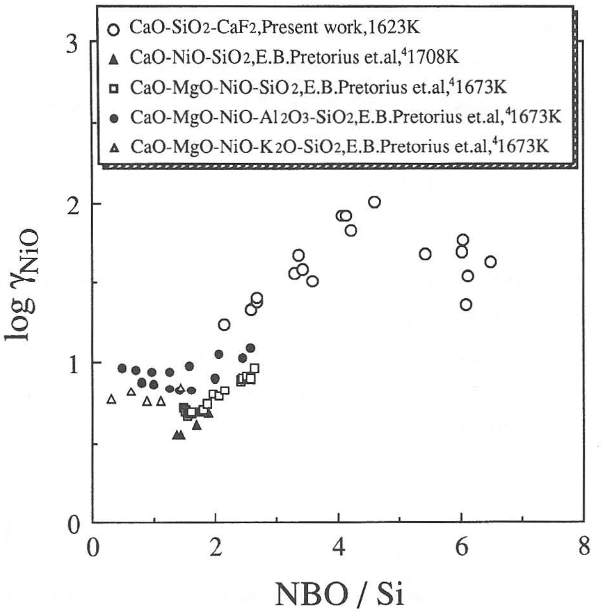


Fig.7. Comparison of the activity coefficients of NiO for various slag systems.

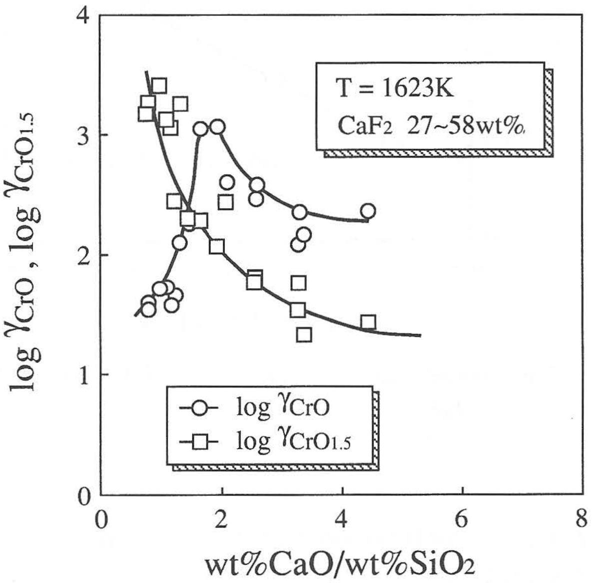


Fig.8. Effect of CaO/SiO2 on the activity coefficients of CrO and CrO1.5 at 1623K.

E. Practical Applications

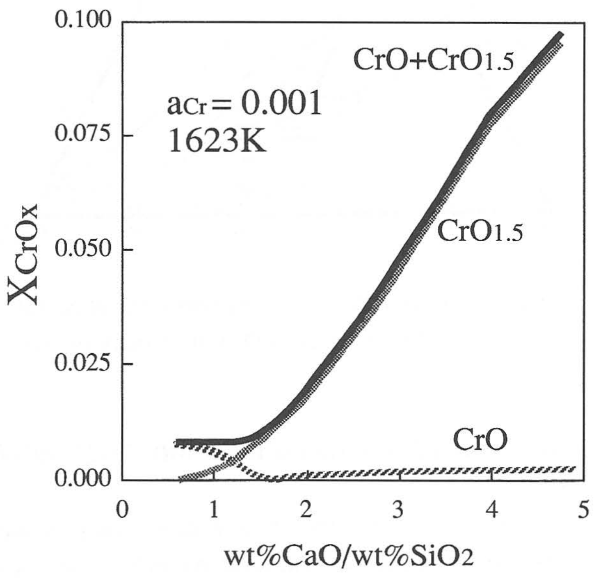
Since nickel is far nobler than chromium or iron, the concentration of NiO in slag should be quite low in a practical steelmaking processes unless its activity coefficient in slag is extremely low. This study showed that NiO in slag shows a positive deviation from ideality, therefore, the loss of nickel to a slag will be marginal even in the refining of high nickel containing iron alloy.

Since chromium takes two different valences in slag,however the behavior of chromium is relatively complex. If temperature and PO2 are fixed, for the slag-metal reaction, the equilibrium concentration of CrO in slag will decrease with basicity and then will reverse to increase at CaO/SiO2=2.0. That of $CrO_{1.5}$ will increase with basicity.

Figure 9 (a) shows the estimated CrOx concentrations in slag equilibrated with metal of aCr=0.001 at PO2=10×10^{-10} atm. This may correspond to the oxidation removal of chromium from metal. CrO1.5 is a predominant oxide and total chromium oxide increases with basicity.

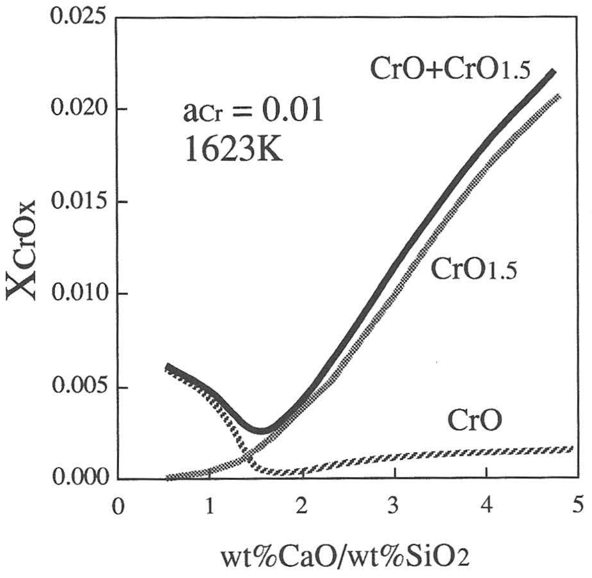
Figure 9 (b) shows the estimated CrOx concentrations in slag equilibrated with metal of aCr=0.01 at PO2=10×10^{-13} atm. This oxygen partial pressure corresponds to a hot-metal dephosphorization. Equilibrium concentration of total chromium oxide takes a minimum at CaO/SiO2=1.7.

Figure 9 (c) shows the estimated CrOx concentrations in slag equilibrated with metal of aCr=0.1 at PO2=10×10^{-15} atm. This corresponds to the reduction of chromium oxides in slag. The concentration of CrO increased and the valley near CaO/SiO2=2.0 became very sharp.

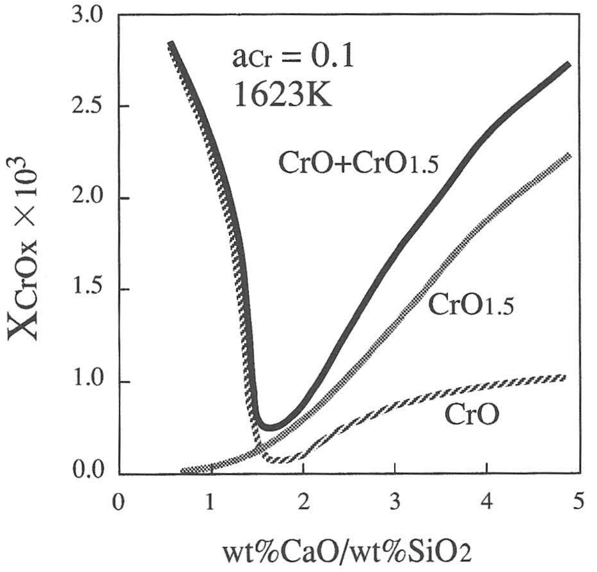


(a) PO2 = 1.0×10^{-10}

Fig.9. Estimated equilibrium concentration of chromium oxides for the CaO-SiO2-CaF2 system at 1623K under various oxygen partial pressures.



(b) PO2 = 6.2 x 10^{-13}



(c) PO2 = 1.0 x 10^{-15}

Fig.9. Estimated equilibrium concentration of chromium oxides for the CaO-SiO_2-CaF_2 system at 1623K under various oxygen partial pressures.

CONCLUSION

1. The activity coefficients of NiO, CrO and $CrO_{1.5}$ in a CaO-CaF_2-SiO_2 system at 1673K were measured by equilibrating molten slag with a CO-CO_2 gas mixture and Ni crucible or Ag-Cr alloy over a wide range of compositions.

2. The activity coefficient of NiO decreased with melt basicity , but changed to increase after basicity rose to above 2.0, which suggests the amphoteric behavior of NiO in this slag system.

3. The amphoteric behavior of CrO and the acidic behavior of $CrO_{1.5}$ were observed.

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