THERMODYNAMIC PREDICTION OF CHROMIUM REDUCTION BEHAVIOUR FROM SLAG

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Introduction

Cr is an important alloying element for high-quality steel materials. A near equilibrium state between the Cr-bearing slag and metal phase is involved in many pyrometallurgy processes. To enhance the Cr yield ratio, it is necessary to understand the thermodynamic behaviour of Cr in the metal and slag phases.

In this research, the reduction behaviour of Cr oxides from $CaO-SiO_2-Al_2O_3/MgO$-based slag when equilibrated with different metal melts was thermodynamically evaluated. The effects of influencing factors such as temperature, slag composition, and metal-melt components like Cr, C, and Si on the final chromium content in the slag (shortened as (%Cr) in this paper) were predicted by using the Equilib module of FactSage software.

Activity coefficient of Cr in Fe-Cr-C(-Si-Al) melts

In the FTstel database of FactSage software, Fe-based liquid metal with high solute concentrations was described using a simple substitutional solution approach based on the Redlich−Kister−Muggianu polynomial expression. By using of these, activity coefficient of Cr (γ_{Cr}, pure liquid substance as standard state) in the Fe-Cr-C(Si/Al) melts was predicted. The effects of carbon content ([%C]), silicon content ([%Si]), and aluminium content ([%Al]) in melts on γ_{Cr} were shown in fig1 (a), (b), (c), respectively.

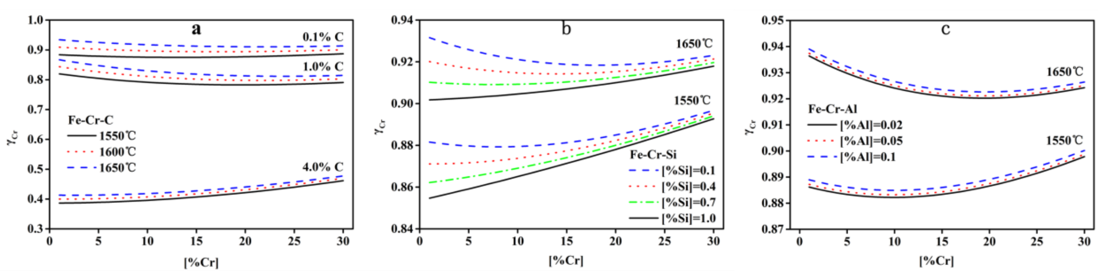

Figure 1: γ_{Cr} under different conditions

As can be seen from Figure 1a, γ_{Cr} greatly decreased with increasing [C]. When [%C] of the Fe-18%Cr-C melt increased from 0.1 to 4.0 at 1600˚C, the corresponding activity coefficient of Cr decreased from 0.88 to 0.37. Figure 1b suggested that the existence

of Si will reduce γ_{Cr}, especially under a low concentration of Cr. However, the opposite is the case in the Fe-Cr-Al melt (Figure 1c). Although the reducibility of Al was superior to that of Si, too much Al can dissolve in the melt and increase the activity coefficient of Cr and then, it is not conducive to the reduction of CrO_x in slag. Further, Figure 1 suggested that γ_{Cr} increased with increasing temperature.

Activity of CrO in CaO-SiO_2-MgO-Al_2O_3-3 wt%CrO system

To understand the distribution behaviour of Cr in slag and metal, a better understanding of its oxide state in slag is important. Cr exists in slag systems mainly in two forms: CrO and Cr_2O_3. Previous studies[1,2] showed that the Cr in CaO-SiO_2-based slag mainly exists in the form of CrO when it equilibrates with a metal melt under a strong reducing atmosphere. This research focused on the properties of CrO-bearing slags. The liquid areas of CaO-SiO_2-MgO/Al_2O_3-3%CrO were thermodynamically predicted by using the FactSage7.0 Phase Diagram module along with the isoactivity lines of CrO in the liquid slag phase under 1600˚C.

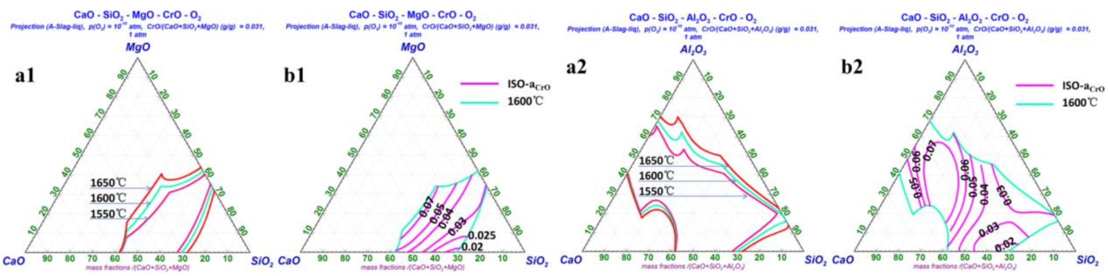

Figure 2: Liquid-phase projections of slags containing 3 wt%CrO and isoactivity lines of CrO

Liquid-phase projections of the CaO-SiO_2-MgO-3%CrO and CaO-SiO_2-Al_2O_3-3%CrO under $PO_2 = 10^{-5}$ Pa, and isoactivity lines of CrO at 1600˚C in these two systems were shown in Figure 2a1, a2, b1, and b2, respectively. It is obvious that the liquid-phase area became larger with an increase in temperature. However, the effect of temperature on the expansion of liquid-phase projection in the high-basicity region was limited when %MgO ≤ 8% (Figure 2a1). For example, the liquid-phase fractions at 1550˚C, 1600˚C, and 1650˚C were similar when the binary basicity (%CaO/%SiO_2) was 1.35. Figure 2b1 showed that the activity of CrO ($a_{CrO,}$ pure liquid substance as a standard state) in the range of 0.02 to 0.07 increased with an increase of basicity and (%MgO) of the slag, indicating that the slag with a high basic-oxide content is conducive to the reduction of CrO and CrO performs basic behaviour. The data in Figure 2a2 and Figure 2b2 revealed that an increase of Al_2O_3 in slag was helpful to increase the ratio of the liquid phase when the binary basicity, (%CaO/%SiO_2), was constant. The activity of CrO was between 0.02 to 0.07 and showed different rules in different liquid-phase regions at 1600˚C. The activity of CrO increased with an increase in basicity when SiO_2% > 20% and Al_2O_3 was constant (Figure 2b2). a_{CrO} increased

slightly with an increase of (%Al_2O_3) when R < 1.0. The effect of Al_2O_3 on a_{CrO} was very limited and can be ignored when R ≥ 1.0.

According to the above results, a constant slag component (CaO/SiO_2=1.4)-8%MgO-15%Al_2O_3-3%CrO (a_{CrO} equals to 0.07 approximately) was selected to discuss the influence of metal melts and temperature on final chromium content in the slag (%Cr) when equilibrating with different metal melts.

Thermodynamic prediction on reduction of CrO from CaO-SiO_2-Al_2O_3-MgO-3%CrO slag system

When the slags containing CrO reacted with the metal melt, the final slag (%Cr) was closely related to the type of metal melt and the temperature. In order to find the best reduction condition, the influence of these factors was evaluated.

Effect of [%C] on (%Cr)

Three different kinds of metal melts were selected to react with (CaO/SiO_2=1.4)-8%MgO-15%Al_2O_3-3%CrO slag in a ratio of 10:1 at 1600˚C. (%Cr) in final slag as functions of [%C] in Fe-C, Fe-5%Cr-C, and Fe-18%Cr-C melts were shown in Figure 3a, (b), and (c), respectively. As shown, in all three cases (%Cr) greatly decreased with increasing [%C]. However, these three melts showed quite different reducing ability. If the [%C] was maintained at 1.0% at equilibrium, the (%Cr) remained at 0.012%, 0.49%, and 2.22% when the slag reacted with Fe-C, Fe-5%Cr-C, and Fe-18%Cr-C, respectively; if the [%C] was further increased to 4%, the (%Cr) remained at 0.00042%, 0.02%, and 0.16%, respectively. This suggests that the metal melt containing a high [%C] and low [%Cr] had the greatest reducibility. It is extremely difficult to obtain as low as 0.1% of (%Cr) when CrO in slag is reduced by high [%Cr] and low [%C] melt.

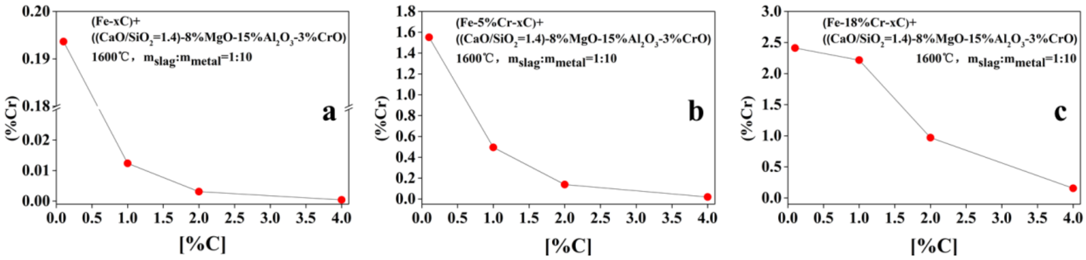

Figure 3: Effect of [%C] in different Cr-containing metal melts on (%Cr)

Effect of [%Si] and temperature on (%Cr)

The effect of [%Si] in high [%Cr] and low [%C] melts (Fe-18%Cr-1.0% C and Fe-18%Cr-0.1% C) on (%Cr) was shown in Figure 4. As shown, (%Cr) decreased significantly when [%Si] increased to be 0.3 and then decreased slowly as [%Si] further increased. It indicates that the introduction of Si into high [%Cr] low [%C] melts (Fe-18%Cr-(0.1, 1.0%)C) had a limited effect on the reduction of CrO in the slag. To achieve a low (%Cr), a high concentration of C in melt is necessary.

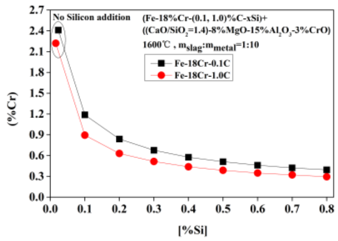

Figure 4: Influence of [%Si] on %Cr

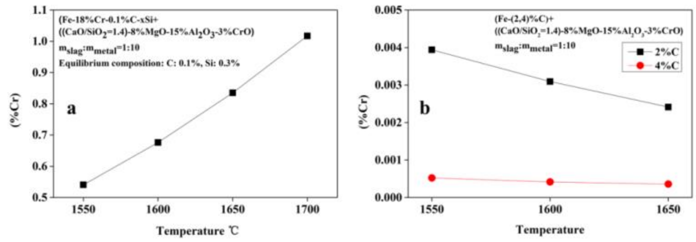

Figure 5: Influence of temperature on (%Cr)

Temperature dependencies of (%Cr) in (CaO/SiO_2=1.4)-8%MgO-15%Al_2O_3-3%CrO slag when it equilibrates with Fe-18%Cr-0.1%C-0.3%Si and Fe-(2%,4%)C were displayed in Figure 5a and 5b, respectively. As shown, opposite tendencies were observed in both cases: with an increase in temperature, (%Cr) increased if the metal was Fe-18%Cr-0.1%C-0.3%Si, while it decreased when the metal is set as Fe-(2%,4%)C. The reason could be explained by that in a metal phase with as high as 18% content of [%Cr] and low [%C], γ_{Cr} significantly increases with increasing temperatures and then Cr in metal was more easily to be oxidised into slag. However, in a metal melt with extremely low [%Cr] and high [%C] such as Fe-(2, 4)%C, the reduction of CrO from slag was greatly promoted due to the low activity of Cr in metal and that a high temperature is conducive to the reaction [C]+(CrO)→[Cr]+(CO).

Conclusions

1. γ_{Cr} decreases with Increasing [%C], increasing [%Si], and decreasing [%Al] in metal phase. And, γ_{Cr} increases with increasing temperature.
2. Activity of CrO in CaO-SiO_2-MgO(Al_2O_3)-3%CrO increases with increasing basicity (%CaO/%SiO_2). (%Al_2O_3) gives little influence on a_{CrO}, while it was helpful to increase the ratio of the liquid phase.
3. Thermodynamically, (%Cr) of slag greatly decreases as the [%C] of a metal increases. For the high [%Cr] and low [%C] metal melt, Si has limited reducibility for CrO in slag. Temperature has different effects on the reduction of CrO in slag and depends on the effective reductant in the melt.

Acknowledgement

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References

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