Viscosity of the CaO–CaF₂ System Containing Chromium Oxide

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Viscosity of the CaO–CaF₂–Cr₂O₃ system (15% < CaO < 25%, 75% < CaF₂ < 85%, 0% < Cr₂O₃ < 10%) was measured by the vibrational resonant amplitude method. From the experimental data on slags viscosity as a function of temperature, liquidus temperatures were determined. Viscosities and liquidus temperatures were found to increase with an increase in the chromium oxide concentration in the slag.

KEY WORDS: viscosity; slag; chromium oxide; liquidus temperature.

1. Introduction

The data on the viscosity and liquidus temperature of slags containing chromium oxides are of importance for the refining of steels containing chromium in the dephosphorization and desulfurization processes. Requirements for fluxes and slags used in the refining processes include high phosphate and sulfide capacities and low viscosity. These requirements are met by the CaO-based fluxes including CaO–CaF₂ flux which are widely used in the steelmaking practice. However, during treatment of steel containing chromium even under low oxidizing conditions, chromium inevitably oxidizes and transfers to the slag phase affecting slags properties. Thus, even small addition of chromium oxide to the binary CaO–CaF₂ significantly decreases its phosphate capacity.¹⁾ Chromium oxide has a similar effect on the sulfide capacity of the CaO-based slags.²⁾ In this study the effect of chromium oxide on the viscosity of the CaO–CaF₂ system and liquidus temperature is investigated.

2. Experimental

2.1. Viscosity and Liquidus Temperature of the CaO–CaF₂–Cr₂O₃ System

Viscosities of CaO–CaF₂–Cr₂O₃ slags were measured by the vibrational resonant amplitude method. This method is based on the fact that the amplitude of forced oscillations of a spindle immersed into the liquid is related to the viscosity of the liquid. The construction of the vibrational viscometer used was described by Arsentiev *et al.*³⁾ Samples for the experiments were prepared from CaO, CaF₂ and Cr₂O₃, calcined at 1050°C in air for 3.5 hr. Three master slags CaO(15wt%)–CaF₂(85 wt%), CaO(25wt%)–CaF₂(75wt%) and CaO(18wt%)–CaF₂(72wt%)–Cr₂O₃(10wt%) were smelted in the

graphite (first two slags) or molybdenum (third one) crucibles. Other samples, whose chemical compositions are given in **Table 1**, were melted from these master slags in the viscometer Tamman-type furnace with a graphite heater. The compositions of samples were chosen to cover the following field of compositions of the CaO–CaF₂–Cr₂O₃ system (wt%): 15% < CaO < 25%, 75% < CaF₂ < 85%, 0% < Cr₂O₃ < 10%.

Measurements were carried out under an argon atmosphere in the molybdenum crucible of 20 mm internal diameter and 35 mm height. The sample mass was approximately 30 g. A spindle was made from the molybdenum rod (300 mm length and 1.5 mm diameter). The depth of immersion was 10 mm. The temperature was measured using a tungsten–rhenium thermocouple and was varied from 1700°C down to 1300°C with rate 1–3°C/min. The viscometer was calibrated using liquids with known viscosity.

From the experimental data on slags viscosity as a function of temperature, liquidus temperatures were determined. For this, the viscosity function of temperature was expressed as

$$\mu = A \exp\left(\frac{E}{T}\right)$$

where A and E are constants. The liquidus temperature was indicated by the sharp change in the slope of the $\log \mu$ vs. $1/T$.

Table 1. Chemical composition (wt%) of samples for viscosity measurements.

No.	1	2	3	4	5	6	7	8	9	10
CaO	15	25	18	18.3	16	21.7	17	22.7	20.3	19.5
CaF ₂	85	75	72	81.7	80.7	78.3	76.3	74	73	77.3
Cr ₂ O ₃	—	—	10	—	9.3	—	6.7	3.3	6.7	3.3

3. Results and Discussion

The slag viscosity measured as a function of temperature is illustrated in Fig. 1. Liquidus temperature was determined from plots of $\log \mu$ against the reciprocal temperature, as shown in Fig. 2. Liquidus temperature and viscosity of the CaO–CaF₂–Cr₂O₃ system (CaO/CaF₂=1/4) as functions of Cr₂O₃ concentration are

Fig. 1. Variation of slag viscosity with temperature. For slag composition see Table 1.

Fig. 2. Illustration of the technique used to determine the liquidus temperature (T_L) for CaO–CaF₂ slag (18.3 wt% CaO, 81.7 wt% CaF₂) using the logarithm of viscosity plotted against reciprocal temperature.

presented in Fig. 3. The addition of chromium oxides to the CaO–CaF₂ system results in the increasing liquidus temperature and viscosity of this system.

Data on the viscosity of the ternary CaO–CaF₂–Cr₂O₃ system were not found in literature. Increase in viscosity with increasing Cr₂O₃ concentration was reported for CaO–CaF₂–Cr₂O₃–Al₂O₃ system⁴⁾ and for CaO–SiO₂–MgO–Cr₂O₃ system.⁵⁾

Mohanty and Kay⁶⁾ studied the activity of chromium oxide in the CaO–CaF₂–Cr₂O₃ system. It follows from their data that liquid phase extends to a much higher Cr₂O₃ concentration (to about 12% at 1500°C, Fig. 4) than was found in this work. Kanzaki *et al.*⁷⁾ studied the solubility of CaO·Cr₂O₃ in the CaO–CaF₂ system at 1500°C. Cr₂O₃ content in the CaO·Cr₂O₃-saturated slags varied from 0.80 to 1.28 wt% with increasing CaO content from 15.6 to 20.6%. This is close to the data obtained in the present work. It is seen from Fig. 4, where data on Cr₂O₃ solubility in the CaO–CaF₂–Cr₂O₃ system are plotted against CaO content at 1500, 1550 and 1600°C.

Fig. 3. Variation of (a) slag viscosity at 1600°C and (b) liquidus temperature with Cr₂O₃ concentration for (%CaO)/(%CaF₂)=1/4.

Fig. 4.

Solubility of chromium oxide in the $\text{CaO}-\text{CaF}_2-\text{Cr}_2\text{O}_3$ system as a function of CaO concentration at 1500°C (curves 1, 2 and 3), 1550°C (curve 4) and 1600°C (curve 5). Curve 1 was drawn using data⁶⁾; curve 2 was taken from Ref. 7); curves 3, 4 and 5: present study.

4. Conclusion

Measurements of viscosity of $\text{CaO}(15-25\%)-\text{CaF}_2(75-85\%)-\text{Cr}_2\text{O}_3(0-10\%)$ slags showed that Cr_2O_3 oxide increases the slag viscosity and liquidus temperature.

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