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Viscosities of Fe_nO-MgO-SiO_2 and Fe_nO-MgO-CaO-SiO_2 slags①

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Abstract: The viscosities of molten Fe_nO-MgO-SiO_2 and Fe_nO-MgO-CaO-SiO_2 semi-synthetic slags for nickel flash smelting were mearured in the temperature range of 1 200-1 450 ℃ by use of a rotational viscometer. The mass ratio of Fe to SiO_2 was fixed at 1.2, calcium oxide and magnesium oxide contents varied in the range of 2%-8% and 9%-12% (mass fraction), respectively. The results show that silicate anions become smaller by increasing CaO content, which results in the viscosity decrease of slag. In the case of addition of MgO the viscosity behaviour is complicated. When MgO content is less than 11%, the viscosity increases with the increase of MgO at all temperatures tested. However, when the MgO content is more than 11%, the viscosity decreases slightly for Fe_nO-MgO-CaO-SiO_2 system. At higher MgO contents, low-viscosity slags can be obtained by adding CaO. As for a given composition, the viscosity decreased with increasing temperature. The higher the temperature, the more MgO can be added before saturation. The effect of Fe_3O_4 on the viscosity is quite significant. The viscosity of slag increases to 300 mPa•s at 1 300 ℃ when Fe_3O_4 content varied from 2.84% to 9.53%. The viscosity values are expressed as the functions of temperature and composition. A comparison between Fe_nO-MgO-SiO_2 and Fe_nO-MgO-CaO-SiO_2 systems are also given.

Key words: nickel flash smelting; high-magnesium slag; viscosity
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1 INTRODUCTION

The viscosity of liquid slags is an important physical property. In nickel flash smelting processes, slags contain mainly iron oxides and silica in addition to MgO, CaO, Cr_2O_3 and Al_2O_3 as well as value metals and other impurities. Many investigations on the viscosity of iron silicate melt were already reported[1-4]. But only few studies are reported on the slags in the composition range occurring in nickel matte smelting. This may mainly be attributed to experimental difficulties in viscosity measurements for the high melting temperature of iron silicate slags with high MgO content. Ji et al[5] measured the viscosities of Fe_nO-MgO-SiO_2 slags in the temperature range of 1 335-1 758 ℃. The slag composition varied from 16.5% to 68.0% Fe_nO and from 8.0% to 31.55% MgO (mass fraction). Zhang et al[7] carried out viscosity determinations of nickel flash smelting slags. Zeng et al[7] and Tan et al[8] investigated the influence of the mass ratio of Fe to SiO_2 and the content of MgO or CaO in the slag on the viscosity under the range of slag contents: w(Fe)/w(SiO_2) 1.1-1.5, CaO 0%-9%, MgO 6%-10%. Ducret et al[9] recently measured the viscosities, liquidus temperature of FeO-Fe_2O_3-SiO_2-CaO-MgO slags saturated with iron for Fe/SiO_2 mass ratio from 1.3 to 1.8, CaO content up to 9%, MgO content up to 12%. However, industrial smelting operations are usually carried out at the ratio of Fe to SiO_2 of 1.2 and the temperature of 1 300-1 350 ℃, and viscosity data are needed in regions away from iron saturation. No previous measurement of the viscosities of Fe_nO-MgO-CaO-SiO_2 slag saturated with silica with the mass ratio of Fe to SiO_2 of 1.2 has been reported in the literature so far.

In this study, the viscosities were measured for the slags of Fe_nO-MgO-SiO_2 and Fe_nO-MgO-CaO-SiO_2 systems at the mass ratio of Fe to SiO_2 of 1.2 and different compositions using rotating cylinder method.

2 EXPERIMENTAL

An industrial slag sample obtained from a flash smelting of Cu-Ni concentrate was used as master slag. Fe and Fe_2O_3 mixed in appropriate stoichiometry as accessory slag. To determine the effect of slag composition on viscosity, CaO and MgO were added in required proportions. The chemicals used in the experiments were at least 99% (mass fraction) pure. Fe and Fe_2O_3 powders were dried at 100 ℃ for 24 h. CaO and MgO powders were calcined at 1 000 ℃ for 6 h in a muffle furnace. After viscosity measurements, slags were cooled quickly and analyzed chemically.

In order to investigate the effect of the individual oxide on the viscosity in Fe_nO-MgO-SiO_2 and semi-

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synthetic Fe_nO-MgO-CaO-SiO_2 slag systems, a constant Fe/SiO_2 mass ratio was maintained.

The rotating cylinder method was employed for viscosity measurements. An electric motor rotates a spindle carrying at the end a molybdenum cylindrical head(20 mm in length and 14 mm in diameter). The torque on the suspended rotating cylinder is measured by an electromechanical transducer.

The temperature was measured by a Pt/Pt-Rh10 thermocouple touching the crucible bottom from outside. The experimental temperature range was from 1 200 ℃ to 1 450 ℃.

Measurements of viscosity were performed using pure molybdenum crucible of 45 mm in diameter and 80 mm in height. A constant argon with (99.999%) flow rate of 1 L/min was maintained throughout the whole experiment. Powdered industrial slag was mixed with a given amount of various pure oxides and melted in a vertical electric furnace at 1 450 ℃ for 2 − 3 h. Then, the rotating cylinder was immersed in molten slag. The tip of the spindle was kept at 3.0 cm above the crucible base and the length of the shaft immersed in the melt was 1.0 cm. The equilibrium time was approximately 0.5 − 1.0 h at each temperature. The temperature was decreased in 30 − 50 ℃ decrements. After all measurements were completed, slag was reheated to 1 400 ℃ for withdraw of the spindle, and then slag was cooled down to room temperature.

3 RESULTS AND DISCUSSION

The viscosities of Fe_nO-MgO-SiO_2 system are shown in Fig. 1 as a function of temperature. As expected, the viscosity decreased with the increase of temperature. It was also found that the viscosities of the slag increased with the increase of MgO content. At 1 400 ℃, viscosity drops to a value similar to that of a magnesia-free iron silicate melt at 1 350 ℃[1]. The result is similar to the Ref. [5].

Fig. 2 shows the effect of CaO content on viscosity in Fe_nO-MgO-CaO-SiO_2 system. It can be seen that adding CaO decreases the viscosities of the slags. The results are in general agreement with that of the Refs. [7, 8, 10]. This effect is more marked for high SiO_2 melts because CaO modifies the Si—O bonds rather than the Fe—O[12]. On the other hand, increasing the CaO content the silicate structure is simplified due to the increase of oxygen and Ca^{2+} content, which results in the decrease of a viscosity. There is another explanation to this phenomena. When CaO breaks the —Si—O—Si— bridge, the Ca^{2+} cations raise the potential barriers of the silicate anions and therefore increase their contribution to slag viscosity[10].

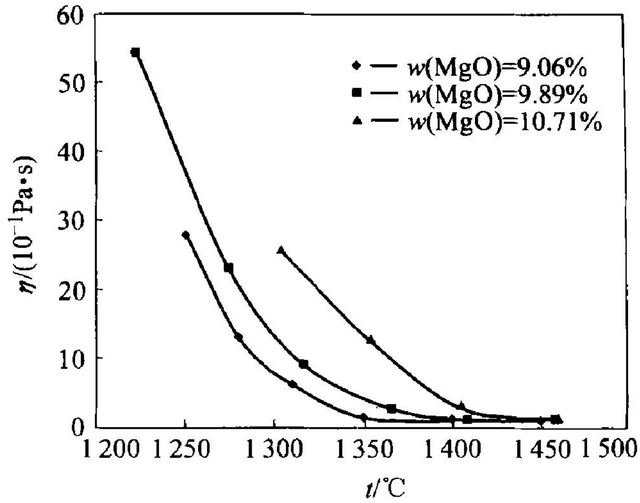

Fig. 1 Effect of MgO content on viscosity(η) of synthetic slags(w(Fe)/w(SiO_2) = 1.2)

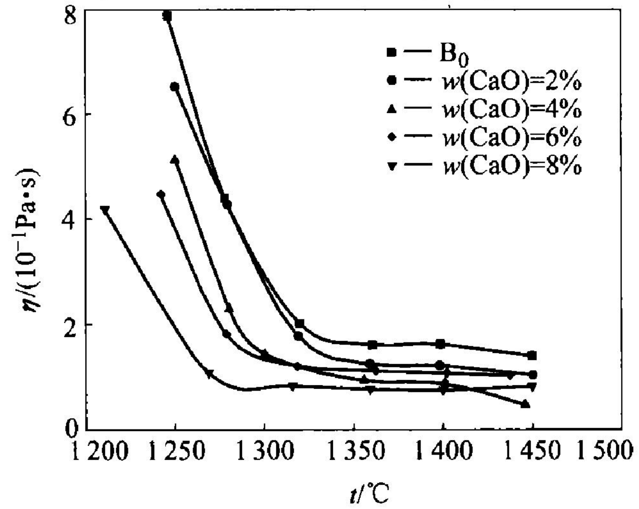

Fig. 2 Effect of CaO content on slag viscosity (B_0 represents a industrial slag; ω(MgO) = 11%; w(Fe)/w(SiO_2) = 1.2)

The effect of MgO content on the viscosity in Fe_nO-CaO-MgO-SiO_2 system at 1 300 ℃ is listed in Table 1. With the increase of MgO from 9% to 11%, viscosities increase at all temperatures tested. However, when the MgO content is more than 11%, the viscosity decreases slightly for the melts with different compositions. Additionally, the effect of MgO is dependent on the CaO content in slag. At high MgO content, the viscosity decreases with the addition of CaO.

As expected, temperature has the greatest effects on viscosity. For a given composition, the viscosity decreases with the increase of temperature and the higher the temperature, the more MgO can be added before saturation.

Williams et al[12] also studied Fe_nO-MgO-CaO-SiO_2 melts containing up to 8% MgO and 15% CaO, but some of the slags were contaminated with zirconia and some of the measurements were in the two phase regions. Previous measurements

Table 1 Measured viscosity values of Fe_nO-MgO-CaO-SiO_2 system

Melt	Composition/ %		Viscosity/ (mPa·s)
	ω(CaO)	ω(MgO)	
1	2.66	9.19	219.3
2	2.49	9.98	426.4
3	2.33	10.75	567.7
4	2.32	11.96	362.0
5	6.49	9.15	150.8
6	6.25	9.95	180.8
7	6.15	10.91	251.2
8	6.33	12.51	229.0
9	8.41	9.30	110.9
10	8.27	10.35	107.9
11	8.25	11.15	206.0
12	8.30	11.96	169.0

on the Fe_nO-MgO-CaO-SiO_2 system have been generally conducted at lower MgO content[6-9].

A comparison between Fe_nO-MgO-SiO_2 and Fe_nO-MgO-CaO-SiO_2 semi-synthetic slags suggests that the viscosity in Fe_nO-MgO-SiO_2 system is higher than that in Fe_nO-MgO-CaO-SiO_2 system mainly because the liquidus temperature of Fe-O-SiO_2 slag systems rises with the increasing of MgO content[7] and CaO tends to decrease the liquidus temperature[9]. The addition of CaO to a magnesia-iron silicate melt resulted in a displacement of the viscosity-temperature curve to a lower temperature range than that recorded for the lime-free melt (Figs. 1 and 2). At 1 300 ℃ the viscosity of the Fe_nO-MgO-CaO-SiO_2 melt is 200 mPa·s lower than that of the Fe_nO-MgO-SiO_2 melt at the equivalent temperature.

Fig. 3 illustrates the effect of Fe_3O_4 content on

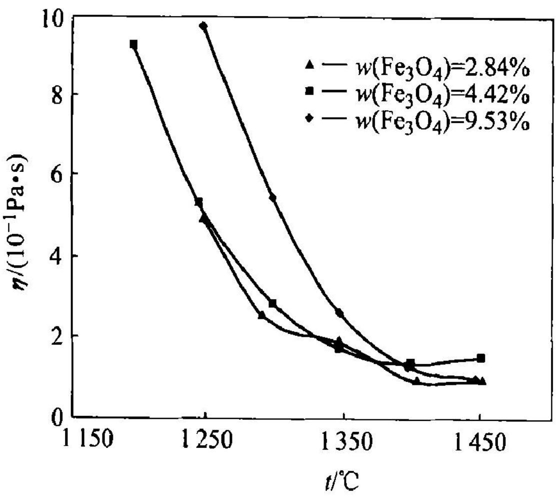

Fig. 3 Effect of Fe_3O_4 content on slag viscosity (ω(MgO) = 11%; ω(CaO) = 6%; w(Fe)/w(SiO_2) = 1.2)

the viscosity of slag in Fe_nO-MgO-CaO-SiO_2 system at different temperatures. The viscosity of slag increases to 300 mPa·s at 1 300 ℃ when Fe_3O_4 content varies from 2.84% to 9.53%. Apparently, viscosity increasing with the increase of Fe_3O_4 content can be explained by the formation of complex anion $Fe_xO_y^{z-}$ from Fe^{3+} cation and O^{2-} anion, and by magnetite crystallization at higher Fe_3O_4 content[13].

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