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Effect of Ce_2O_3 and $\text{CaO}/\text{Al}_2\text{O}_3$ on the Phase, Melting Temperature and Viscosity of $\text{CaO}-\text{Al}_2\text{O}_3$ -10 Mass% SiO_2 Based Slags

Abstract: The melting temperature and viscosity of $\text{CaO}-\text{Al}_2\text{O}_3$ -10 mass% SiO_2 based slag system with various concentrations of Ce_2O_3 have been studied using the melting point detector and the rotating crucible viscometer. And X-ray diffraction analysis has been used for phase identification. The results show that cerium is stable in Ce^{3+} state existing mainly as CeAlO_3 and $\text{Ce}_{4.67}(\text{SiO}_4)_3\text{O}$ phase in slags and CeAlO_3 phase appears in green color. The melting temperature gently decreases with Ce_2O_3 additions in 1.57 of $\text{CaO}/\text{Al}_2\text{O}_3$. Moreover, the melting temperature increases first and then decreases with the increasing of $\text{CaO}/\text{Al}_2\text{O}_3$ from 1.17 to 1.52 at 4.47 mass% Ce_2O_3 . In addition, at 1.57 of $\text{CaO}/\text{Al}_2\text{O}_3$, the viscosity increases at the beginning and then decreases with the increasing Ce_2O_3 content from 4.39 to 11.48 mass%. Furthermore, at 4.47 mass% Ce_2O_3 , the viscosity decreases at the first and then increases with the increasing $\text{CaO}/\text{Al}_2\text{O}_3$ from 1.17 to 1.52. Meanwhile, from the slopes of the Arrhenius relationship for viscosity, the activation energy range of viscous flow is from 179.07 to 433.70 kJ/mol. On the basis of these results, slag composition of 45.64 mass% CaO -39.02 mass% Al_2O_3 -10.73 mass% SiO_2 -3.83 mass% Ce_2O_3 is melting temperature of 1361 °C and viscosity of 0.398 Pa·s (1500 °C), which has superiority and is more suitable for the actual refining process.

Keywords: Ce_2O_3 , phase, melting temperature, viscosity

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1 Introduction

The fluidity characteristic of slag, which contains the melting temperature and viscosity, is important physico-

chemical property that determines the stability and productivity in the steelmaking. Its role in slag/metal separation, inclusion absorption and refining ability in the steelmaking cannot be overstated. Thus, a fundamental understanding of slag melting temperature, viscosity and essential factors that influence this property is significantly important to maximize productivity and ensuring optimum steelmaking operations.

Particularly, in Al-killed steel, Al_2O_3 is one of the main inclusions which deteriorate steel performance as well as result in the submerged entry nozzle clogging during continuous casting [1]. In the process of steel refining, these harmful Al_2O_3 inclusions can be removed by the absorption of the molten covering slag to reduce the harmfulness of alumina inclusions. Moreover, reducing the activity of Al_2O_3 and improve the fluidity properties of refining slag are verified as positive contributions to absorption of Al_2O_3 inclusions [2–4].

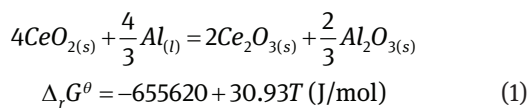
Previous research has shown that Ce_2O_3 addition decreases the activity of Al_2O_3 due to the formation of $\text{Ce}_2\text{O}_3\text{-Al}_2\text{O}_3$ compounds [5]. On this basis, the design of addition Ce_2O_3 to traditional $\text{CaO}-\text{Al}_2\text{O}_3\text{-SiO}_2$ refining slag would enhance the Al_2O_3 inclusions absorbability of refining slag. However, to our best knowledge, present researches have mainly focused on the effect of rare earth oxides on the mold flux of continuous casting [6, 7] and effect of rare earth oxides on the glass and ceramic [8, 9]. And only Shimizu et al. [10] has measured the viscosity and surface tension of $\text{RE}_2\text{O}_3\text{-MgO-SiO}_2$ (RE Y, Gd, Nd and La) melts at high temperature. Here, this paper intends to research on the effect of Ce_2O_3 and $\text{CaO}/\text{Al}_2\text{O}_3$ on the melting temperature and viscosity of $\text{CaO}-\text{Al}_2\text{O}_3$ -10 mass% SiO_2 based refining slags.

Therefore, in the present work, refining slag containing Ce_2O_3 has been prepared under laboratory conditions. And X-ray diffraction analysis has been used for the phase identification of slag. The effect of 5–15 mass% of the Ce_2O_3 addition in 1.8 of $\text{CaO}/\text{Al}_2\text{O}_3$ and 1.2–1.8 of the $\text{CaO}/\text{Al}_2\text{O}_3$ mass ratio with 5 mass% Ce_2O_3 on the melting temperature and viscosity of $\text{CaO}-\text{Al}_2\text{O}_3$ -10 mass% SiO_2 based refining slags have been investigated.

2 Experimental

2.1 Sample preparation

Since CeO₂ is stable in air and the laboratory supplying material, it should be converted to Ce₂O₃ for that Ce₂O₃ is stable in slag in the steelmaking process. The samples were synthesized using reagent grade chemicals of CaO, SiO₂, Al₂O₃, CeO₂ and Al. Aluminum is used as a reducer which reduces CeO₂ to Ce₂O₃. The reduction equation and related standard Gibbs free energy (1500~2000 K) is described in Eq. (1).



As listed in Table 1 column aim, the CaO/Al₂O₃ mass ratios were fixed at 1.2, 1.5 and 1.8, which are the typical of commercial refining slag used in LF refining, and the mass contents of Ce₂O₃ were fixed at 5, 10 and 15 mass% in order to investigate the effect of component Ce₂O₃ and the CaO/Al₂O₃ mass ratio on the physicochemical properties of slag. The samples were premelted at 1773 K (1500 °C) under 0.2 L/min of argon in a graphite crucible to reduce the CeO₂ and obtain a homogeneous slag sample of CaO-Al₂O₃-10 mass% SiO₂-Ce₂O₃. To remove excess moisture and oxygen in argon, the gas was passed through the columns of CaSO₄ and Mg turnings heated at 723 K (450 °C), respectively. After 2 hours, the homogenized samples were quenched, crushed and screened for the primary experiments. The chemical composition and phase of the slags were analyzed after the premelting using X-ray fluorescence (XRF) spectroscopy and X-ray diffraction (XRD), respectively. The composition of premelted CaO-Al₂O₃-SiO₂-Ce₂O₃ slags for melting temperature and viscosity measurements were listed in Table 1 column actual.

2.2 Melting temperature measurements

The melting temperature was measured with a hemispheric method by melting point detector. The details of the experimental apparatus for melting temperature measurements are shown in Fig. 1.

The slag sample was ground and screened for particles of size less than 0.075 mm, and made into Φ3 × 3 (mm³) cylindrical specimens. Then, the specimen was put on the spacer and put into the silicon carbide heating furnace. The heating rate was 5 °C/min and Pt was used as a substrate in argon protecting. The T~t curve was measured when the temperature was higher than 600 °C. The deformation of the specimen was observed through the screen, and the temperature was recorded as softening temperature, hemispherical temperature and flow temperature corresponds to the height of specimen decreased to 5/6, 1/2 and 1/3 of the original height. The system error was controlled less than 5 °C, and every specimen was measured by three times to ensure measurement accuracy. Moreover, the hemisphere temperature was taken as the melting temperature for ease of comparison [11].

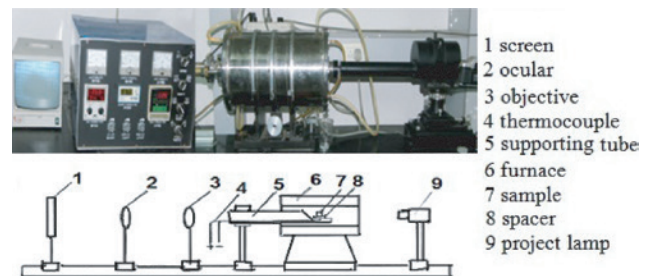


Fig. 1: Experimental apparatus for melting temperature measurements

Table 1: Aim and actual composition of CaO-Al₂O₃-SiO₂-Ce₂O₃ slags for melting temperature and viscosity measurements, mass%

No.	Aim					Actual (after premelting)					
	CaO	Al ₂ O ₃	SiO ₂	Ce ₂ O ₃	CaO/Al ₂ O ₃	CaO	Al ₂ O ₃	SiO ₂	Ce ₂ O ₃	Impurities	CaO/Al ₂ O ₃
1	54.64	30.36	10	5	1.8	50.40	33.12	11.09	4.39	1.00	1.52
2	51	34	10	5	1.5	48.45	34.09	11.64	5.19	0.63	1.42
3	46.36	38.64	10	5	1.2	45.64	39.02	10.73	3.83	0.78	1.17
4	51.43	28.57	10	10	1.8	50.23	30.99	9.74	8.66	0.38	1.62
5	48.21	26.79	10	15	1.8	46.25	29.50	10.92	11.48	1.85	1.57

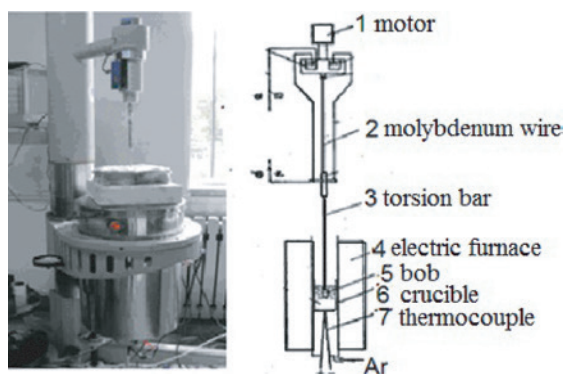


Fig. 2: Experimental apparatus for viscosity measurements

2.3 Viscosity measurements

The viscosity was measured using a rotating spindle connected to a calibrated field digital rheometer. The details of the experimental apparatus are shown in Fig. 2. The viscometer was calibrated using different silicone oil standards with viscosities of 0.985 to 4.85 Pa·s at 298 ± 1 K.

A 130 g slag sample premelted, quenched, crushed, ground and screened before was prepared and placed in the graphite crucible with inside dimension 80 mm in height and 40 mm in diameter. The crucible rested on an alumina platform and was surrounded by a cylindrical alumina muffle. A MoSi₂ electric furnace was used to heat and melt the samples to 1773 K (1500 °C) at a heating rate of 10 °C/min and held sufficiently for more than 30 min in an Ar gas atmosphere to achieve thermal equilibrium. At that time, it was stirred by the rotor at a speed of 200 r/min. Then each viscosity measurement was performed during the cooling cycle at a cooling rate of 5 °C/min under Ar atmosphere.

3 Results and discussion

The melting temperatures and viscosities of the $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{Ce}_2\text{O}_3$ slag system were measured. Five different slag compositions were chosen based on three different levels of Ce_2O_3 and three different levels of $\text{CaO}/\text{Al}_2\text{O}_3$ ratio. The range of Ce_2O_3 was varied between 5 and 15 mass% and the $\text{CaO}/\text{Al}_2\text{O}_3$ mass ratio between 1.2 and 1.8. The viscosity measurements were performed in a wide temperature range starting from 1650 to 1773 K. The slag post-experimental compositions used in the present investigation and measured after premelting are shown in Table 2. The melting temperature and viscosity values at 1773 K of the present investigation are also presented in the same table. It should be mentioned here that the chemical compositions of slags mentioned in the discussion are pre-experimental compositions only, as listed in Table 1 column actual.

3.1 Phase detection

The appearance and XRD analysis of the $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{Ce}_2\text{O}_3$ slag system were described in Fig. 3. As shown in

Table 2: The melting temperatures and viscosity of $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{Ce}_2\text{O}_3$ quaternary slags

No.	Melting temperature (°C)	Mean (°C)	η (Pa·s) at 1773 °K
1	1358/1360/1362	1360	0.416
2	1346/1347/1351	1348	0.363
3	1358/1362/1363	1361	0.398
4	1353/1356/1356	1355	0.497
5	1352/1353/1357	1354	0.289

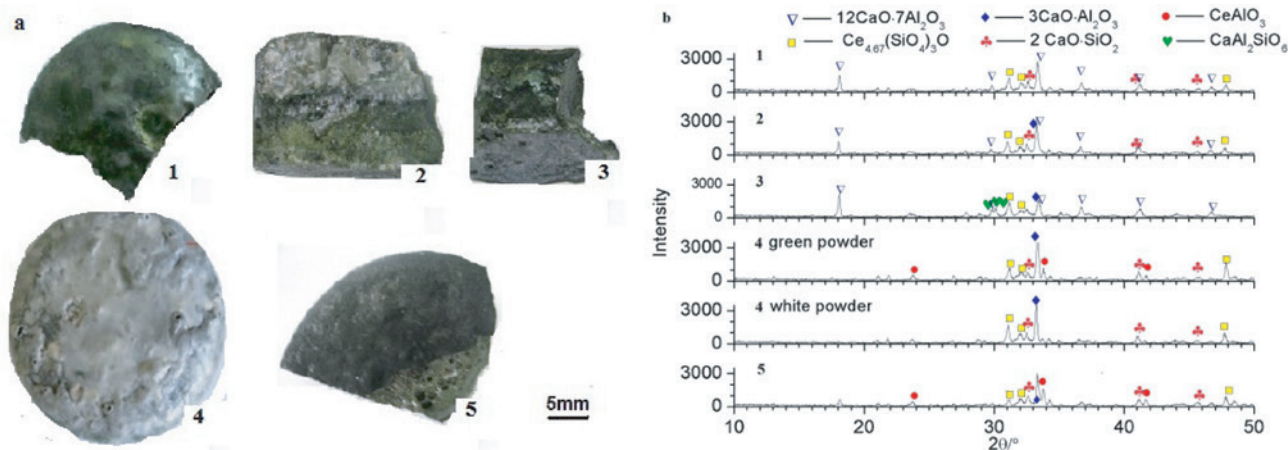


Fig. 3: (a) The appearance of $\text{CaO}-\text{Al}_2\text{O}_3-10 \text{ mass\% SiO}_2-\text{Ce}_2\text{O}_3$ slag system; (b) XRD analysis

Fig. 3(a), No. 1 sample has a large number of pores in surface, texture hard, well distributed in black green color and appears as green powder after ground. However, No. 2 sample has obvious layered phenomenon which the upper layer is gray in color and the bottom layer is green in color. As the same, No. 3 sample has well distribution feature alternate with black, green and gray and appears also as a green powder after ground. In addition, No. 4 sample appears main white and minor yellow in color on surface, and appears light green at the bottom layer which appears as a gray powder after ground. Moreover, No. 5 sample appears as green color and metallic luster on the surface, and has a large number of pores distributed of all sizes in surface.

As shown in Fig. 3(b) and compared the XRD analysis results, it can be observed that the main phases in the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-Ce}_2\text{O}_3$ slag were $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$, $3\text{CaO}\cdot \text{Al}_2\text{O}_3$, CeAlO_3 , $\text{Ce}_{4.67}(\text{SiO}_4)_3\text{O}$, $2\text{CaO}\cdot \text{SiO}_2$ and $\text{CaAl}_2\text{SiO}_6$ and the relative content of each phase is changing with the altering of the Ce_2O_3 content and $\text{CaO}/\text{Al}_2\text{O}_3$ mass ratio. For No. 1, 2 and 3 samples, which fix the Ce_2O_3 content at 4.47 mass%, it can be noted that the relative intensities of $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ and $2\text{CaO}\cdot \text{SiO}_2$ were decreasing and $\text{CaAl}_2\text{SiO}_6$ phase is adding in No. 3 sample with $\text{CaO}/\text{Al}_2\text{O}_3$ mass ratio decreasing from 1.52 to 1.17. Similarly, for No. 1, 4 and 5 samples, which fix the $\text{CaO}/\text{Al}_2\text{O}_3$ mass ratio at 1.57, it can be noticed that the relative intensities of CeAlO_3 and $\text{Ce}_{4.67}(\text{SiO}_4)_3\text{O}$ were increasing and there is adding $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ phase in No. 1 with Ce_2O_3 content increasing from 4.39 to 11.48 mass%. In addition, the different colors of layered slag were detected separately and the CeAlO_3 phase is only found in green color layer. In summary, cerium is stable in Ce^{3+} state in slags and the tetravalent cerium wasn't detected in all of slag samples.

3.2 Melting temperature

3.2.1 Results of melting temperature measurement

The results of the melting temperature measurement are presented in Table 2. The melting temperature range of $\text{CaO-Al}_2\text{O}_3\text{-10 mass% SiO}_2\text{-Ce}_2\text{O}_3$ slag measured is from 1346°C to 1363°C , which means the slag can melt homogeneously at the steelmaking temperature, and the mean melting temperatures of No. 1–5 samples are 1360°C , 1348°C , 1361°C , 1355°C and 1354°C , respectively.

3.2.2 Effect of Ce_2O_3 and $\text{CaO}/\text{Al}_2\text{O}_3$ on melting temperature

The effect of different Ce_2O_3 content and $\text{CaO}/\text{Al}_2\text{O}_3$ mass ratio on melting temperature of $\text{CaO-Al}_2\text{O}_3\text{-10 mass% SiO}_2$ based slag were shown in Fig. 4. Fig. 4(a) shows the melting temperature of $\text{CaO-Al}_2\text{O}_3\text{-10 mass% SiO}_2$ based slag with increasing Ce_2O_3 additions when $\text{CaO}/\text{Al}_2\text{O}_3$ mass ratio fixed at 1.57. Moreover, it can be seen from Fig. 4(a) that the addition of Ce_2O_3 decreases melting temperature slightly in the content range from 4.39 to 11.48 mass%. On the basis of the XRD analyses, the causes of the melting temperature slightly decreasing may be due to that the decrease of $2\text{CaO}\cdot \text{SiO}_2$ phase or the increase of $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ phase as increasing Ce_2O_3 content can decrease the melting temperature, but the increase of CeAlO_3 phase as increasing Ce_2O_3 content can increase the melting temperature. Those comprehensive factors lead to the appearance of melting temperature slightly decreasing. As the same, Fig. 4(b) shows the melting temperature of $\text{CaO-Al}_2\text{O}_3\text{-10 mass% SiO}_2$ based slag with the increasing $\text{CaO}/$

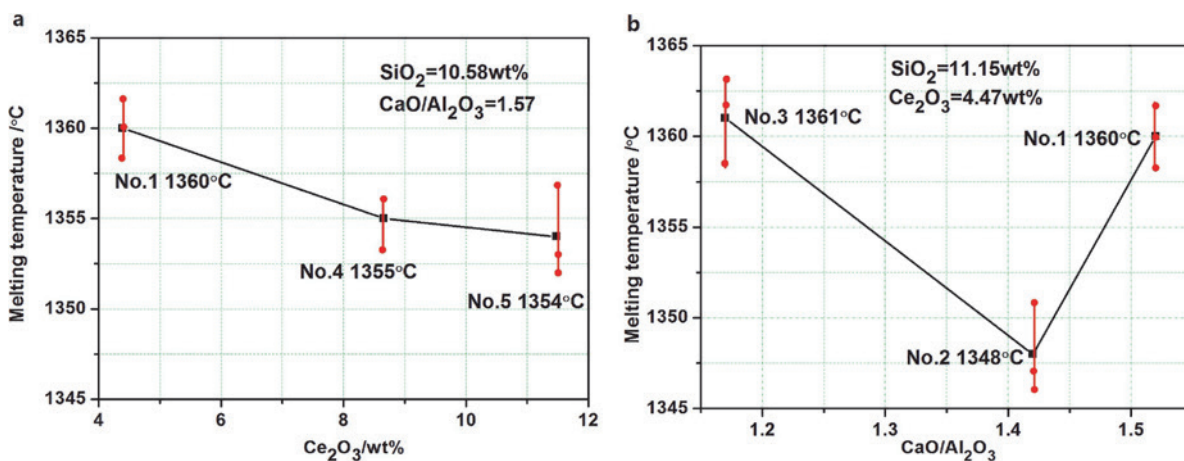


Fig. 4: The effect of $\text{CaO}/\text{Al}_2\text{O}_3$ and Ce_2O_3 content on melting temperature of $\text{CaO-Al}_2\text{O}_3\text{-10 mass% SiO}_2\text{-Ce}_2\text{O}_3$ slag system

Al_2O_3 mass ratio when Ce_2O_3 mass% fixed at 4.47. In addition, it can be noted from Fig. 4(b) that the melting temperature decreases first and then increases with increasing of $\text{CaO}/\text{Al}_2\text{O}_3$ mass ratio from 1.17 to 1.52 at 4.47 mass% Ce_2O_3 . Based on the XRD analyses, the major reasons for this may be due to that a higher value of the $\text{CaO}/\text{Al}_2\text{O}_3$ mass ratio would promote the percentage of $2\text{CaO}\cdot\text{SiO}_2$ phase, while the smaller one may facilitate the formation of CaAlO_3 phase (melting point is about 2300 K [12]), both of which are compounds with high melting temperature, resulting in the increase of melting temperatures.

A comparison among different additions of Ce_2O_3 and $\text{CaO}/\text{Al}_2\text{O}_3$ reveals that Ce_2O_3 to be more effective at decreasing the melting temperature at high content of Ce_2O_3 and low $\text{CaO}/\text{Al}_2\text{O}_3$ mass ratio. In general, $\text{CaO}\text{-Al}_2\text{O}_3\text{-10 mass% SiO}_2\text{-Ce}_2\text{O}_3$ slag system with proper composition could have relatively low melting temperature and No. 2 sample slag with a composition of 48.45 mass% CaO -34.09 mass% Al_2O_3 -11.64 mass% SiO_2 -5.19 mass% Ce_2O_3 has the lowest melting temperature value of 1348 °C.

3.3 Viscosity of $\text{CaO}\text{-Al}_2\text{O}_3\text{-10 mass% SiO}_2\text{-Ce}_2\text{O}_3$ slag

3.3.1 Results of viscosity measurement

The viscosity of the $\text{CaO}\text{-Al}_2\text{O}_3\text{-10 mass% SiO}_2\text{-Ce}_2\text{O}_3$ quaternary slag at 1773 K (1500 °C) is also present in Table 2. The viscosity range of $\text{CaO}\text{-Al}_2\text{O}_3\text{-10 mass% SiO}_2\text{-Ce}_2\text{O}_3$ slag measured in this experiment is 0.289 to 0.497 Pa·s and the viscosities of No. 1–5 samples are 0.416 Pa·s, 0.363 Pa·s, 0.398 Pa·s, 0.497 Pa·s and 0.289 Pa·s, respectively. In addition, the conventional $\text{CaO}\text{-Al}_2\text{O}_3\text{-SiO}_2\text{-MgO}$ refining

slag has the same viscosity range of 0.3 to 0.5 Pa·s. Therefore, this comparison reveals that refining slag remains good fluidity properties with the appropriate addition of Ce_2O_3 at high temperature.

3.3.2 Effect of Ce_2O_3 and $\text{CaO}/\text{Al}_2\text{O}_3$ on viscosity

The effect of different Ce_2O_3 content and $\text{CaO}/\text{Al}_2\text{O}_3$ mass ratio on viscosity of $\text{CaO}\text{-Al}_2\text{O}_3\text{-10 mass% SiO}_2$ based slag at 1773 K were shown in Fig. 5. Fig. 5(a) shows the viscosity of $\text{CaO}\text{-Al}_2\text{O}_3\text{-10 mass% SiO}_2$ based slag with increasing Ce_2O_3 additions with a $\text{CaO}/\text{Al}_2\text{O}_3$ mass ratio fixed at 1.57. Moreover, it is found from Fig. 5(a) that the viscosity increases at the beginning and then decreases with the increasing Ce_2O_3 content from 4.39 to 11.48 mass% with a $\text{CaO}/\text{Al}_2\text{O}_3$ mass ratio fixed at 1.57. Similarly, Fig. 5(b) shows the viscosity of the $\text{CaO}\text{-Al}_2\text{O}_3\text{-10 mass% SiO}_2$ based slag with an increasing $\text{CaO}/\text{Al}_2\text{O}_3$ mass ratio with Ce_2O_3 content fixed at 4.47 mass%. In addition, it can be noted from Fig. 5(b) that the viscosity decreases at the first and then increases with the increasing $\text{CaO}/\text{Al}_2\text{O}_3$ mass ratio from 1.17 to 1.52 with Ce_2O_3 content fixed at 4.47 mass%, which is similar to the evolution of melting temperature.

The causes for these may be due to that the hindrance effect of cation and the interaction force effect between cation and oxygen ion can both affect the viscosity, and the roles of the two factors change at a different composition range [13]. Meanwhile, enough basic oxide (Ce_2O_3 or CaO) present to generate weak non-bridging oxygen bond would lead to the decrease of viscosity. However, the stable tetrahedron formed in the charge-compensation of Al^{3+} ion by the Ce^{3+} ions and Ca^{2+} ions would lead to the increase of viscosity [14]. In addition, the replacement of

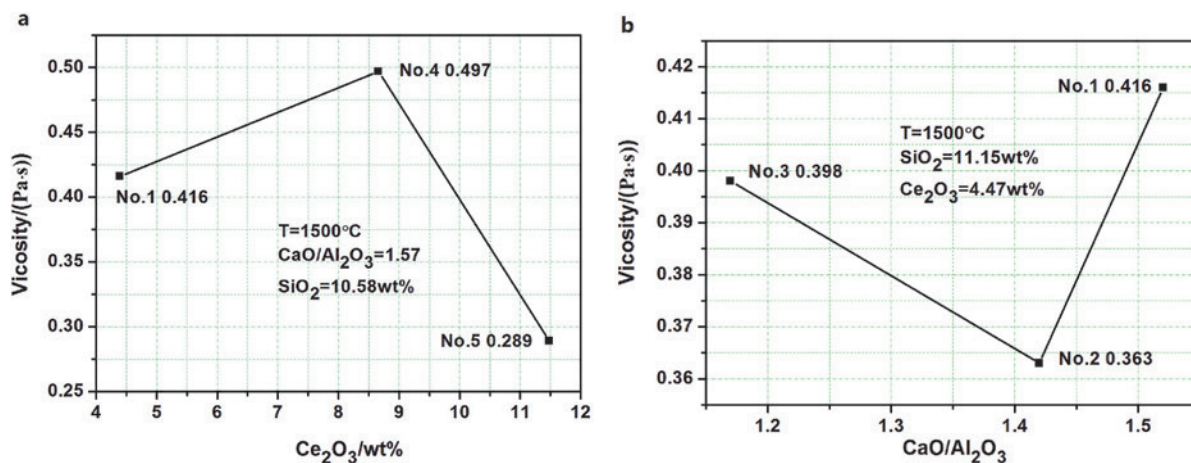


Fig. 5: Effect of $\text{CaO}/\text{Al}_2\text{O}_3$ and Ce_2O_3 content on viscosity of $\text{CaO}\text{-Al}_2\text{O}_3\text{-10 mass% SiO}_2\text{-Ce}_2\text{O}_3$ slag system

strong Si-O bond by weak Al-O bond can decrease viscosity, but the decrease of non-bridging oxygen content or the enhancement of the degree of polymerization as increasing Al_2O_3 content can increase viscosity [15]. The coexistence of those factors in the fully composition range leads to the complex variety of viscosity with composition.

In general, $\text{CaO-Al}_2\text{O}_3$ -10 mass% SiO_2 - Ce_2O_3 slag system with proper composition could have the same viscosity range of conventional $\text{CaO-Al}_2\text{O}_3$ - SiO_2 - MgO refining slag and No. 5 sample slag with the composition of 46.25 mass% CaO -29.50 mass% Al_2O_3 -10.92 mass% SiO_2 -11.48 mass% Ce_2O_3 has the lowest viscosity value of 0.289 Pa·s.

3.3.3 Effect of temperature on viscosity

In the afore-mentioned effect of Ce_2O_3 content and $\text{CaO}/\text{Al}_2\text{O}_3$ on the viscosity at 1773 K shown in Fig. 5, it was clear that the depolymerization effect of constant Ce_2O_3 additions was less pronounced at low or high value of the $\text{CaO}/\text{Al}_2\text{O}_3$ mass ratio at 1773 K. The viscous behavior of molten slag can be affected [16] by (1) the modification of the molten slag by additions of certain fluidizers such as CaF_2 and Ce_2O_3 , (2) the operational temperature. At higher temperatures, increased thermal energy is provided that some silicates and aluminates network bonds can dissociate and thus depolymerize compared with that at lower temperatures. Thus, there is both a temperature effect and a compositional effect on the molten slag structure and subsequently the viscous behavior. However, it was also speculated that there is a certain limit where the temperature effect on the viscous behavior becomes negligible similar to the compositional effects.

Fig. 6 shows the effect of temperature on the viscosity curve of $\text{CaO-Al}_2\text{O}_3$ -10 mass% SiO_2 - Ce_2O_3 slag system. It can be illustrated from Fig. 6 that viscosity increases with decreasing temperature. In addition, the viscosity of present study keeps smooth and steady in the temperature range of 1460 °C–1500 °C. However, the viscosity increases dramatically when the temperature decreases to below the transition temperature, which is because of the precipitation of phases with high melting point. Transition temperatures of No. 1, 2, 3, 4 and 5 sample slag are 1405 °C, 1458 °C, 1400 °C, 1390 °C and 1405 °C, respectively. Moreover, it can be noted from Fig. 6 that No. 3 sample has a relative wide range of temperature stable at low viscosity.

However, it seems not so quantitative that the effect of temperature on viscosity. Therefore, the temperature dependences of viscosity described by an Arrhenius type relationship Eq. (2) were shown in Fig. 7.

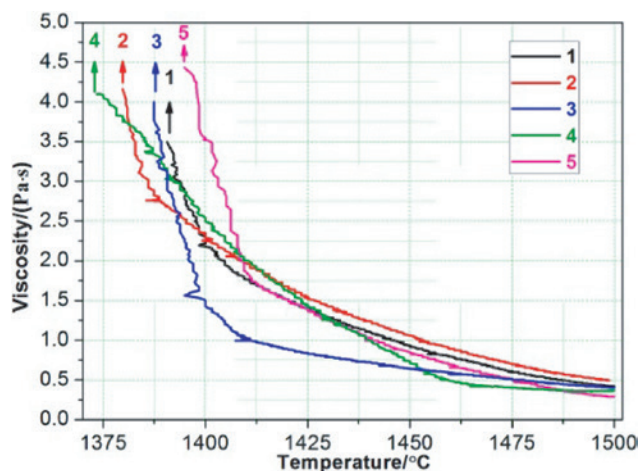


Fig. 6: The effect of temperature on the viscosity curve of the $\text{CaO-Al}_2\text{O}_3$ -10 mass% SiO_2 - Ce_2O_3 slag system

$$\eta = \eta_0 \exp(\Delta E_\eta / RT) \quad \ln \eta = \ln \eta_0 + \Delta E_\eta / RT \quad (2)$$

where η , η_0 , ΔE_η , R and T are viscosity, constant, activation energy of viscous flow, gas constant and absolute temperature, units of which are Pa·s, Pa·s, J·mol⁻¹, J·mol⁻¹·K⁻¹ and K, respectively.

Fig. 7(a) shows the natural logarithm of viscosity ($\ln \eta$) as a function of reciprocal temperature ($1/T$) and the apparent activation energy of viscous flow calculated according to Eq. (2). Using the Arrhenius-type given in equation (2), five activation energies for viscous flows are obtained by Eq. (2) to create fit curve in Fig. 7(a), (b), (c), (d) and (e), which are 290.14 kJ·mol⁻¹, 88.39 kJ·mol⁻¹, 179.07 kJ·mol⁻¹, 273.45 kJ·mol⁻¹ and 433.70 kJ·mol⁻¹, respectively. Since R-Square of No. 2 sample is 0.86 less than 0.99, thus No. 2 sample is in conformity with the Arrhenius type relationship equation and is not in uniform state.

Compared with each other sample except No. 2 sample, the activation energy for No. 3 sample was found to be the lowest value. Therefore, the temperature has the smallest influence on the viscosity of No. 3 sample at high temperature range, that is to say, No. 3 sample slag has wider low viscosity temperature range. Although No. 5 sample slag has the lowest viscosity at 1500 °C, but the viscosity of No. 5 sample slag increases significantly with the temperature decreasing, especially when temperatures below 1450 °C. However No. 3 sample slag maintains at low viscosity and increases at a slow speed with the temperature decreasing. Therefore, considered the stability of viscosity, No. 3 sample slag with a composition of 45.64 mass% CaO -39.02 mass% Al_2O_3 -10.73 mass% SiO_2 -3.83 mass% Ce_2O_3 has superiority, which is more suitable to the actual refining process.

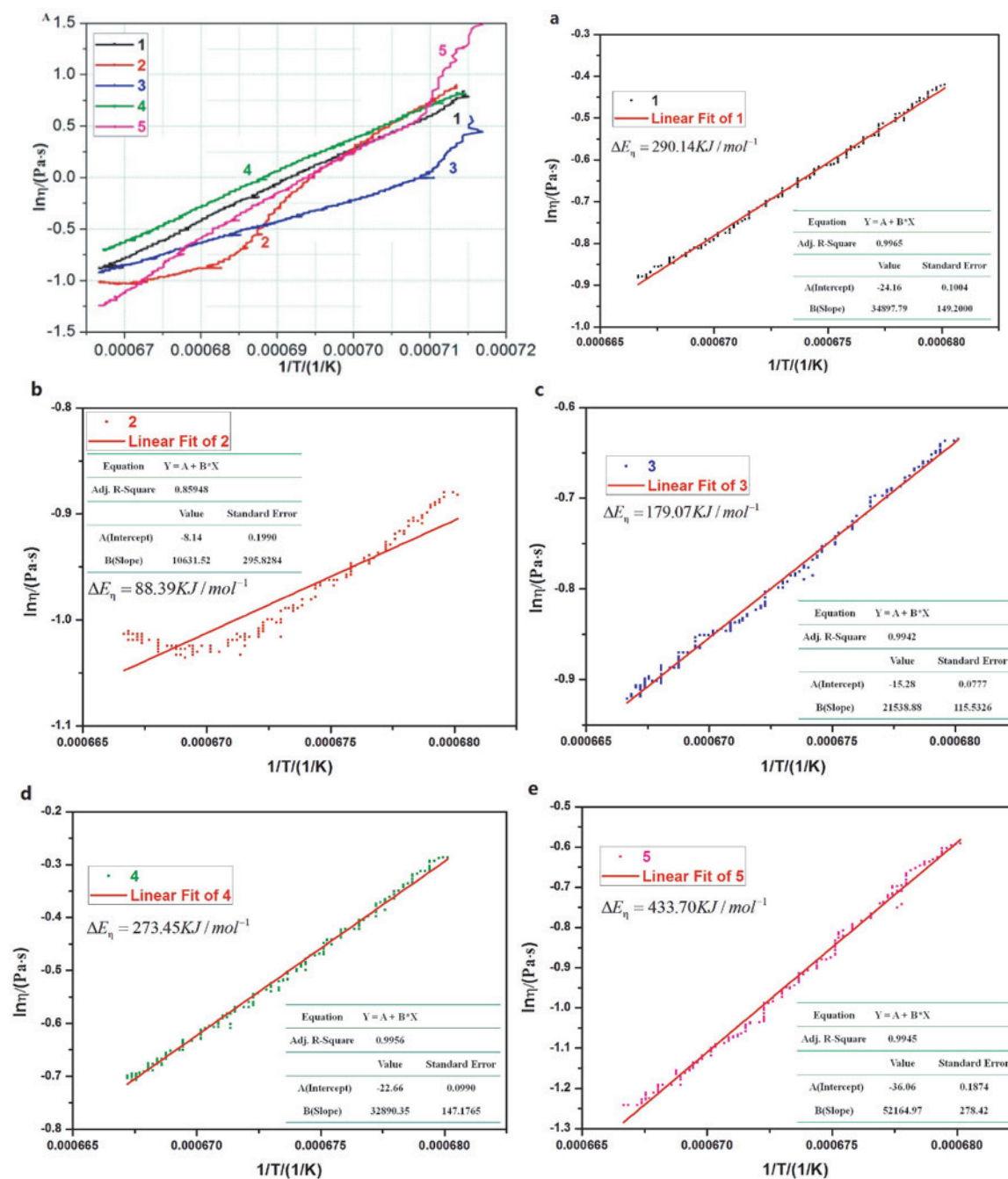


Fig. 7: Natural logarithm of viscosity as a function of reciprocal temperature in the $\text{CaO-Al}_2\text{O}_3$ -10 mass% SiO_2 - Ce_2O_3 slag system

4 Conclusions

1. Cerium is stable in Ce^{3+} state existing mainly as CeAlO_3 and $\text{Ce}_{4.67}(\text{SiO}_4)_3\text{O}$ phase in $\text{CaO-Al}_2\text{O}_3$ -10 mass% SiO_2 based slag system and the green color of the slag is caused by CeAlO_3 phase.
2. The melting temperature range of $\text{CaO-Al}_2\text{O}_3$ -10 mass% SiO_2 - Ce_2O_3 slag system studied in the present is from

1357 °C to 1366 °C. The melting temperature gently decreases with increasing of Ce_2O_3 additions with a $\text{CaO}/\text{Al}_2\text{O}_3$ mass ratio fixed at 1.57, and increases first and then decreases with the increasing of $\text{CaO}/\text{Al}_2\text{O}_3$ from 1.17 to 1.52 at 4.47 mass% Ce_2O_3 .

3. The viscosity range of $\text{CaO-Al}_2\text{O}_3$ -10 mass% SiO_2 - Ce_2O_3 slag system studied in the present is from 0.289 Pa·s to 0.497 Pa·s at 1500 °C. The viscosity decreases at the

first and then increases with the increasing $\text{CaO}/\text{Al}_2\text{O}_3$ from 1.17 to 1.52 at 4.47 mass% Ce_2O_3 , and increases at the beginning and then decreases with the increasing Ce_2O_3 content from 4.39 to 11.48 mass% with a $\text{CaO}/\text{Al}_2\text{O}_3$ mass ratio fixed at 1.57.

4. The activation energy range of viscous flow is from 179.07 kJ/mol to 433.70 kJ/mol. Slag with a composition of 45.64 mass% CaO -39.02 mass% Al_2O_3 -10.73 mass% SiO_2 -3.83 mass% Ce_2O_3 has melting temperature of 1361 °C, viscosity of 0.389 Pa·s (1500 °C) and activation energy of 179.07 kJ·mol⁻¹, which has superiority and is more suitable for the actual refining process.

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