

MELTING FEATURES AND VISCOSITY OF SiO_2 -CaO-MgO- Al_2O_3 -FeO NICKEL SLAG IN LATERITE METALLURGY

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Abstract

Physic-chemical properties of slag at high temperature were very important for the production of ferronickel alloy by pyrometallurgical process. It determines the operation efficiency, metal recovery ratio, energy consumption and the distribution of elements (like S and P) between the slag and metal. In the present work, the effect of slag basicity on melting features and viscosity of the slag was investigated. The basicity of the SiO_2 -CaO-MgO- Al_2O_3 -FeO quinary slag system varied from 0.76 to 0.99. The results showed that: 1) all the slag samples began to soften at the same temperature; 2) the softening temperature, melting temperature and flowing temperature decreased with the increase of basicity from 0.76 to 0.92, after that, the temperatures would increase sharply. 3) the inflection point temperature of viscosity-temperature curve became larger and larger with the increase of basicity within 0.76 ~ 0.99.

Keywords: Nickel laterite, Slag basicity, Melting features, Viscosity

1. Introduction

Nickel plays an important role in modern manufactures, such as airplane, computer, stainless steel and so on [1]. It is the essential element for stainless steel production, which accounts for 65% of the nickel consumption in the world [2], hence, the growing demand of stainless steel calls for more and more nickel [3, 4].

Nickel is usually extracted from two distinct ore types: nickel sulphide deposits and oxide nickel laterite deposits. The great majority of world's known nickel resources are contained in laterite deposits [3]. The laterite ores are normally classified into two groups: the high-iron laterite ore and high-magnesia laterite ore [1, 3]. Typical composition of high-magnesia laterite ore is in the range 1-3%, and these ores are suitable for pyrometallurgical process to produce ferronickel [1, 5].

Normally, laterite ores contain high silica and magnesium, especially for the high-magnesium laterite ore, which would lead to large amount of slag. And the physic-chemical properties of the slag has a crucial influence on the operation efficiency since the slag properties can significantly affect the nickel and iron recovery ratio [6-10], energy consumption, sulfur and phosphorus distribution ratio between slag and metal etc [11, 12]. Therefore, it is necessary to investigate the properties of the slag to optimize the production process. The physic-chemical properties

of slag include smelting feature, viscosity, density etc. These properties depend on chemical composition and structure of the slag [13,14]. The influences of basicity of the slag on melting temperature and viscosity were mainly investigated in this study. The basicity was defined as $[\omega(\text{MgO})+\omega(\text{CaO})]/\omega(\text{SiO}_2)$.

2. Experimental

2.1 Materials and Preparation of the Slag

The chemical composition of the material is shown in Table 1. The slag was from a domestic ferroalloy plant. According to the CaO-MgO- SiO_2 phase diagram, the raw slag is located in the forsterite region, near to the pyroxene region with low melting temperature. Hence, reagent-grade SiO_2 , CaO, MgO was used to adjust the composition of the slag in order to reach pyroxene region. On this basis, five different kinds of slag were investigated. Firstly, the mixture (raw slag and reagent) was re-melted at 1450 °C in MgO crucible within Ar atmosphere for 1 hour. After homogenization, the slag melt was quenched by water and then crushed. The chemical composition of the re-melted slag shown in Table 2 would change a little, which was mainly due to the influence of MgO crucible during melting and can be neglected. Then the slag were milled to particles of <0.074mm and shaped by a cylindrical mould to obtain 3×3mm samples for melting features measurement.

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Table 1. Chemical Composition of the Raw Slag (Mass%)

Composition	SiO ₂	CaO	Al ₂ O ₃	MgO	FeO	Ni	Cr ₂ O ₃
Content/%	42.16	18.84	5.99	20.8	7.72	0.04	1.5

Table 2. Chemical Compositions and basicity of the Slag Studied in the Present Work

Sample	SiO ₂ /%	CaO/%	Al ₂ O ₃ /%	MgO/%	FeO/%	Basicity
1#	47.89	20.26	6.06	16.05	5.96	0.76
2#	46.13	19.83	5.92	17.51	6.5	0.81
3#	44.37	19.39	5.77	18.97	7.04	0.86
4#	42.61	18.95	5.63	20.43	7.58	0.92
5#	41.28	18.45	5.47	22.45	7.56	0.99

2.2 Experimental Apparatus and Procedure

2.2.1 Melting Features

Melting features measurement system includes three parts: sample hold, heating system and image system, being shown in Figure 1. Measuring mechanism of this system is that the sample height will change with the material melting since temperature rising. Sample was placed in the center of the heating furnace, and the heating rate was 15°C/min. The softening temperature, melting temperature, flowing temperature are defined as the temperature at which the sample height decrease to 75%, 50%, 25% of the original height respectively. And the initial softening temperature is considered as the temperature at which the sample height starts to decrease.

2.2.2 Viscosity

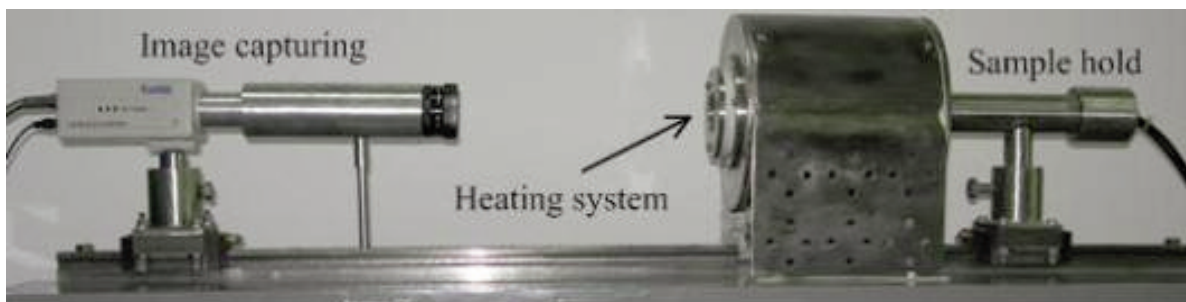
The rotating cylinder method was employed for viscosity measurements. The experimental apparatus, measurement principle and the calibration method had been explained in detail in earlier literatures [11, 12, 15, 16]. In each run, 120g slag powder was hold in MgO crucible (φ45×60mm), and it was placed in a graphite crucible. The graphite crucible was located

into the reaction chamber of MoSi₂ furnace in an Ar atmosphere in the heating process. The temperature was controlled by a Pt-30mass%Rh/Pt-6mass%Rh thermo couple and a proportional integral differential (PID) controller. The temperature fluctuation was about ±2°C. In order to make the slag melt completely, the slag was molten for 2 hours when the temperature reached to 1470°C which was based on the melting temperature. Then, the molybdenum spindle was immersed into the slag and was held in the middle of the melt. When the temperature was kept stable for about 20 minutes, then the viscosity was continuously measured while the temperature fallen at the speed of 5°C per minute. When the viscosity up to 2 Pa.s, the measurement was stopped, then the temperature was reheated to 1450°C. After keeping the temperature unchanged for about 1 hour, the isothermal viscosity was measured. Finally, the spindle was taken out from the melt slag.

3. Results and Discussion

3.1 Melting Features

Figure 2. shows the effect of basicity on the melting features of SiO₂-CaO- MgO-Al₂O₃-FeO slag. It is clear that all the slag have the same initial softening temperature at about 1230°C, which means that there is a same low melting temperature component in different slag. The softening temperature, melting temperature and flowing temperature decreased with the increase of basicity from 0.76 to 0.92, and as basicity reach to 0.99 then the temperatures rise sharply. The lowest and the highest melting temperature would appear when the basicity is 0.92 and 0.76, respectively. The temperature difference between lowest and highest melting temperature is about 30 °C. The temperature interval between initial softening temperature and softening temperature was bigger than 40 °C, but the

**Figure 1.** Melting features measurement system

temperature difference between softening temperature and melting temperature or between melting temperature and flowing temperature was smaller than 10°C. From above, it can obtain that the main material phases of the samples have the similar melting temperature and the melting speed of slag is fast.

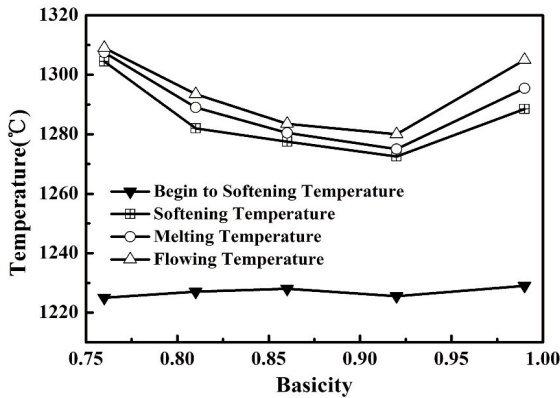


Figure 2. The effect of basicity on the melting feature of slag

3.2 Viscosity

If a slag is melted at high temperature and then cooled slowly, the slag viscosity linearly increases up to a specific temperature, and then abruptly increases below that temperature. Thermodynamically, the temperature should be the liquidus temperature of the slag, that is, the maximum temperature at which liquid and solid phase can coexist in equilibrium. If the slag is cooled further, more solid phase will precipitate and increase the slag viscosity [12].

Figure 3. shows the viscosity of the slag by varying basicity as a function of temperature. From Figure 3, it can be observed that the inflection point temperature increases with the increase of basicity when it is in the range of 0.81 and 0.99. When the basicity is 0.76 and 0.81, the slag has a lower inflection temperature and a wider solid-liquid coexisting region than others as temperature is below 1470°C. When basicity of slag varies from 0.76 to 0.92, the difference of the inflection temperature is about 90°C, which is from 1360°C to 1450°C. The slag has the smallest viscosity, and the corresponding basicity is 0.76, when the temperature is in the range of 1370°C and 1470°C. On the other hand, when the temperature is more than 1370°C the viscosity of the slag, when basicity is 0.76 and 0.81, is smaller than 0.4 Pa.s, which can meet the requirements of the smelting of nickel laterite ore well. Normally, the smelting temperature of the production of ferronickel alloy is between 1450°C and 1500°C, therefore, in

order to reduce energy consumption trough decreasing melting temperature, it is better to control the basicity of the slag being lower than 0.9.

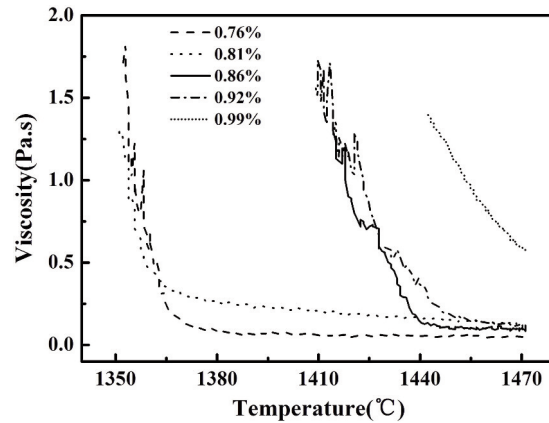


Figure 3. Viscosity of different slag by varying basicity as a function of temperature

The effect of basicity on melting temperature and viscosity is different, which may due to the melting temperature is mainly depended on low melting temperature material, while the viscosity is largely related to the high melting temperature material. The phenomenon can be explained from the phase diagram (Figure 4,) of $\text{SiO}_2\text{-CaO-MgO-Al}_2\text{O}_3\text{-FeO}$ slag system calculated by Factsage software. Table 3 gives the composition, temperature, and main material phase of four Eutectic points, which are marked with number 4, 7, 12, 13 in Figure 4. The chemical Compositions of the Slag Studied in the Present Work are shown as the black circle in the phase diagram, and the black triangle is the raw slag. From Figure 4 and Table 3, it can obtain that the material phase of the slag in this study maybe include Amonoxide, Aolivine, Ca_2SiO_4 , $\text{Ca}_2\text{MgSi}_2\text{O}_7$ (akermanite), Orthopyroxene, $\text{CaMgSi}_2\text{O}_6$ (diopside). The melting

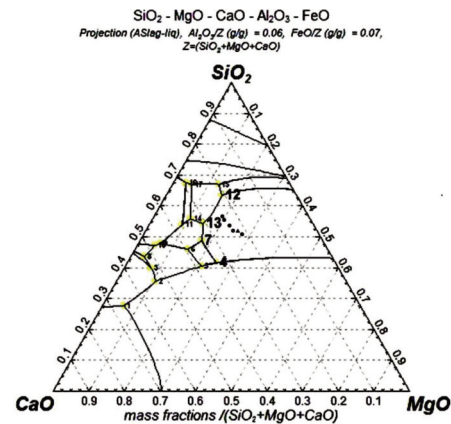


Figure 4. Phase diagram of $\text{SiO}_2\text{-CaO-MgO-Al}_2\text{O}_3\text{-FeO}$ slag system

Table 3. Four Phase Intersection Points with ASlag-liq

Point	SiO ₂ /%	CaO/%	MgO/%	Temperature/°C	Phase
4	36.81	29.56	22.12	1422	Amonoxide; Aolivine
7	43.1	30.09	15.31	1321	Aoliveine;Ca ₂ SiO ₄ ;Ca ₂ MgSi ₂ O ₇ (akermanite)
12	56.19	18.5	13.89	1275	AOlivine;Orthopyroxene;CaMgSi ₂ O ₆ (diopside);
13	47.96	27.35	13.19	1271	AOlivine; Ca ₂ MgSi ₂ O ₇ (akermanite); CaMgSi ₂ O ₆ (diopside)

temperature of these slag was depended on the melting property of these material. The melting temperature of Ca₂MgSi₂O₇ (akermanite) is lower and the Amonoxide is higher. The initial softening temperatures of each slag are the same, that maybe all the slag contain Ca₂MgSi₂O₇ (akermanite), but as the content exist discrepancy, so the melting temperatures are different. The melting temperatures of the slag are between 1276°C and 1309°C, which are within the temperatures of eutectic point 7, 12, and 13. It means the measurements and calculation is consistent. The existence of Amonoxide at eutectic point 4, whose eutectic temperature is 1422°C that is the reason for the inflection temperature is higher than 1440°C when the basicity is more than 0.86.

4. Conclusions

The effect of basicity of the slag on melting features and viscosity of the slag was investigated in present study. The results show that:

(1) The softening temperature, melting temperature, flowing temperature decrease with the increase of basicity when the basicity varies from 0.76 to 0.92, and when basicity up to 0.99, the temperatures increase sharply.

(2) The inflection point temperature of viscosity-temperature curve increase with the increase of basicity when the basicity is in range of 0.76 to 0.99.

(3) The basicity should be kept lower than 0.9 in the pyrometallurgical process of production of ferronickel alloy.

Acknowledgements

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