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Effect of MgO/Al_2O_3 on Fluidity of SFCA-Based Binder Phase

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Abstract: The fluidity of sinter binder phase is one of the main properties that determine the quality of sinter, and it is also an important index to characterize the quality of sinter. So far, iron and steel enterprises mainly produce high alkalinity sinter, and its binder phase is mainly composite calcium ferrite based binder phase. Therefore, the research object of this paper is the composite calcium ferrite based binder phase of high alkalinity sinter. The effect of MgO/Al_2O_3 on the fluidity of high calcium composite calcium ferrite based binder phase was investigated from three aspects: fluidity index, liquid phase formation temperature and melting time by using chemical pure reagent and melting point velocimeter. The results show that in the range of MgO/Al_2O_3 from 0.46 to 0.68, with the increase of the ratio of MgO to Al_2O_3, the fluidity index first increases and then decreases, and the maximum value is obtained at MgO/Al_2O_3=0.65; The melting time decreases first and then increases. At the same time, the minimum value is obtained at MgO/Al_2O_3=0.65, and the influence on the melting time becomes more and more obvious with the increase of MgO/Al_2O_3 ratio; the characteristic temperature of liquid phase formation increases briefly and then decreases.

Keywords: Fluidity, MgO/Al_2O_3 Ratio, Calcium Ferrite, Sintering Liquid Phase

1. Introduction

At present, iron and steel enterprises mainly produce high-basicity sinter with binder phase of silico-ferrite of calcium and aluminum (SFCA) [1-5]. The effect of CaO on the fluidity of liquid phase in Ferrites with different compositions was studied. Furthermore, the influence of SiO_2 was investigated, and the matching principle of CaO, SiO_2 and basicity of ferrite liquid phase was clarified. Objecting to high-basicity sinter, single cause study of melting characteristics of different $nCaO:nFe_2O_3$, w(MgO), $w(SiO_2)$ and $w(Al_2O_3)$ ferrite binder phases were investigated by Li et al [6, 7]. As the binder phase changes with sintering conditions, especially the continuous dissolution of MgO, SiO_2 and Al_2O_3, SFCA with high calcium or low calcium will be formed. Therefore, for different types of SFCA, systematic research on chemical composition, melting characteristics and fluidity plays an important role in guiding raw material preparation and improving sinter quality.

Based on recent studies on the formation of SFCA [8, 9] and the influence of MgO and Al_2O_3 on sintering properties [10-13], in this thesis, calcium ferrite was made from chemical reagent. On this basis, systematically investigated of influence of MgO/Al_2O_3 on fluidity index, melting time and liquid phase formation temperature of SFCA-based bine phase with high calcium and fixed SiO_2 content by changing the proportion of MgO and Al_2O_3. The effect of MgO/Al_2O_3 on the melting and fluidity behavior of SFCA-based binder phase was revealed.

2. Experimental Scheme

2.1. Experimental Materials

The experimental materials were made from analytical reagent, and the proportioning scheme is shown in Table 1.

Table 1. *Raw material composition of SFCA (mass %).*

Sample No.	CF	Fe_2O_3	MgO	Al_2O_3	SiO_2	MgO/Al_2O_3
1#	44.13	43.82	2.39	3.51	6.15	0.68
2#	44.13	39.30	4.12	6.30	6.15	0.66
3#	44.13	36.71	4.12	8.89	6.15	0.46
4#	44.13	38.18	5.24	6.30	6.15	0.83
5#	44.13	35.59	5.24	8.89	6.15	0.59
6#	44.13	27.58	7.32	14.82	6.15	0.49
7#	44.13	25.26	9.64	14.82	6.15	0.65

2.2. Experiment Equipment

A smelting point determining instrument was adopted in the experiment, and the structure diagrammatic sketch is shown in Figure 1.

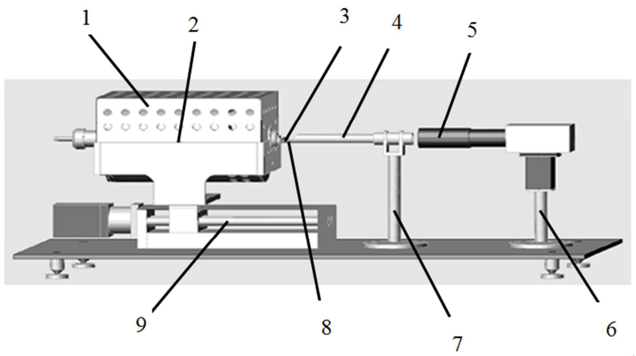

Figure 1. *Appliance sketch map of measuring melting point and rate.*

1-- heating furnace; 2--furnace temperature-measuring thermocouple; 3--sample; 4--corundum tube; 5--CCD electron camera; 6--camera bracket; 7--corundum tube bracket; 8--sample temperature-measuring thermocouple; 9--sliding rail.

2.3. Experimental Procedure

1) Experimental steps for preparation of calcium ferrite

Firstly, CaO and Fe_2O_3 (analytical reagent, $n(CaO):n(Fe_2O_3)=0.8:1.0$) were mixed and ground with anhydrous ethanol. And they were put into the crucible made of Al_2O_3 after drying. The crucible was heated to 1250°C (heating rate is 10°C/min) in air and kept at the constant temperature for 24 hours to prepare calcium ferrite.

2) Experimental steps for fluidity

Then SFCA was prepared according to table 1. The prepared reagent is mixed evenly, added with a certain amount of anhydrous ethanol, adjusted to paste shape and made into cylinders of Ø3mm×3mm by mould. Samples were fed into RDS-5 melting point/rate measuring instrument together with corundum gasket. The time, image, temperature and other parameters of cylindrical sample in the process of heating to over-melting were collected, and the average value was calculated with the results of three times of experiment for each sample. Then the fluidity index and melting time is recorded to evaluate its fluidity.

2.4. Data Representation

In this study, the fluidity of SFCA-based binder phase was represented by three characteristic parameters: fluidity index-F, melting time-t and liquid phase formation temperature-T.

The fluidity index is defined as [1]:

$$F = \frac{A_a}{A_b}$$

Where, $A_a$is the area after sample flowing; $A_b$is the area before sample flowing. The larger the fluidity index is, the stronger the fluidity is.

Melting time, the time it takes for the specimen to deform to complete flow, defined as [14]:

$$t = t_e - t_s$$

Where, t_e is the time it takes for the shrinkage 80%; $t_s$is the time it takes for the shrinkage 10%. The shorter the melting time, the better the fluidity.

Furthermore, there are three characteristic parameters of liquid phase formation temperature T during sample melting:

(1) T20: Temperature corresponding to the shrinkage of 20% is the starting temperature of effective liquid phase formation;

(2) T50: Temperature corresponding to the shrinkage of 50% is the termination temperature of effective liquid phase formations;

(3) Flowing temperature: Temperature corresponding to the shrinkage of 80%.

3. Results and Discussion

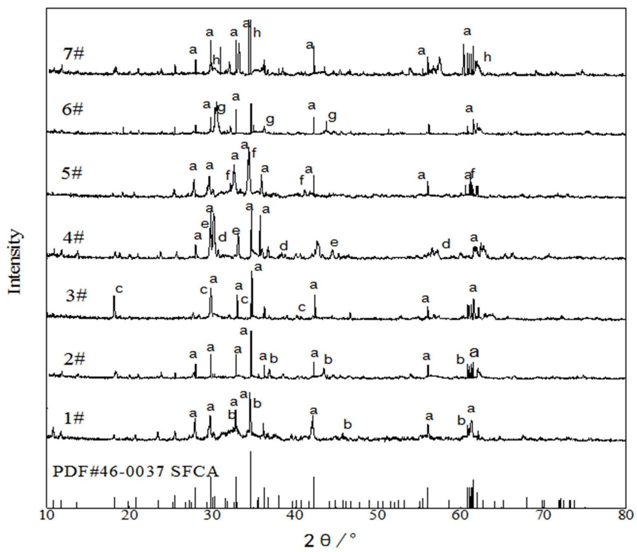

Figure 2. *XRD patterns of sample under 1250°C×24h.*

a: SFCA ($Ca_{2.3}Mg_{0.8}Al_{1.5}Fe_{8.3}Si_{1.1}O_{20}$); b: calcium diferrite; c: hedenbergite; d: diopside; e: calcium silicate; f: $Ca_2Fe_7O_{11}$; g: kirschsteinite; h: magnoferrite

The XRD diffraction analysis of calcium ferrite samples prepared according to Table 1 is shown in Figure 1. From the analysis of the pattern curve in the figure, it is known that the main components of the pattern are compound calcium ferrite. From the comparison of the curves in Figure 1, Style 1 and Style 6 contain the highest purity of calcium ferrite, in addition to a small amount of calcium diferrite. Style 3 contains a certain amount of hedenbergite. Style 4 contains more calcium silicate. Style 5 contains more $Ca_2Fe_7O_{11}$. Sample 7 contains not only the main mineral compound calcium ferrite, but also a small amount of hedenbergite.

3.1. Influence of MgO/Al_2O_3 on Fluidity Index of SFCA-based Binder Phase

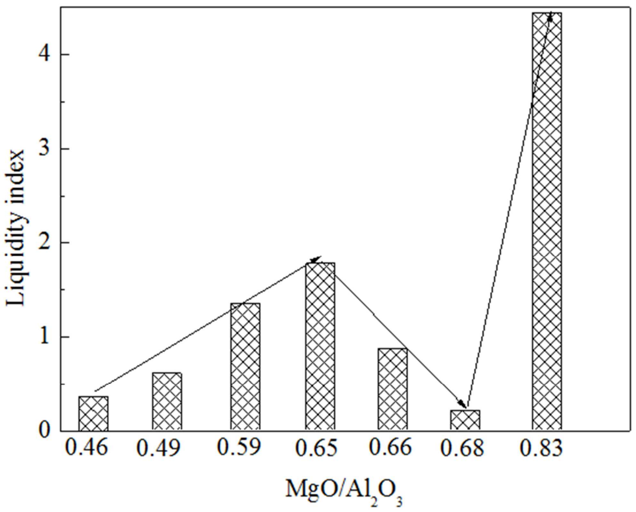

Figure 3. *Fluidity index of SFCA under different MgO/Al_2O_3.*

As can be seen from Figure 3, When MgO/Al_2O_3 is 0.46~0.65, the increase of fluidity index MgO/Al_2O_3 increases linearly. When MgO/Al_2O_3 is 0.65~0.68, the fluidity index decreases with the increase of MgO/Al_2O_3 ratio. The MgO/Al_2O_3 is 0.68~0.83, and the fluidity index increases rapidly with the increase of MgO/Al_2O_3 ratio. Especially at MgO/Al_2O_3 is 0.83, the fluidity index of composite calcium ferrite has obviously exceeded the reasonable range. According to the composition ratio of Table 1 and the phase composition of Figure 1, it is considered that when MgO/Al_2O_3 is 0.46~0.65, the formation of high melting point phase decreases with the increase of MgO/Al_2O_3 value, and the phase composition approaches. The complete low-melting composite calcium ferrite phase ($Ca_{2.3}Mg_{0.8}Al_{1.5}Fe_{8.3}Si_{1.1}O_{20}$), the melting point of the system is lowered, so the fluidity index increases; When MgO/Al_2O_3 is continuously increased to 0.68, the high melting point phase begins to form in the system, and is melted in the liquid phase system in the form of a heterogeneous phase, which reduces the flow ability of the liquid phase; When MgO/Al_2O_3 is increased to 0.83, only a very small amount of diopside and calcium silicate phase are formed in the system, and the proportion of composite calcium ferrite is much higher than that of the other six groups, resulting in a heterogeneous phase in the liquid phase. The fulcrum is reduced, the melting point is the lowest, and the fluidity index is the highest (close to 4.5).

Figure 4 is the effect of fixed MgO content (wt%=4.12), changing the Al_2O_3 content on the fluidity index of the composite calcium ferrite-based binder phase. It can be seen from Figure 4 that with the increase of Al_2O_3 content, the flow index shows a downward trend. Within a reasonable range (0.46~0.66), the downward trend of the liquidity index is not obvious. Combined with the data analysis in Figure 2, it can be seen that the fluidity index of the calcium ferrite-based binder phase is closely related to the change of MgO/Al_2O_3 value, and there is no obvious regularity with the specific MgO and Al_2O_3 content. The liquid phase formation temperature and melting time are the same. Corresponding relationship, it's not described in this article to avoid repetition.

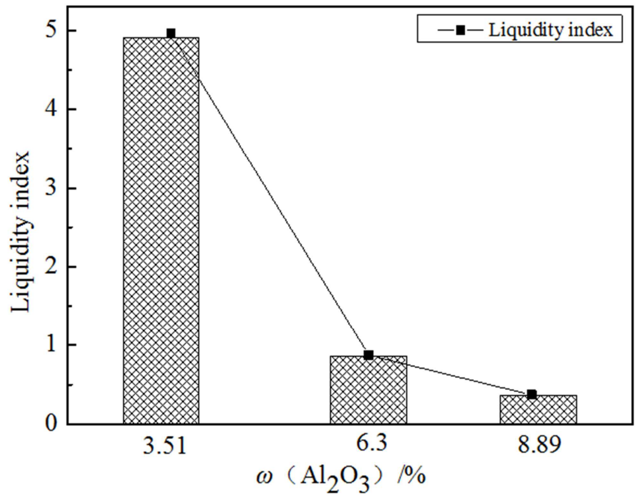

Figure 4. *Effect of Al_2O_3 content on the fluidity index of composite calcium ferrite based binder.*

According to the research on the basic characteristics of existing sintering [15], the fluidity index of sintered ore is generally controlled within the range of 0.7~1.6. Therefore, when the ratio of MgO/Al_2O_3 is in the range of 0.49~0.66, the composite calcium ferrite is sticky. The phase has good fluidity.

3.2. Influence of MgO/Al_2O_3 on Liquid Phase Formation Temperature of SFCA-based Binder Phase

As shown in Figure 5, the initial temperature, the termination temperature of liquid phase formation and the flow temperature of the sample increase first and then decrease with the increase of MgO/Al_2O_3, and all peak values occur when MgO/Al_2O_3 is 0.49. The initial temperature and the termination temperature of liquid phase formation decrease rapidly when MgO/Al_2O_3 is in the range of 0.65-0.68. The two characteristic temperatures are greatly affected by MgO/Al_2O_3, and the flow temperature hardly changes at this stage. When MgO/Al_2O_3 is in the range of 0.68 and 0.85, the initial temperature, termination temperature of liquid phase formation and flow temperature tend to be staying stable. With the change of MgO/Al_2O_3, there are two peaks for the gap between flow temperature and liquid phase termination temperature where MgO/Al_2O_3 are 0.49 and 0.68 respectively. Generally, the temperature gap of flow temperature and termination temperature of liquid phase formation shows an upward trend with the increase of MgO/Al_2O_3.

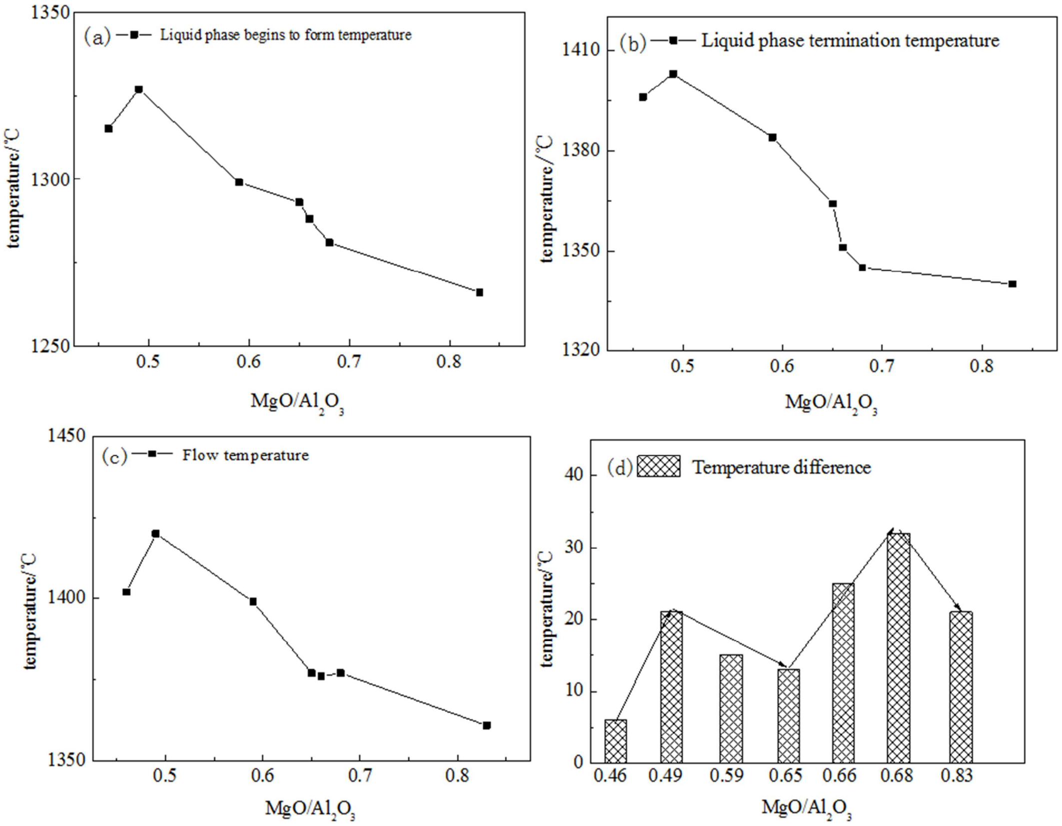

Figure 5. *Initial and termination temperature of liquid phase formation and flow temperature of liquid phase.*

In order to explore the specific causes of the phenomena shown in Figure 6, viscometer was used to test 7 groups of samples in table 1. Experimental results are shown in Figure 5.

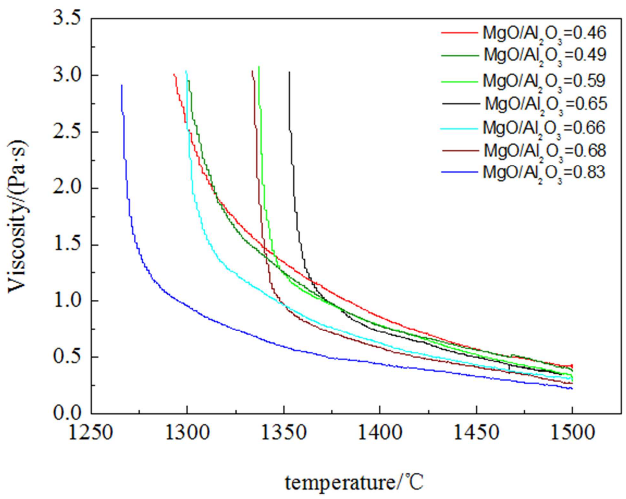

Figure 6. *Temperature-viscosity curves of SFCA with different MgO/Al_2O_3.*

The analysis shows that the main reason for this change is that the melting process is a process in which the regular structure of the sample is destroyed from the outside to the inside. With the increase of temperature, a series of abrupt changes occur in the sample. It is shown in Figure 5 that the viscosity curve of sample changes smoothly when MgO/Al_2O_3 is less than 0.49, showing the characteristics of long slag. There are obvious turning points in the viscosity curves, showing the characteristics of short slag when MgO/Al_2O_3 is greater than 0.49. The melting temperature increases first and then decreases with the increase of MgO/Al_2O_3.

In the early stage of melting, the melting of samples is affected by viscosity and melting temperature. With the increase of MgO/Al_2O_3, the liquid phase formation stages show a short increase, and then tend to a gentle decline. In the later stage, the melting of sample is mainly accomplished by the wetting action between melted liquid phase and surrounding unmelted part. The characteristic temperature of sample is largely affected by the wettability of SFCA. With the increase of MgO/Al_2O_3, the non-uniform phase particles during melting process are reduced, the solubility of interface increased, the wettability improved, and the melting process carried out more smoothly.

The high melting point substances have little effect on the initial formation temperature of liquid phase, but have great influence on the termination formation temperature and flow temperature. Therefore, the high melting point substances produced with the increase of MgO/Al_2O_3 will affect the termination formation temperature and flow temperature.

3.3. Influence of MgO/Al_2O_3 on Melting Time of SFCA-based Binder Phase

The melting time also has an important effect on the fluidity and liquid phase formation of SFCA-based binder phase. A shorter melting time means a better the fluidity and a stronger generation ability of liquid phase. Because the time to reach the highest sintering temperature in sintering production is relatively short and the reaction process is in non-equilibrium state, more liquid phases are required in a short time.

As shown in Figure 6, the melting time decreases first and then increases with the increase of MgO/Al_2O_3. When MgO/Al_2O_3 is 0.65, the melting time is the shortest. When MgO/Al_2O_3 is small, it shows a slight effect on the melting time, and the effect becomes more obvious with the increase of MgO/Al_2O_3. When MgO/Al_2O_3 is in the range of 0.46~0.65, the melting time decreases with the increase of MgO/Al_2O_3 because of the decrease of non-uniform phase particles, which results in the decrease of liquid surface tension, the enhancement of bubble reconstruction ability and the increase of contact polymerization probability. It is beneficial to improve liquid flow ability and shorten melting time. When MgO/Al_2O_3 is in the range of 0.65~0.68, the increase of MgO/Al_2O_3 promotes the formation of silicate-aluminate network structure, which leads to the increase of liquid phase viscosity and the difficulty of melting process, thus improving the melting time of SFCA samples. When MgO/Al_2O_3 is larger than 0.68, the melting time decreases again with the increase of MgO/Al_2O_3, which is because the number of free O^{2-} increases gradually, leading to the disintegration of complex silica-oxygen complex anions in the sample and reduction of the viscosity.

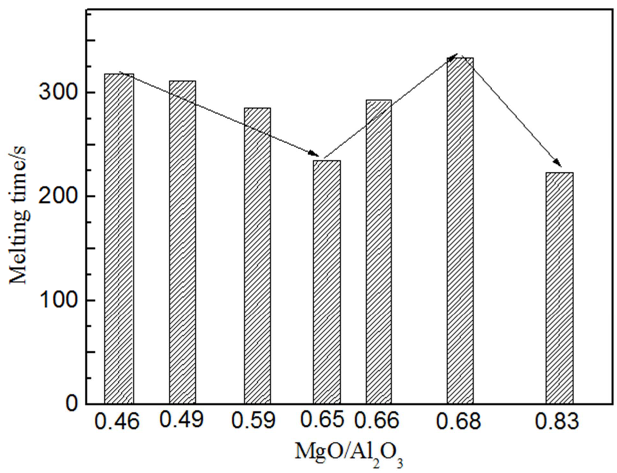

Figure 7. *Effect of MgO/Al_2O_3 ratio on the melting time of SFCA.*

4. Conclusions

The effect of MgO/Al_2O_3 on the fluidity index, liquid phase formation temperature and melting time of the composite calcium ferrite-based binder during sintering process was investigated by using analytical reagent as experimental material. The conclusions of the experimental study are as follows:

1) The liquidity index increases first and then decreases with the increase of the ratio of MgO/Al_2O_3 in the range of 0.46-0.68, and reaches the maximum value when MgO/Al_2O_3 is 0.65. Considering the liquidity index, the binder phase has better liquidity when MgO/Al_2O_3 in the range of 0.49-0.66.
2) The initial formation temperature, the termination formation temperature and the flow temperature of the binder phase increased first and then decreased with the increase of MgO/Al_2O_3. They increase briefly when MgO/Al_2O_3 in the range of 0.45-0.5 and decreased in 0.5-0.85.
3) The melting time decreased first and then increased with the increase of MgO/Al_2O_3 in the range of 0.46~0.68, and the minimum value was obtained when MgO/Al_2O_3 was 0.65. Moreover, the effect of MgO/Al_2O_3 ratio on melting time is smaller when the ratio is small, and become more obvious with the increase of MgO/Al_2O_3.

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