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EFFECT OF CAO/SIO$_2$ RATIO ON MELTING PROPERTY AND STRENGTH OF SINTER WITH VANADIUM-TITANIUM IRON ORE ADDITION

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Melting behavior is the precondition of liquid phase reaction, which is the foundation of sinter consolidation. Melting property measurement and sinter pot test were adopted to determine the melting temperature and strength of sinter with 13 % and 40 % vanadium-titanium ore addition at different CaO/SiO_2 ratio. The results showed that, the increasing CaO/SiO_2 ratio positively influences the melting property. Due to the difference of TiO_2 content, the influence of increasing CaO/SiO_2 ratio on strength appears in different curves which are not the same as prediction. The sinter strength variations were not only influenced by melting property, but also by mineral texture. The influences of TiO_2 on melting property, strength, mineral texture especially SFCA were still needed a further study.

Key word: vanadium - titanium iron ore, CaO/SiO_2, strength, sinter, mineral texture

INTRODUCTION

Vanadium - titanium (V - Ti) sinter production was developed from sinter with low CaO/SiO_2 ratio to sinter with high CaO/SiO_2 ratio, which is the same as the development of ordinary ore sinter based on calcium ferrites theory that is reported to be optimal for sinter strength and iron-making in a blast furnace .The main reactions happened in the sintering of ores mixture is the liquid phase reaction, which is the foundation of sinter consolidation and similar to the generation of slag . In addition, the melting behavior is the precondition of liquid phase reaction.

For V-Ti sinter, the previous work [1] pointed out that there is a larger difference between V - Ti and ordinary sinter for the special mineral texture especially perovskite ($CaO{\cdot}TiO_2$), which consumes CaO sources and causes the decrease in calcium ferrite. Meanwhile, it has a higher fragility without the bonding effect, which causes the poor strength of V-Ti sinter. Meanwhile, according to the thermodynamic calculation, the generation of perovskite is prior to calcium ferrites. Meanwhile, Du [2] points out that the generation of perovskite and calcium ferrites was also influenced by the concentration of TiO_2.

Up to now, the influence of the CaO/SiO_2 ratio on melting property of the sinter mixture with V-Ti ores addition and its relationship with V-Ti sinter strength are still unclear. Thus, in present study, the melting property of sinter with V-Ti ore addition at different CaO/SiO_2 ratio was determined using the method similar to the measuring method of slag. In addition, the tumbler strength (TI) of sinter with V-Ti ore addition at different CaO/SiO_2 ratio was determined, and the difference in the tendency in strength by increasing CaO/SiO_2 ratio was analyzed and discussed.

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EXPERIMENTAL WORK

Raw materials

The chemical composition of raw materials was listed in Table 1.

Table 1 **Chemical composition of raw materials /mas. %**

Raw materials	TFe	FeO	CaO	SiO_2	MgO	Al_2O_3	TiO_2	V_2O_5
V-Ti ore	61,42	28,63	0,32	2,54	1,20	2,95	5,12	1,01
Ore A	62,99	26,56	0,49	5,30	1,01	3,36	-	-
Ore B	63,85	27,86	0,05	5,48	0,17	3,66	-	-
Ore C	61,81	22,21	1,39	3,66	3,54	2,44	-	-
Shaft furnace dust	62,56	-	0,31	8,16	0,58	0,92	-	-
Magnesite	-	-	1,20	3,50	42,00	-	-	-
Quicklime	-	-	80,0	5,00	1,10	-	-	-

EXPERIMENTAL METHODS

Melting property tests

Up to now, there is no standard method to measure the melting property in the mixture of solid and liquid phases. Thus, an indirect method was adopted according to the relationship between the height of the sample and the temperature. This method is always used to measure the melting properties of the slag / coal ash. The measurement system for melting property is consisted of image

capturing, the sample holder, and heating system, shown in Figure 1. The heater is made of $MoSi_2$, and the maximum temperature achieved is 1 400 °C.

The experimental ore matching schemes are shown in Table 2. About 100 g mixture of each scheme was dried for 2 h at 110 °C, and then was grinded to – 0,074 mm by using a sealed crusher. The mixture was shaped into tablets with Φ 3 mm × 3 mm by using two steel moulds under a pressure of 15 MPa for 2 min.

The sample was heated in the heating system according to the program fixed in the controller, shown in Figure 2. The air atmosphere was adopted during the measurement. First, samples were put on the sample holders which were then pushed into the heating zone. In this measurement, the heating rate was fixed at 10 °C /min to 1 000 °C, 8 °C / min to 1 200 °C, 5 °C /min to 1 400 °C, then push the sample out to cool to room temperature. The sample would shrink in the measurement due to the melting behavior. According to the method used for measuring the melting features of slag / coal ash and the definition on the effective formation of liquid phase [3, 4], the temperatures for initial melting, half height, and end of melting were defined individually as the temperature when the height of the sample becomes 70 %, 50 % and 40 % of the original height. In this measurement, half height temperature is defined as the melting temperature as the index for evaluating the melting property. Figure 3 shows the images captured in the measurement system. For the purpose of ensuring the accuracy of the results, each scheme was repeated three times, and the average result of the three samples was the final result.

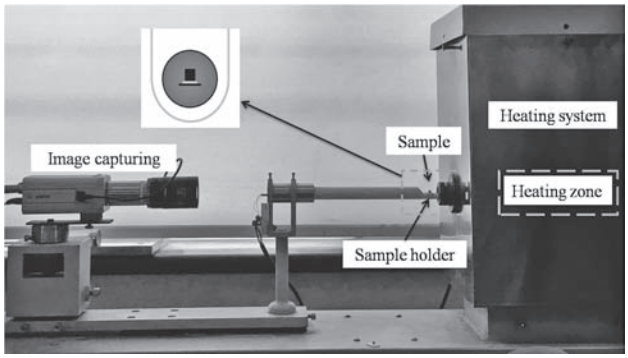


Figure 1 Measurement system for melting property

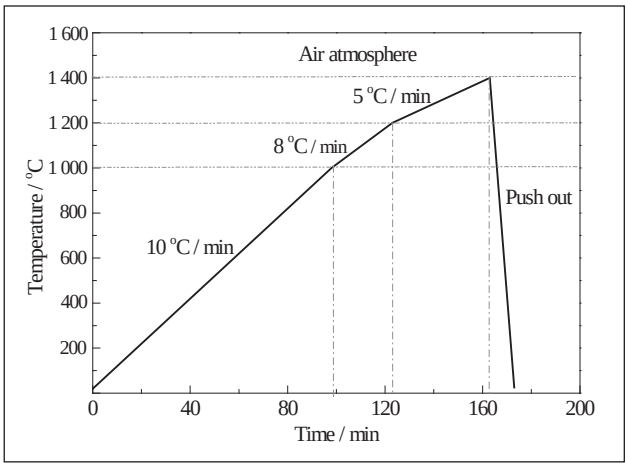


Figure 2 Temperature system and atmosphere for melting property

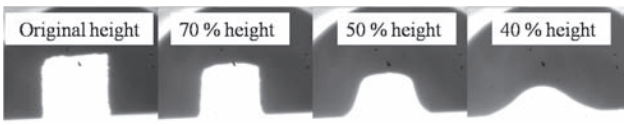


Figure 3 Image captured in the measurement for melting property

Sintering pot Tests

Experiment schemes are shown in table 2, experimental parameters and methods are consistent with reference [1].The difference of items A and B was 27 % V-Ti ore replaced by 12 % Ore B and 15 % Ore C. The tumbler strength (TI) was determined in accordance with ISO - 3271.

Table 2 **Experimental ore matching schemes/ mas. %**

Items	CaO/SiO_2	V-Ti ore	Ore A	Ore B	Ore C	shaft furnace dust	others
A	1,9/2,1/ 2,4/2,7	40	20	0	0	4,5	16,5
B	1,9/2,1/ 2,4/2,7	13	20	12	15	4,5	16,5

RESULTS AND DISCUSSION

Melting property

The melting property results of A and B were shown in Figure 4. It is found that with CaO/SiO_2 ratio increasing, the melting temperatures of A and B decrease from 1 340 °C, 1 328 °C to 1 310 °C, 1 280 °C, respectively. And the tendency influenced by CaO/SiO_2 ratio was similar .This may be attributed to the increase in low-melting substance formation in melt with the CaO/SiO_2 ratio rising, which accelerates the formation of liquid phases and the tablet of sinter mixture would shrink at a

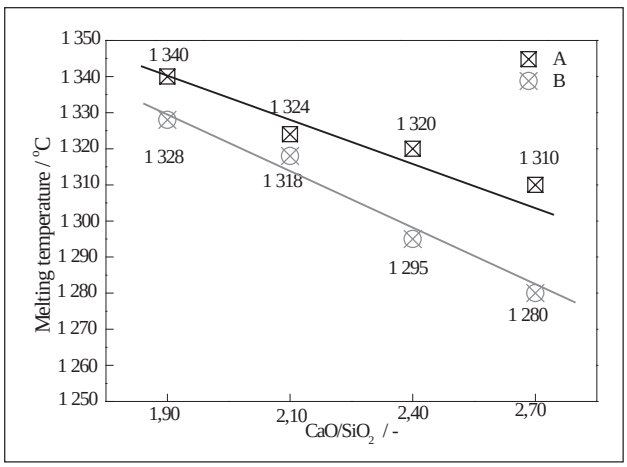


Figure 4 Melting temperatures of sinter mixture with V-Ti ore addition at different CaO/SiO_2 ratio

low temperature. Meanwhile, the melting temperature of B is lower than that of A at the same CaO/SiO_2 ratio. The probable reason is that the shrinkage not only relates to the mass of liquid phase formation, but also the viscosity of the liquid phases, the contact angle between the liquid phase and the sample tablet and some other factors [5]. A and B have different TiO_2 content (in form of 40 %V-Ti ore addition and 13 %V-Ti ore addition), which will influence the viscosity of the liquid phases. The difference between A and B in TiO_2 content may be the reason causing the difference in melting temperature at the same CaO/SiO_2 ratio. Due to the TiO_2 region is too small (TiO_2 1,0 ~ 2,3 %) and the other factors also influence the melting temperature. Therefore, the influence of TiO_2 on melting property needed to be studied further.

So, increasing the CaO/SiO_2 ratio positively influences the melting property of sinter across the range from 1,90 to 2,70, no matter with 13 % or 40 % V-Ti ore addition. And a better sinter strength was predicted for more liquid phases supplied along with a better melting property.

Strength

Figure 5 shows the tumbler strength of sinters A and B at different CaO/SiO_2 ratio. As can be observed, the sinter strength of B rises continuously from 54,8 % to 64,8 %, which is opposite to the tendency of melting temperatures along with the increase of CaO/SiO_2 ratio in the range of 1,90 to 2,70. While, the sinter strength of A having a little drop first and a subsequently rapid rise presents a "V" shape with CaO/SiO_2 ratio increasing. The varied tendency of A was different from that of B and does not consist with the prediction, which should be opposite to the tendency of melting temperatures as shown in Figure 4. This may be attributed to the influence of mineral texture. The precious work [1] indicated that perovskite ($CaO{\cdot}TiO_2$) was one key factor influencing the sinter strength in V-Ti sinter. The interaction

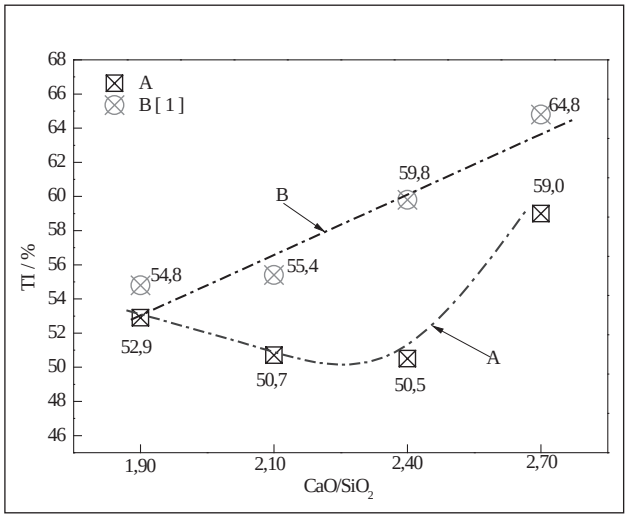
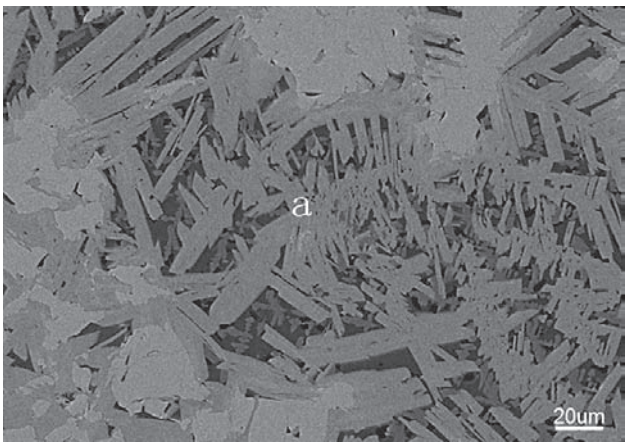


Figure 5 Tumbler strength of sinter with V-Ti ore addition at different CaO/SiO_2 ratio



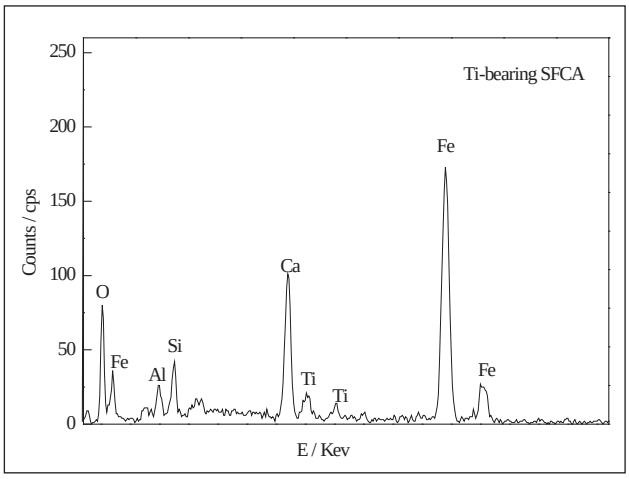


Figure 6 SEM -EDS of Ti-bearing SFCA (Sinter A at CaO/SiO_2 ratio = 2,70)

between calcium ferrite (positive effect) and perovskite (negative effect) may be the reason causing the difference between curve A and B. For sinter with 13 % V-Ti ore addition (~ 1,0 % TiO_2), the influence of TiO_2 was little compared with the influence of CaO/SiO_2 ratio, and the variation in mineral texture in sinter B caused by CaO/SiO_2 ratio and its influence in strength has been discussed in reference [1]. While for 40 % V-Ti addition (~ 2,3 % TiO_2), the negative effect of TiO_2 was larger than positive effect by increasing CaO/SiO_2 ratio at some CaO/SiO_2 ratio value. Thus, the curve A appears a "V" shape.

Additional, there is one worthy phenomenon to be mentioned, the SFCA found in sinter A (~ 2,3 TiO_2) at CaO/SiO_2 ratio 2,70 was a Ti-bearing SFCA, shown in Figure 6. The difference between Ti-bearing SFCA and ordinary SFCA and their influence on sinter strength needed a further study. Meanwhile, the mechanism of perovskite and calcium ferrite formation, their competitive mechanism and their influence on the sinter strength also still needed a further study.

CONCLUSIONS

1) Increasing the CaO/SiO_2 ratio positively influences the melting property of sinter across the range from 1,90 to 2,70, no matter with 13 % or 40 % V-Ti ore addition.

2) Due to the different of TiO_2, the influence of CaO/SiO_2 ratio increasing on sinter strength of A and B appear different curves and not the same as the prediction according to the melting property tendency of TiO_2 at ~ 2,3 %.
3) The sinter strength variations was not only influenced by melting property, but also influenced by mineral texture. The influence of TiO_2 on melting property, strength, mineral texture especial SFCA at different CaO/SiO_2 ratio needed a further study.

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Note: Song-tao Yang is responsible for English language, Shenyang, China