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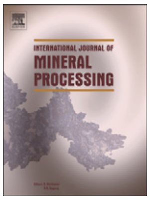

Softening and melting properties of different burden structures containing high chromic vanadium titano-magnetite

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ABSTRACT

The present work studied the softening and melting properties of different burden structures including pellet, sinter and mixed burden (pellet mixed with sinter) with a pellet ratio of 33.65%. The content of high chromic vanadium titano-magnetite in sinter and pellet was different. The experimental results indicated that the compositions of the burden have an important effect on the softening and melting properties. The softening and melting properties of pellet burden structure were improved when the high basicity sinter was added into the acid pellet forming mixed burden. The softening and melting properties of mixed burden with a pellet ratio of 33.65% were better than other burden structures. The initial softening temperature, the temperature interval of softening, the starting melting temperature, the temperature interval of melting, and maximum differential pressure were 1100 °C, 130 °C, 1250 °C, 130 °C and 15.7 kPa, respectively. By comparing the contents of Ti, V and Cr of iron that had dripped through the different burden structures, the content of valuable components (Ti 0.349%, V 0.244% and Cr 0.094%) was highest of the pig iron collected from the mixed burden.

1. Introduction

Vanadium and titanium which are widely used in metallurgy, aerospace, national defense and military fields are recognized as important strategic resources (Lv et al., 2013). The vanadium titano-magnetite is the main raw materials for producing pigment and vanadium. At the same time, many scholars have been dedicated to studying on comprehensive utilization of titanium slag to prepare titanium material (Liu et al., 2013; Zhang et al., 2007). Now, a large number of un-mined vanadium titano-magnetite with high content of chrome was discovered in Panzhihua district of china. The high chromic vanadium–titanium magnetite has the characteristics of high vanadium, high iron, high chromium and low titanium, so development of smelting high chromic vanadium–titanium magnetite has great significance for extraction of Fe, V, Ti, and Cr.

The blast furnace with an efficient countercurrent exchanger of heat, mass and oxygen is the most common means of producing hot metal. Now the process of blast furnace is the main operating means for melting vanadium titano-magnetite to separate iron, vanadium and titanium. Actually, the cohesive zone was identified as a dominant factor for blast furnace operation according to subsequent studies (Leimalm et al., 2010; Zuo, 2000). The softening and melting of iron-bearing materials including the iron oxide reduction, deformation, the formation of iron and slag and various chemical reactions in the blast furnace are quite a complex process. The burden structures made up by different iron raw materials have great effect on the position, structure and shape of cohesive zone, also the permeability of stock column.

To improve the quality of the blast furnace burden, considerable effort has been invested in studies of softening and melting properties. A number of laboratory tests have been developed to obtain information about softening and melting characteristics of iron-bearing materials. Du et al. (2010) reported that adding V–Ti pellet has effect on the burden structure of blast furnace. Several previous studies analyzing the softening and melting of lump ore, sinter, pellet and mixed burden such as those of An et al. (2013), Shatokha and Velychko (2012) and Loo et al. (2011), show that the mechanism of formation of liquid slag and metal phases is determined by the gangue amount and composition of the iron ore materials. Diao (1996) had reported that the temperature interval produced from initial dripping to the end was very large and a great differential pressure was generated in the process of melt-down. Meanwhile, the viscosity of slag increased due to the formation of Ti(C,N), which leads to the difficulties in the separation of the pig iron and slag and other issues when the vanadium–titanium magnetite was acted as ironmaking raw materials. Gan et al. (2000) has revealed that the ratio of SiO_2/TiO_2 has great effect on the softening start temperature of vanadium–titanium sinter.

In order to reveal the effect of high chromic vanadium–titanium magnetite on the melting characteristics of the burden structures,

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softening and melting tests of pellet, sinter and mixed burden have been carried out in the laboratory.

2. Materials and methods

Samples for experiments were sinter and pellet which were composed of the high chromic vanadium titano-magnetite and other common iron powdered ores. The composition of samples is shown in Table 1. Samples are 10–12.5 mm in diameter.

Fig. 1 shows the measuring device for high temperature properties. The device was mainly composed of the high temperature furnace body, gas control system, temperature control system and data recording system. The softening and melting properties of different burden structures were tested in the graphite crucible (85 mm O.D., 75 mm I.D., 120 mm height). To simulate the charging rules of the blast furnace, first the dried coke having 10–2.5 mm in diameter was placed on the bottom of the graphite crucible forming a layer thickness of 30 mm. Second samples including sinter, pellet and mixed burden with a pellet ratio of 33.65% of 500 g were charged in a graphite crucible and formed a layer of ore, whose thicknesses (H_0) were measured as the initial height of burden structures. Third the dried coke with the thickness of 15 mm was tiled on the samples. In order to guarantee the reducing gas passing through the burden efficiently and ensure the generated liquid iron and slag dripping down smoothly from the crucible, about 25 holes with the diameter of 5 mm were uniformly drilled at the bottom of the graphite crucible. To collect the liquid iron and slag dripping down from samples another graphite crucible (85 mm O.D., 70 mm I.D., 80 mm height) was placed below the upper graphite crucible. The temperature in the reaction site was monitored using an S-type thermocouple. The pressure lever with disc on the bottom was placed onto the upper coke. And when the experiment started, the displacement sensor could continuously measure the displacement changes of the pressure lever, which stands for the thickness changes of the burdens. According to the displacement changes, the shrinkage ratio would be successively calculated by the computer and is expressed as: shrinkage ratio $= H_1 / H_0 \times 100\%$, where H_0 is the original height of burden and H_1 is the displacement of the displace sensor.

Table 2 summarizes experimental conditions which consult the experiment of Chu et al. (2013). Heating rate was 10 °C/min at the temperature of less than 900 °C, 3 °C/min from 900 °C to 1020 °C and 5 °C/min from 1020 °C to the end of the experiment, respectively. Gas flow was 3 L/min of N_2 below 400 °C, then 9 L/min of N_2, 3.9 L/min of CO, 2.1 L/min of CO_2 from 400 °C to 900 °C, 10.5 L/min of N_2 and 4.5 L/min of CO from 900 °C to the end. The load of 0.5 kg/cm^2 below 900 °C and the pressure of 1.0 kg/cm^2 would be given when the temperature of burden exceeds 900 °C.

3. Results and discussion

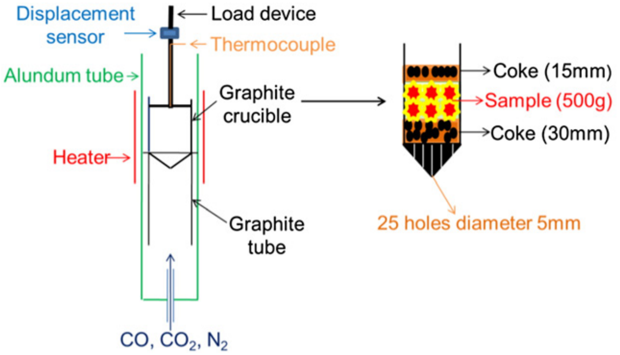

Fig. 1. Measuring apparatus for temperature properties under load.

Shigaki et al. (1990) proposed that the melt-down of the ores could determine the inner shape of the cohesive zone of the blast furnace and affect the permeability and distribution of gas there. Softening start temperature (T_4), softening temperature (T_{40}), melting start temperature (T_S), and dropping temperature (T_D) should be measured. The softening start temperature (T_4) and the softening temperature (T_{40}) are the temperatures at which the shrinkage ratio of raw material layer reaches 4% and 40% respectively. The temperature accompanying differential pressure with a massive jumping is considered as the melting start temperature (T_S). The pig iron is dripping from the graphite crucible at a certain temperature which is regarded as the dropping temperature (T_D). $T_{\Delta p}$ is the temperature at which the pressure drop of a sample has reached maximum value. Fig. 2 shows the relationships between differential pressure, contractibility rate of different burden structures and the temperature.

The volumetric expansion of the burdens took place at the temperature below 1000 °C. The maximum expansion ratios of pellet burden, mixed burden and sinter burden were 4.44%, 1.76% and 1.53% at the temperature 867 °C, 897 °C and 881 °C, respectively. The expansion mechanism of burdens is mainly caused by reduction swelling and thermal swelling (Sharna et al., 1992). However, the reduction swelling caused by a large amount of long iron whiskers formed during the reduction plays an important role. The phase transformation from Fe_2O_3 to Fe_3O_4 took placed during the reduction stage, which the crystal was converted from rhombohedron of trigonal system to cube of isometric system with the volume swelling up to 11%. The maximum expansion ratio of pellet was larger than the sinter. The result would be illustrated by comparing the content of TFe and phase composition of pellet and sinter. From Table 1 the contents of TFe were 61.86% and 46.42% in the pellet and sinter. Fig. 3 shows the ore phase compositions of the pellet and sinter. The element of Fe mainly existed in pellet in the form of Fe_2O_3 but in sinter in the form of Fe_2O_3 and Fe_3O_4. It indicates that the reduction swelling of pellet was larger than sinter caused by the phase transformation from Fe_2O_3 to Fe_3O_4. Wang and Sohn (2011) had reported that the swelling index decreased with an increase in %CaO, when the content of SiO_2 was in the range of 4% to 8%. In the present study, the content of SiO_2 was 5.25% in the pellet and 5.51% in the sinter. But the content of CaO was 0.05% and 11.7% in the pellet and

Table 1
Chemical composition of samples/(mass%).

Composition	TFe	CaO	MgO	SiO_2	TiO_2	V_2O_5	Cr_2O_3
Sinter	46.42	11.70	2.56	5.51	1.84	0.318	0.18
Pellet	61.86	0.05	0.31	5.25	2.56	0.405	0.28

Table 2
Experimental conditions and runs.

Heating up time/min	40	50	40	Above 120
Pressure/(kg/cm^2)	0.5	1.0	1.0	
Compositions and flow of gas	N_2 100% 3 L/min	N_2 60% 9 L/min CO 26% 3.9 L/min CO_2 14% 2.1 L/min	N_2 70% 10.5 L/min CO 30% 4.5 L/min	
Heating rate	10 °C/min to 400 °C	10 °C/min to 900 °C	3 °C/min to 1020 °C	5 °C/min to the end

Symbols	Meaning	Units
T_4	The initial softening temperature	°C
T_{40}	The end of softening temperature	°C
T_S	The melting start temperature	°C
T_D	The melting end temperature	°C
$T_{\Delta p}$	The temperature at which the pressure drop is maximum value	°C
T_{40}–T_4	The softening temperature interval	°C
T_D–T_S	The melting temperature interval	°C
P_{max}	The maximum value of pressure drop	Pa
$S = \Delta P \times \Delta T$	The integral of pressure drop function in melting temperature interval	Pa × °C