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Effect of carbon species on the reduction and melting behavior of boron-bearing iron concentrate/carbon composite pellets

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Abstract: Iron nugget and boron-rich slag can be obtained in a short time through high-temperature reduction of boron-bearing iron concentrate by carbonaceous material, both of which are agglomerated together as a carbon composite pellet. This is a novel flow sheet for the comprehensive utilization of boron-bearing iron concentrate to produce a new kind of man-made boron ore. The effect of reducing agent species (i.e., carbon species) on the reduction and melting process of the composite pellet was investigated at a laboratory scale in the present work. The results show that, the reduction rate of the composite pellet increases from bituminite, anthracite, to coke at temperatures ranging from 950 to 1300°C. Reduction temperature has an important effect on the microstructure of reduced pellets. Carbon species also affects the behavior of reduced metallic iron particles. The anthracite-bearing composite pellet melts faster than the bituminite-bearing composite pellet, and the coke-bearing composite pellet cannot melt due to the high fusion point of coke ash. With anthracite as the reducing agent, the recovery rates of iron and boron are 96.5% and 95.7%, respectively. This work can help us get a further understanding of the new process mechanism.

Keywords: iron ore pellets; iron ore reduction; boron; bituminite; anthracite; coke

1. Introduction

Boron, which is one of the less available elements in the earth, is an important substance used widely in chemical industry, ceramics, glass, metallurgy, medicine, war industry, aerospace, and nuclear applications [1]. The traditional boron resource, szaibelyite ore, of China is going to run out, and its grade becomes much lower than before. It is estimated that the boron mine gap in China will be about 1.5-2.0 million tons by 2020. There is 0.28 billion tons of low-grade ludwigite deposit in Liaoning and Jilin Province in northeast China, which accounts for 57.88% boron reserve and 1% iron reserve in China. This low-grade ludwigite is the main alternate resource of szaibelyite ore, which is a kind of complex ore of iron, boron, magnesium, and uranium, but cannot be directly utilized as a single ore by traditional methods because of its low grade. The average boron and iron contents of the ore are 7.23wt% and 30.65wt%, respectively [2].

At present, the boron-bearing iron concentrate and boron concentrate can be obtained by an ore dressing method from the crude iron ore. The boron concentrate is a good raw material for the boron industry after activation roasting. The boron and iron separation of the boron-bearing iron concentrate is the key problem. It can be realized through a selective reduction and melting method, and then, the boron-bearing pig iron and boron-rich slag can be obtained. The pig iron and activated boron-rich slag are raw materials for steel making and borax production. This is one of the most appropriate flow sheet for the comprehensive utilization of low grade ludwigite.

Based on the iron nugget process (i.e., ITmk3) [3-6] and the characteristics of boron-bearing iron concentrate, the authors proposed a novel flow sheet of comprehensive utilization of boron-bearing iron concentrate by carbon-bearing composite pellet reduction and melting technology (BCCRM). The preliminary exploration has been completed, but the reduction-melting mechanism and relevant factors have not been studied deeply [7]. The main purpose of the present work is to study the effect of carbonaceous species on the reduction-melting behavior of the boron-bearing iron concentrate/carbon composite pellet and get a further understanding of the mechanism.

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2. Experimental

2.1. Raw materials

Boron-bearing iron concentrate used in this study was obtained from Dandong, Liaoning Province, China. The chemical composition of the complex ore sample is shown in Table 1. Most of the iron ore concentrate particles (98%) were below 200 mesh in size. The mineralogical analysis of the concentrate was investigated by X-ray diffraction (XRD). The result indicated that the main crystalline phases were magnetite (Fe_3O_4), szaibelyite ($Mg_2(OH)$-$[B_2O_4(OH)]$), and chrysotile ($Mg_3[Si_2O_5](OH)_4$).

Three kinds of carbonaceous materials (anthracite, low volatile bituminite, and coke) were used as the reducing agents in the experiment. The chemical compositions of the reducing agents are listed in Table 2. The fineness of the reducing agents is 100% passing 0.5 mm.

Table 1. Chemical composition of boron-bearing iron concentrate **wt%**

B_2O_3	TFe	MgO	SiO_2	Al_2O_3	FeO	CaO	P	S
6.90	47.20	19.20	5.32	0.15	18.90	0.34	0.020	0.16

Note: TFe stands for the content of total Fe in the ore sample.

Table 2. Proximate and ash analysis results of the reducing agents **wt%**

Carbonaceous material	Proximate analysis				Ash analysis				
	FC_d	V_d	A_d	S	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO
Anthracite	81.40	6.40	11.10	0.34	46.10	32.16	9.51	4.26	0.65
Bituminite	74.30	12.48	12.50	0.21	45.24	23.35	9.54	6.56	1.92
Coke	86.20	1.64	12.16	0.69	49.70	31.63	6.44	4.49	0.80

Note: FC_d stands for the fixed carbon, V_d the volatile matter, A_d the ash, and S the total sulphur.

2.2. Experimental procedure

The experiment included isothermal reduction and high-temperature isothermal reduction-melting. The ore/anthracite composite pellet, ore/bituminite composite pellet, and ore/coke composite pellet were corresponded to the symbols of P_A, P_B, and P_C, respectively.

For the isothermal reduction experiment (i.e., the first set of experiments), the pellets were made using boron-bearing iron concentrate and three different kinds of reducing agents as the raw materials with a fixed carbon/reducible oxygen mole ratio (C/O) equal to 1.0. The agglomeration process was performed through a manual ball press under the pressure of 15 MPa. The dry green pellet presented a column shape. The experiment was carried out in a thermogravimetric system with a shaft $MoSi_2$ resistance furnace, under a high purity N_2 flow of 3 L/min as the purge gas, one pellet at each run. The pellet was put in a corundum crucible, and the crucible was suspended by Fe-Cr-Al-Mo wire, attached to an electronic balance, and heated at different temperatures. The course of reaction was expressed in terms of reaction fraction (f), which is defined as the weight loss measured at a given time (t) with respect to the maximum possible weight loss.

Some samples were cooled carefully and cut, and the cross section was examined in a scanning electronic microscope with an energy dispersive spectroscope (SEM-EDS).

For the isothermal reduction-melting experiment (i.e., the second set of experiments), the pellets with the C/O of 1.2 were used. The pellet was put into the corundum crucible and heated at 1400°C. To improve the carburization of the pellet and obtain the slag sample, a certain quantity of graphite granules was put under the pellet. The schematic diagram of the experimental apparatus is depicted in Fig. 1.

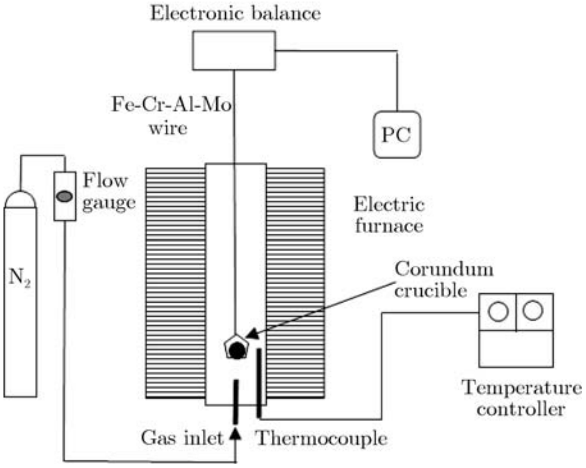

Fig. 1. Schematic diagram of the experimental apparatus.

3. Results and discussion

3.1. Isothermal reduction experiments

The reduction behaviors of composite pellets containing different kinds of reducing agents at the relatively low temperatures are shown in Fig. 2. It can be observed that the reduction rate is greatly improved with the temperature increasing from 950 to 1300°C. The values of reaction fraction gradually increase with the time prolonging. The reduction finishes within ~20 min for P_B at 1300°C. It is clear that the reduction rate of P_B is higher than that of P_A and P_C. The reduction reaction of P_C presents the slowest in the experiment, especially at the low temperature range. The heating temperature should be higher than 1100°C to get a faster reduction rate. When the temperature is high, the effects of temperature and carbon species on the reduction rate become smaller.

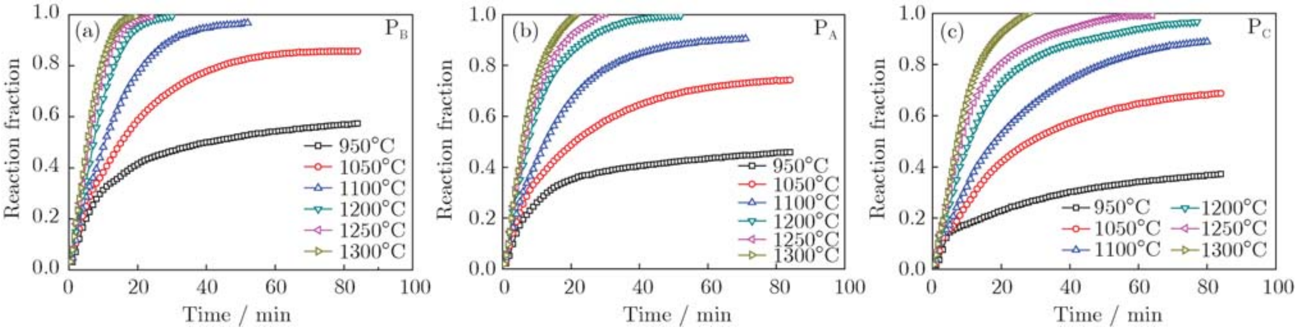

Fig. 2. Effect of carbon species on the reduction of boron-bearing iron concentrate: (a) bituminite; (b) anthracite; (c) coke.

The reactions in the composite pellets include the direct reductions and indirect reductions. The indirect reductions are shown as

$$3Fe_2O_3 + CO = 2Fe_3O_4 + CO_2 \tag{1}$$

$$Fe_3O_4 + CO = 3FeO + CO_2 \tag{2}$$

and

$$FeO + CO = Fe + CO_2 \tag{3}$$

accompanied by the Boudouard reaction of

$$C + CO_2 = 2CO \tag{4}$$

The direct reductions are shown as

$$3Fe_2O_3 + C = 2Fe_3O_4 + CO \tag{5}$$

$$Fe_3O_4 + C = 3FeO + CO \tag{6}$$

and

$$FeO + C = Fe + CO \tag{7}$$

At the initial stage, the carbothermic reduction is dominated by the direct reduction, whose product breaks the contact between iron ore and coal particles. Then, the direct reduction reaction may stop [8]. At present, it is generally agreed that the reduction of iron oxides by carbon proceeds through the gaseous intermediates CO and CO_2. Therefore, in a viable reduction process, the indirect reduction and the carbon solution loss reaction should dominate the reduction rate. It is reasonable to believe that the Boudouard reaction plays an important role in the reduction process.

The effect of carbon species on the reduction rate of the pellet is mainly related to their reactivity with CO_2, i.e., Boudouard reaction. Generally speaking, the reducing agent with a higher volatile content has a better reactivity, which is good for reduction. The reactivities of three kinds of pulverized reducing agents were assessed by thermogravimetric method. The result is shown in Fig. 3. Bituminite contains the highest volatile matter of 12.48%, and it has the best reactivity. However, coke is just on the opposite. As shown in the derivative thermogravimetric (DTG) curve of Fig. 3, the reactivity of three reducing agents differs much at low temperature range, and the difference gradually disappears with the increase in temperature. The thermogravimetric (TG) results agree well with the reduction experiments.

To guarantee a high reduction rate, the reactivity of the reducing agent, which is in a close relation to its nature and temperature, should be as high as possible. From DTG results shown in Fig. 3, the maximum reactivity points of the three reducing agents are between 1150°C and 1200°C. Theoretically, the reduction rate of the pellet is high at the temperature above 1150°C; thus, the reduction begins to proceed at a relatively fast speed based on the gaseous intermediates CO and CO_2.

From results shown in Fig. 2, it can be concluded that bituminite is an appropriate reducing agent for the reduction of the boron-bearing concentrate/carbon composite pellet in the present experiment condition, due to its relatively higher volatile content. The reduction reaction is fast in the bituminite/ore pellet, so the energy consumption should be low in practical industrial production.

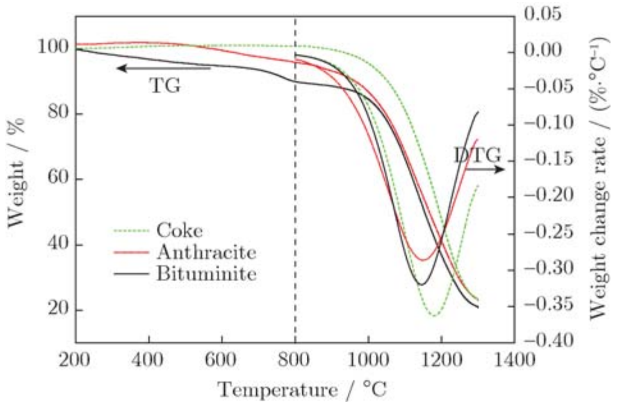

Fig. 3. Reactivity thermogravimetric curves of the pulverized reducing agents.

3.2. Microscopic examination of the reduced pellets

Fig. 4 presents the cross-sectional SEM images (backscattered electrons) of the final reduced anthracite-bearing composite pellets at 950, 1100, 1200, and 1300°C. The chemical analysis was carried out by EDS. When the pellet is reduced at 950°C for 88 min, the final reaction fraction is about 0.46. The main phases of the whole pellet are wustite and gangue. It can be seen that the sample presents very little and small metallic iron particles on the edge of wustite. For the pellet reduced at 1100°C, the final reaction fraction is about 0.90. Metallic iron can be easily observed and aggregates to a spherical shape. The diameter of iron particles are about 10-15 μm. When the pellets complete the reduction at 1200 and 1300°C, the final reaction fraction is nearly equal to 1.0. The metallic iron particles grow up and join together, forming a chain or net structure.

Fig. 5 shows the SEM images (backscattered electrons) of the final reduced composite pellets bearing the different reducing agents at 1200°C. It can be seen that the structure of the reduced bituminite-bearing composite pellet is denser than those bearing anthracite and coke. The metallic iron particles of the reduced bituminite-bearing composite pellet randomly scatter throughout. However, the metallic iron particles reduced by coke aggregate to a round chain shape. The metallic iron microstructure reduced by anthracite presents an intermediate state between the bituminite-bearing and coke-bearing composite pellets.

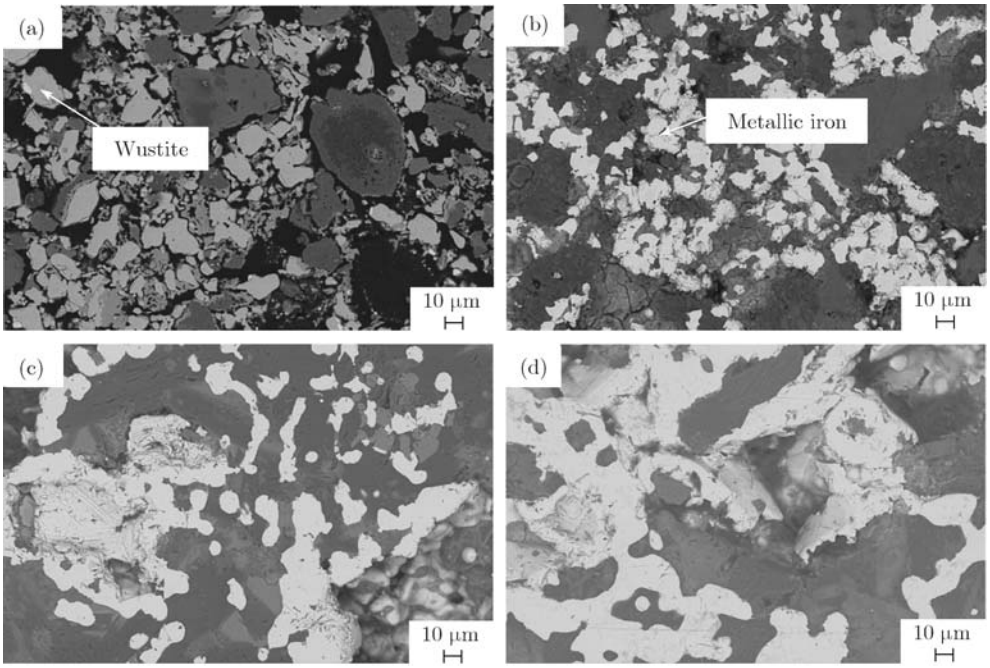

Fig. 4. SEM images (backscattered electrons) of the final reduced anthracite-bearing composite pellets: (a) 950°C; (b) 1100°C; (c) 1200°C; (d) 1300°C.

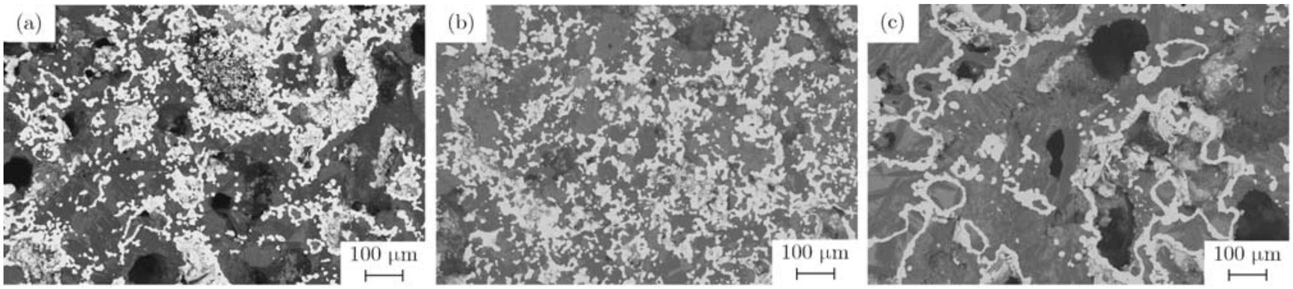

Fig. 5. SEM images (backscattered electrons) of the final reduced pellets at 1200°C: (a) P_A; (b) P_B; (c) P_C.

Based on SEM analysis, it can be concluded that the microstructure of the final reduced pellet mainly depends on reduction temperature, and carbon species also have very important effect. The metallic iron particle becomes coarse with the increase of temperature. When the pellet is heated above 1200°C, the nonmetallic material in the final reduced pellet formed by the iron gangue, reducing agent ash, and unreduced iron oxide separates into two phases, the light gray one and the dark gray one. The light gray phase contains silicon, magnesium, iron, and oxides. The dark gray phase contains lots of magnesium, oxides, and a little of silicon. Boron is a kind of light element, and cannot be analyzed out by EDS. According to the mass balance, the boron element mainly gathers in the dark gray phase. The iron content in the light gray phase decreases with the increase of reduction temperature.

3.3. Isothermal reduction-melting experiments

The iron making process generally consists of four stages, heating stage, reduction stage of iron ore, carburization of reduced iron, and melting stage of carburized iron and slag. The iron nugget formation process from the carbon composite pellet also includes the typical four stages. Iron ore carbothermic reduction can be performed well with the advantage of pulverized carbonaceous material and iron ore agglomerated together, especially using high reactivity coal as the reducing agent. Actually, the most important stages in the iron nugget process of the boron-bearing concentrate/carbon composite pellet are the stages of carburization and iron-slag melting separation due to the high content of MgO in the boron-bearing concentrate.

There is a good deal of literatures on the carburization and iron-slag melting separation in the iron nugget formation process [9-13]. It becomes clear that, the slag composition is not only related to their own melting, but also affects the carburization and consequently the melting separation of molten slag and iron-carbon alloys. There is a complicated interrelation between slag melting and carburization. Most importantly, the iron and slag separation depends on the liquidus temperature of slag, and the carburization can be improved through an extra method.

In the view of Iguchi and Endo [14], the carburization ability of carbonaceous material decreased from graphite, coke, to coal char. Therefore, in the present work, the carburization ability increased from bituminite, anthracite, to coke. The different kinds of contained carbonaceous materials also influenced the carburization of reduced iron, though the pellet was positioned on the layer of graphite granule. The beginning time of melting decreased with the increase in carbon content, i.e., C/O, in the previous study [7].

The liquidus temperature of the B_2O_3-MgO-SiO_2 slag system forming from stable gangue minerals in the composite is about 1450°C [15], and it provides the possibility of iron and slag melting separation. When the heating temperature is 1400°C, the anthracite-bearing composite pellet begins to melt at 10 min, and the bituminite-bearing composite pellet begins to melt at 11 min. The morphology of iron nugget and slag separation of the anthracite-bearing composite pellet reduced for 15 min is shown in Fig. 6. It can be observed that the iron nugget and slag are separated in a clean manner. The nugget and slag are both in a relatively regular shape. B_2O_3 is difficult to be reduced in the experimental condition and concentrated with the gangue minerals, forming the so-called boron-rich slag. The chemical composition of the iron nugget and boron-rich slag obtained from the anthracite-ore composite pellet is listed in Tables 3 and 4, respectively. The B_2O_3 content is as much as 20wt% in the slag, and it makes the slag meet the requirement of grade I szaibelyite ore [16]. The recovery rates of iron (in iron nugget form) and boron are 96.5% and 95.7% (in slag form), respectively.

Fig. 6. Morphology of iron nugget and slag separation (anthracite, 1400°C, 15 min).

Table 3. Chemical composition of the iron nugget (anthracite, 1400°C, 15 min) wt%

C	Si	Mn	B	S	P	Fe
3.57	0.018	0.038	0.065	0.27	0.079	Residual

Table 4. Chemical composition of boron-rich slag (anthracite, 1400°C, 15 min) wt%

MgO	B_2O_3	SiO_2	Al_2O_3	FeO	CaO
50.72	20.01	19.44	2.62	2.02	1.66

However, the coke composite pellet cannot melt, even having no melting trend at 1400°C. From the view point of carburization, the phenomenon is incredible. When the reduction temperature increases from 1400 to 1450°C, the molten iron nugget has separated from the unmolten slag. The melting point of slag made from the coke-bearing composite pellet may be much higher than 1450°C. The most possible reason for the different phenomenon may be that, the ash fusion points of reducing agents are different. The ash fusibility of the three kinds of carbonaceous materials is shown in Table 5. The ash consists of about 6wt% material in the slag, which is mainly made from the gangue (i.e., stable oxides) of boron-bearing iron concentrate, the ash of carbonaceous material, and the unreduced iron oxide. The fusion points (i.e., HT) of bituminite ash and anthracite ash are 1320°C and 1350°C, respectively. The fusion point of coke ash is much higher than 1500°C. The high fusion point ash represses the melting of slag, but the low fusion point ash may improve it. The pellet, with the mixture ratio of bituminite and coke by mass of 1.1, begins to melt when reduced for 11 min at 1400°C, and the morphology is almost the same with the separation product of bituminite and anthracite composite pellets. On the other hand, the melting behavior also becomes worse at 1400°C if 1wt% CaO is introduced into the anthracite-bearing composite pellet. Consequently, the slag in the present study is very sensible to the high fusion point material due to its high content of MgO. To get a clean separation of iron nugget and slag, the reducing agent with the ash fusion point lower than 1400°C can be preferred, and no other high fusion point materials should be added in.

Table 5. Ash fusibility of the carbonaceous materials °C

Carbonaceous material	DT	ST	HT	FT
Anthracite	1300	1320	1350	1380
Bituminite	1105	1350	1375	1395
Coke	1460	>1500	—	—

Note: DT is the deformation temperature, ST the softening temperature, HT the hemispherical temperature, and FT the fluid temperature.

According to the reduction-melting experiment results, the anthracite-bearing composite pellet makes iron and slag separate earlier than the other two type pellets. On one hand, the differences in reduction rate of three kinds of pellets are smaller at high temperature. On the other hand, the carburization rate of anthracite is higher than that of bituminite. The carburization stage is more important than the reduction stage in the iron nugget process. Therefore, anthracite is a more appropriate reducing agent in the experiment.

4. Conclusions

(1) The reduction rate of the boron-bearing iron concentrate/carbon composite pellet increases with the increase of reactivity of the carbonaceous materials with CO_2 and reaches the reduction end in less than 30 min at 1300°C. The bituminite composite pellet proceeds the fastest at all the temperatures ranging from 950 to 1300°C, and the coke composite pellet proceeds the slowest. The low volatile bituminite is an appropriate reducing agent for the direct reduction of boron-bearing iron concentrate.

(2) The microstructure of the final reduced pellet mainly depends on reduction temperature. When the temperature is higher than 1200°C, slag components in the pellet can separate into two phases. Carbon species also have an important effect on the microstructure.

(3) The anthracite composite pellet melts faster than the bituminite composite pellet. The anthracite composite pellet begins to melt at 10 min, and the bituminite composite pellet begins to melt at 11 min. The coke composite pellet cannot melt even at 1450°C due to the high fusion point of coke ash. Therefore, the ash fusion point influences the melting behavior of the composite pellet greatly, and it should be lower than 1400°C in the iron nugget process.

Acknowledgements

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