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Investigation of solidification mechanism of fluorine-bearing magnetite concentrate pellets

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ABSTRACT

The compressive strength of the roasted fluoride-containing iron ore pellets reached to 2463 N/P at roasting temperature 1080 °C for 10 min with appropriate preheating conditions. However, its compression strength drastically dropped no matter increasing or decreasing the roasting temperature and time. Unfortunately, the narrow suitable roasting temperature range seriously affects the normal pellets productions, while the low compressive strength of pellets limits their application in the blast furnace. In the present study, The SEM-EDS, TG-DSC techniques, and thermodynamic software were adopted to systematically investigate the roasting behaviors of fluoride-bearing iron concentrate pellet and the formation mechanism of liquid phases in the pellets during the roasting process. Furthermore, according to the EDS results and the phase diagram analysis, the low-melting-point phase $Ca_4Si_2F_2O_7$ was generated with the existence of fluorine and $Na(K)AlSi_3O_8$ was formed with the existence of alkali metal. These low-melting-point phases can react with the $CaAl_2Si_2O_8$, $CaSiO_3$, SiO_2, and CaF_2 to form the complex eutectics which had lower melting points. Briefly, the excessive amount of liquid phases in pellet generated from the fluorine and alkali metals primarily caused the poor roasting properties of the fluoride-containing pellet.

1. Introduction

As the increasing consumption of the iron and steel productions, the need for iron ore resources also increases [1]. Thus, many special iron ore resources including vanadium titanomagnetite ore, high phosphorus oolitic hematite ore, and fluorine-bearing magnetite are exploited and investigated in order to be used for producing iron productions [2–5]. In China, most of the iron productions are produced by the blast furnace process. The dominant blast furnace burden contains sinter and pellets [6,7]. Moreover, the pelletizing process is very widely used, and the roasted pellets are durable and easy to handle, which performs well in the blast furnace due to their good bed permeability (solid state) and reducibility [8]. Pellets become an indispensable component of the blast furnace burden due to their large production and good quality [9].

Fluorine-bearing magnetite is a famous and special iron ore which is mainly found in Baiyun'Ebo and Huanggang regions in Inner Mongolia, China [10–13]. The fluorine-bearing magnetite is used to produce iron and steel productions after sintering or pelleting processes, where is mainly utilized in Baotou Steel [14]. However, during the production of fluorine-bearing iron concentrate pellets in Baotou Steel, serious problems such as narrow range of suitable roasting temperature, low compression strength, easy adhesions and poor softening performance have emerged. The fluorine also has a negative impact on the composition and microstructure of pellet [15], and the existence of fluorine can promote the generation of fusible phases and destruct the refractory materials in the blast furnace [16,17].

The previous researchers considered that the existence of fluorine and alkali metals were the major reason of the problems in the pellets production [18]. In order for the utilization of fluorine-bearing iron ore, many researchers studied for its beneficiation for removal of fluorine and adding additives into pelletization. The results of beneficiation tests showed that the fluorine content in the iron concentrate could be reduced to 0.39 wt% [19]. After the beneficiation process, the serious problems during the pellets production were reduced but still has not been solved thoroughly [18]. In addition, Xu et al. [20] investigated the effects of MgO on the properties of fluorine-bearing iron concentrate pellets and showed that the compression strength of roasted pellets and preheated pellets were improved when the content of MgO was increased from 0.83 wt% to 2.0 wt%, and its strength also increased as the increase of the preheating time. While the results from Wu et al. [21] indicated that the pelletizing performance was improved with the addition of dolomite powder. The compression strength of pellets decreased with the increase of MgO content, which was opposite with the results of Xu et al. [20]. Moreover, it also showed that the compression strength of the pellets decreased while the roasting temperature continued to increase. Briefly, it can be seen that the fundamental solidification mechanism of the fluorine-bearing iron concentrate pellet is not clear. Thus, it is essential to investigate its solidification mechanism for the utilization of this special iron ore.

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Table 1
Chemical composition of fluorine-bearing iron concentrate (wt%).

TFe	FeO	SiO_2	Al_2O_3	CaO	MgO	MnO	F	K_2O	Na_2O	P	S
61.91	26.36	4.93	1.74	3.04	0.51	0.46	1.56	0.290	0.156	0.074	0.13

Table 2
Chemical composition of bentonite (wt%).

TFe	SiO_2	Al_2O_3	CaO	MgO	K_2O	Na_2O	FeO	P	S	Ig
2.36	54.58	9.90	5.18	2.72	0.86	1.68	0.22	0.083	0.072	14.46

Table 3
Grain size distribution and specific surface area of fluorine-bearing iron concentrate.

<0.074 mm/wt%	0.045–0.074 mm/wt%	<0.045 mm/wt%	Specific surface area/$cm^2.g^{-1}$
85.19	14.67	70.52	1683.37

Table 4
Grain size distribution of bentonite (wt%).

<0.074 mm	0.045–0.074 mm	<0.045 mm
26.77	19.89	53.33

In the present paper, the roasting properties of the fluorine-bearing iron concentrate pellets, the phase compositions, and the elements distributions were investigated. The SEM-EDS and TG-DSC techniques were adopted to investigate the formation of liquid phases in the pellets. The mechanism of liquid phase formation was also discussed with related phase diagrams. The findings will provide a technical basis for developing techniques or methods to improve the roasting properties of fluorine-bearing iron concentrate pellets.

2. Materials and methods

2.1. Materials

The fluorine-bearing iron concentrate and bentonite used in this study were provided by Huanggang Mining Company (Inner Mongolia, China). The bentonite was adopted as the pelletizing binder in this study. The chemical compositions of the fluorine-bearing iron concentrate and bentonite are listed in Tables 1 and 2. As shown in Table 1, the fluorine-bearing iron concentrate contains 1.56 wt% fluorine, whose total iron grade is as high as 61.91 wt% and its K_2O and Na_2O are 0.29 wt% and 0.156 wt%, respectively. The size distribution of the fluorine-bearing iron concentrate and bentonite are shown in Tables 3 and 4. The specific surface area of fluorine-bearing iron concentrate is 1683.37 $cm^2.g^{-1}$.

The microstructure of fluorine-bearing iron concentrate was observed by SEM and shown in Fig. 1. It is clearly seen that there are lots of fine particles and a number of angular fragments on the surface of large grains. In general, this kind of microstructure is beneficial to the pelletizing of iron concentrate.

2.2. . Methods

2.2.1. Balling

The balling test was taken as follows, firstly, 5 kg of fluorine-bearing iron concentrate was blended with a given amount of bentonite (1.75 wt%) and water. After mixed thoroughly, the mixtures were balled into 10–15 mm green pellets in a laboratory disc pelletizer, which had 1000 mm diameter and 200 mm edge height. The green pellets were dried in an oven at 110 °C for >4 h to obtain dry balls.

2.2.2. Pre-heating and roasting

The dry green pellets of about 10–12 mm in diameter were chosen for the following preheating and roasting experiments. The preheating and roasting tests were carried out in a horizontal electrically heated tube furnace with an internal diameter of 50 mm. Fig. 2 shows the schematic diagram of the horizontal tube furnace. The preheating temperature and roasting temperature were controlled by an intelligent temperature controller, that is to say we can setup the target temperature and temperature rising speed. The dry balls were placed into a corundum crucible, pushed into the preheating zone slowly and preheated under the planned conditions. The preheated pellets were removed from the furnace and cooled in the air, or directly driven into the roasting zone for roasting as planned. At last, the roasted pellets were taken out and cooled naturally in the air [22].

The compression strengths of cooled preheated and roasted pellets were determined by an LJ-1000 material experimental machine [22] and the compression strength of each experiment was from an average value of 20 pellets. Furthermore, part of the cooled roasted pellets of each test was stochastically chosen for the SEM-EDS analysis and the chemical composition analysis.

2.2.3. Analysis and characterization

The structure, phase composition and elements distributions of the samples were characterized by a scanning electron microscope (SEM, Quanta200, FEI, Netherland) equipped with energy dispersive analysis of X-ray (EDAX). The TG-DSC experiment was conducted with a Thermal Analyzer (NETZSCHSTA 449 C, Germany) at a heating rate of 10 °C/min from 20 °C to 1200 °C in argon gas, and the gas flow rate was

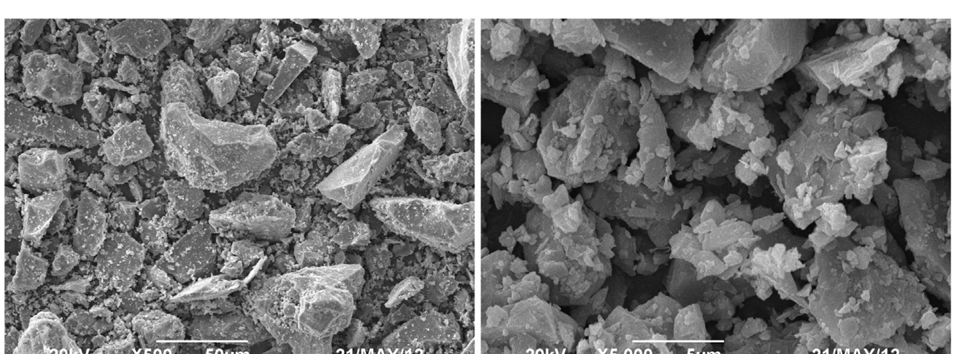

Fig. 1. SEM micrographs of fluorine-bearing iron concentrate.