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Research Paper

Crystallization properties of molten blast furnace slag at different cooling rates

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HIGHLIGHTS

- Crystallization properties are crucial for recycle usage of blast furnace slag.
- The critical cooling rate was experimentally investigated.
- The crystallization kinetics was analyzed.
- The phase change under different isothermal temperatures was discussed.

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ABSTRACT

Blast furnace slag, as a potentially active gelling material, is an important functional material for cement concrete making. However, the effective utilization of blast furnace slag depends on its amorphous formation ability in the cooling process with phase change. In the present study, single hot thermocouple technique is employed to investigate the crystallization properties of molten blast furnace slag under various cooling rates based on isothermal cooling and continuous cooling experiments. The slag with basicity of 0.934 is adopted and its characteristic temperatures are obtained. The crystal growth rate increases and then turns to drop with an increase in the isothermal temperature. The critical cooling rate of the testing blast furnace slag is about 9 °C/s. The results of continuous cooling experiments indicate that the critical cooling rate is about 6 °C/s. Meanwhile, shortened crystal incubation time and lower crystal onset temperature are reached with increasing cooling rate. The generated crystal in the testing blast furnace slag is Gehlenite showing columnar or plate-like structures.

1. Introduction

Blast furnace slag (BF slag) is one of the main solid by-products during iron and steel making process. Generally, it has an output of about 0.3 ~ 1.0 ton/ton pig iron [1] and contains a great deal of high-grade sensible heat accounting for 10% of waste energy in steel industry and 28% of high-temperature waste heat since it is exhausted with critically high temperature of about 1450–1550 °C in molten state [2]. Effective waste heat recovery from the molten BF slag is now a major task faced by the iron and steel making industry. Up to date, the mainstream technique for the BF slag treatment is known as water quenching, in which the slag is directly poured into cooling water. The subsequent fast cooling rate not only results in powerful thermal stress to crush the slag flow into granules but also induces the phase transformation toward amorphous glass inside the slag granules. Consequently, most of water quench slag having amorphous glass is further used as the raw materials of cement [3–5] because of cementitious activity of glass. However, the direct bleed-off of cooling water and emission of vapor during water quenching process gives rise to huge waste of water and residual heat. This definitely limits its application prospect due to growing shortage of water source and energy source.

Aiming at the waste heat recovery and water saving, a prospectively substitutional technology called heat recovery with dry granulation has been promoted for the BF slag [6], in which the molten BF slag is firstly granulated and then air is used as heat transfer medium to achieve the heat recovery from the slag. In the last decades, researchers worldwide have devoted to the dry granulation heat recovery technology and various dry granulation techniques including rotating drum process [7], air blast process, rotating cup atomizer (RCA) process [8] have been developed and experimentally investigated. Unfortunately, no matter what kind of granulation technique is adopted, a severe question is confronted, that is, the cooling rate by air is quite lower than that by water quenching. The existed researches have evidenced that phase transformation in the molten material depends on its cooling rate. Fast cooling

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results in glass with high activity in the BF slag [9] while various crystals appear at a lower cooling rate [10], thereout, the minimum cooling rate required for glass transition is named as critical cooling rate [11]. As thus, the dry granulation heat recovery technology for BF slag is rising to a challenge of failure in slag vitrification due to quite lower air cooling rate. Moreover, according to the national standard of China, the BF slag can be used for cement production only when the content of amorphous glass in slag is more than 70% [12]. Therefore, to promote application of the dry granulation heat recovery technology and to provide valuable guidance to system design as well as subsequent utilization of BF slag, it is crucial to understand the crystallization properties of BF slag under various cooling rates and to find out the critical cooling rate.

The existing methods for investigating crystallization properties of materials mainly include differential scanning calorimetry (DSC) [13,14], viscosity–temperature curve method [15] and single hot thermocouple technique (SHTT) [16,17]. The DSC method is of a high measurement accuracy while with a limited cooling rate range. The fastest cooling rate it can realize is less than 30 °C/min. The viscosity–temperature curve method takes the temperature of curve inflection point as the crystallization temperature. However, the factors affecting the actual liquid viscosity are quite many during the cooling process, giving rise to an uncertain crystallization temperature. Furthermore, both the DSC method and the viscosity–temperature curve method fail to observe in situ the crystallization evolution of the experimental material. Hot thermocouple technique is a new method developed in recent decade with the characteristics of intuitive observation, rapid response, high accurateness as well as easy operation. It can not only achieve a variety of cooling ways and cooling rates but also realize the in situ observation of the crystallization progress. The maximum cooling rate it can reach is 150 °C/s, which is higher than the critical cooling rate of most oxide slags. Consequently, SHTT attracts growing attention of the researchers in material field to visually investigate the crystallization process of different slags. Liu et al. [17] and Kölbl N et al. [18] adopted SHTT to study the crystallization properties of mold flux slag at different cooling rates. The crystallization properties of metallurgical slag was investigated by Klug et al. [19] using SHTT and the critical cooling rates of CaO-Al$_2$O$_3$ artificial slag and CaO-SiO$_2$ artificial slag were obtained. SHTT was also used by Jung et al. [20] to study the crystallization properties of CaO-Al$_2$O$_3$-MgO-FeO artificial slag. Their results indicated that the increase in the content of MgO led to higher crystallization temperature and longer crystal incubation time. Moreover, the crystal phase obviously changed when FeO content was more than 15 mass%. Furthermore, some other investigations [21–23] have been carried out basing on SHTT to study the effects of slag compositions such as the change of Al$_2$O$_3$/SiO$_2$, Na$_2$O, Be$_2$O$_3$ and TiO$_2$.

It is noted that only a few researches focused effort on the crystallization properties of BF slag under different cooling rates, especially using SHTT. Hu et al. [24] studied crystallization behavior of Perovskite in the synthesized high-titanium-bearing BF slag using confocal scanning laser microscope with cooling rate of 30 K/min. The continuous cooling crystallization kinetics of a molten BF slag was studied by Zhang et al. [25] using different models based on DSC data. Qin et al. [26] obtained the critical cooling rate of BF slag and carried out a kinetics study of crystallization process. Li et al. [27] focused on the crystallization behavior of Rutile in the synthesized Ti-bearing blast furnace slag at different isothermal temperatures using SHTT. Kashiwaya et al. [16] performed SHTT experiments to analyze the effect of cooling rate on the crystal phase transformation. Sun et al. [28] propose a multi-stage control method for waste heat recovery from high temperature slags based on SHTT. Obviously, the previously limited studies have not well uncovered the detailed crystallization properties of BF slag with various compositions under different cooling conditions, such as crystallization evolution, the crystal growth rate as well as the crystallization kinetics. Considering the request from the dry granulation heat recovery technology for the BF slag, in the present study, the SHTT method was adopted to investigate the crystallization process of molten BF slag by conducting both the isothermal cooling experiments and continuous cooling experiments. The effect of cooling rate on the detailed crystallization properties including crystal growth rate, crystal phases and morphologies as well as critical cooling rate were discussed.

2. Experimental apparatus and methods

2.1. Experimental apparatus

Experimental apparatus of the SHTT method is shown in Fig. 1. The SHTT system consisted of a thermocouple system and an observation system, as shown in Fig. 1a. The thermocouple system was composed of a thermocouple, a furnace and a temperature controller. The thermocouple was formed by welding the resistance wires of PtRh30 and PtRh6 with the diameter of 0.5 mm, as shown in Fig. 1b. The semicircular region at the top of the thermocouple was the melting region of testing medium. Moreover, the thermocouple played the roles of both the heating element and the temperature measuring element during experiments. The heating and the cooling processes were controlled by the temperature controller. The observation system was composed of a microscope, a camera, a processor and a display. The evolutions of the crystalline phase in the molten BF slag over cooling process were recorded by the microscope and the camera under different cooling rates. Under light illumination, the molten BF slag will appear specular

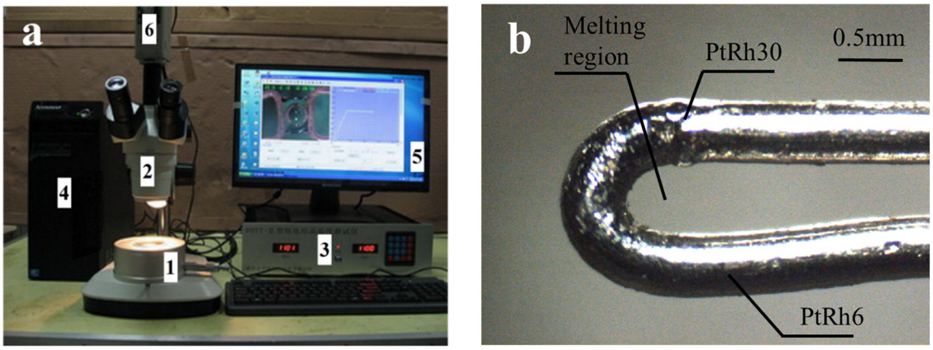

Fig. 1. Experiment apparatus of SHTT method. (a) Experimental system 1. Furnace. 2. Microscope. 3. Temperature controller. 4. Processor. 5. Display. 6. Camera. (b) Pt–Rh thermocouple model.