Fuel 223 (2018) 360–365

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Prediction on crystallization behaviors of blast furnace slag in a phase change cooling process with corrected optical basicity

Bin Ding[b], Hong Wang[a,b,*], Xun Zhu[a,b,*], Xian-Yan He[b], Yu Tan[b], Qiang Liao[a,b]

[a] Key Laboratory of Low-grade Energy Utilization Technologies and Systems, Chongqing University, Chongqing 400030, China
[b] Institute of Engineering Thermophysics, Chongqing University, Chongqing 400030, China

ARTICLE INFO

Keywords:
Blast furnace slag
Crystallization behaviors
Corrected optical basicity
Correlation

ABSTRACT

Up to now, centrifugal granulation and heat recovery technology is the most feasible one to achieve the simultaneous harvest of high-temperature waste heat and high-quality glassy blast furnace (BF) slag. For the phase change cooling process, both the slag components and the cooling rate play dominate roles in the solidification and crystallization behaviors of BF slag, which guides the determination of operational condition in the centrifugal granulation and heat recovery system. Therefore, an accurate prediction on crystallization behaviors of BF slag with various components is convenient to confirm the optimal cooling condition and is crucial to popularize the technology. In the present study, the corrected optical basicity (Λ_{corr}) is adopted to represent the slag component. As the results, a series of correlations between crystallization behaviors (including critical cooling rate, phase type, crystal phase content and crystallization temperature region) and the corrected optical basicity are obtained by fitting the experimental data. Moreover, the correlations are mainly available in the range of Λ_{corr} = 0.643–0.681, and the theoretical results fit well with the experimental data.

1. Introduction

Iron-making industry plays a significant role in the economic development in many developing countries. The production of pig iron leads to a plenty amount of blast furnace (BF) slag, which are the mineral residues of iron preparation in the blast furnace. For instance, in 2015, the output of pig iron in the world was more than 1153 million tons accompanying with nearly 384 million tons of BF slag production [1]. BF slag contains significant amounts of high-grade thermal energy, owing to the high slagging temperature (about 1500 °C) [2]. This means that the total heat carried by BF slag is equivalent to about 22.3 million tons of standard coal [3], which is the last part that fails to be recovered in the iron-making industry.

For the treatment of molten slag, the cooling rate plays a dominant role in the atomic structure of BF slag. Specifically, glassy phase with an open atomic structure presents in the slag once the cooling rate is fast enough to prevent the ions arranging themselves. Moreover, the glassy slag can be adopted to produce cement, which is attributed to the similar component and good hydration activity. Whereas, the ions have adequate time to arrange themselves in a slow cooling rate, resulting in the appearance of crystal phase. The hydration activity of the crystal slag is limited by the compact structure. Therefore, it has usually been used as aggregate for road construction and landfilling purposes. At present, the melting BF slag is quenched by water to obtain the high value-added glassy phase. Unfortunately, it undergoes many shortcomings, such as thermal energy waste, water consumption and toxic gases (SO_2 and H_2S) emission [4,5].

Up to now, many dry heat recovery technologies characterized by slag granulation and air cooling have been energetically developed to solve the mentioned problems, such as mechanical crushing method [6,7], air blast method [8] and centrifugal granulation method [9–11]. Among them, centrifugal granulation method is the most feasible one due to the compact structure, reliable operation, high heat recovery efficiency and low power consumption [9–12]. In the centrifugal granulation and heat recovery system the melting BF slag is broken into small droplets with a diameter of 1–5 mm by a high-speed rotating cup/disk, then the small droplets are fast cooled by air [13,14]. However, the cooling air with a high speed is essential to form glassy phase, due to the low heat transfer ability of air. It is inevitable to debase the quality of the recovered heat and increase the energy consumption of fan. Therefore, determining an optimal speed of cooling air is crucial to a win-win result of the BF slag utilization, waste heat recovery and energy consumption. It has to point out that the component of BF slag varies in different Iron works [8] and presents significant effect on the crystallization behaviors [15,16]. Correspondingly, the determination of the cooling air optimal speed should be based on the BF slag

---

* Corresponding authors at: Key Laboratory of Low-grade Energy Utilization Technologies and Systems, Chongqing University, Chongqing 400030, China.
E-mail addresses: hongwang@cqu.edu.cn (H. Wang), zhuxun@cqu.edu.cn (X. Zhu).

https://doi.org/10.1016/j.fuel.2018.03.038
Received 14 November 2017; Received in revised form 23 February 2018; Accepted 6 March 2018
0016-2361/

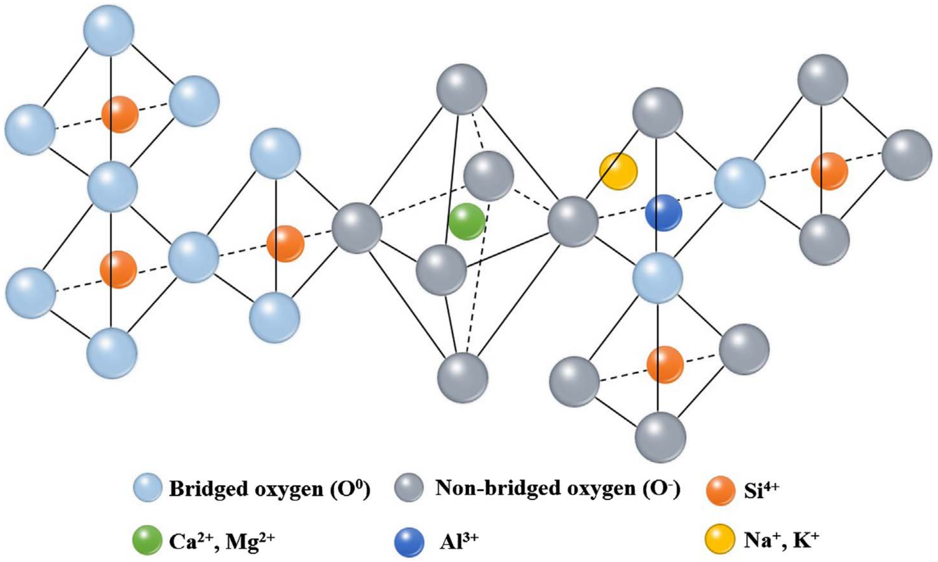

Fig. 1. Schematic drawing of the BF slag melt structure [27].

component. Therefore, a model to predict the crystallization behaviors of BF slag with various components is convenient to confirm the optimal cooling condition and is crucial to popularize the centrifugal granulation technology.

The characterization of the crystallization behaviors of slag mainly consists of critical cooling rate, phase type of the precipitated crystals, crystallization temperature region and the crystal phase content evolution under various cooling rates. However, up to now, the prediction of slag crystallization behaviors has mainly focused on the critical cooling rate. For example, Esfahani et al. [17] established a correlation for estimating the critical cooling rate from the BF slag liquidus temperature and viscosity. Unfortunately, the popularization of the empirical correlation was limited by the great difficulty and high cost in acquiring the liquidus temperature and viscosity. By contrast, Qin et al. [18] provided a correlation for predicting the critical cooling rate from the binary basicity and the mass percent of the MgO and Al_2O_3. That means the application sphere of the correlation was quite limited, owing to ignore the effect of trace elements (for example, TiO_2). Furthermore, it has to point out these correlations were suitable for the BF slag under isothermal/continuous cooling condition. However, the crystallization behaviors of BF slag in a phase change cooling process were quite different, owing to the interplays between phase change heat transfer and crystal phase growth [19–21]. Specifically, the critical cooling rate of BF slag in a phase change cooling process was about 50% of that under the continuous cooling condition [22]. Unfortunately, up to now, an overall prediction of BF slag crystallization behaviors in a phase change cooling process has not been reported.

In the present study, the relationship between slag component and crystallization behaviors was investigated based on the results from the existed researches [19–26]. Moreover, the corrected optical basicity was adopted to represent the slag component. Therefore, a series of correlations between crystallization behaviors (including critical cooling rate, phase type, crystal phase content and crystallization temperature region) and the corrected optical basicity were obtained.

2. Acquisition of BF slag crystallization behaviors

In the existed experimental work, a directional solidification apparatus was adopted to explore the crystallization behaviors of BF slag in a phase change cooling process [19], where the crystallization region was obtained by the thermocouples placed inside the BF slag. Moreover, the crystal phase content and phase type of sliced samples from different locations were acquired by the X-ray diffraction (XRD) test. In addition, the characteristic temperatures (liquidus temperature and glassy transition temperature) were obtained by the differential scanning calorimetry (DSC) test. Based on these, the coupling relationships between the crystallization behaviors and the phase change cooling process were found out. Moreover, the critical cooling rate, evolutions of crystal phase content and phase type, crystallization temperature region were then obtained. Furthermore, the effect of Al_2O_3 content, MgO/Al_2O_3 ratio and CaO/SiO_2 ratio on the crystallization behaviors were discussed [20–22]. The content of CaO, SiO_2, Al_2O_3 and MgO in the existed researches was 36.12%–42.14%, 30.10%–36.41%, 7.21%–16.99% and 7.21%–14.41%, respectively. Corresponding the binary basicity (CaO/SiO_2 ratio) and MgO/Al_2O_3 ratio was 1.0–1.4 and 0.5–2.0. Moreover, the content of the trace elements (such as TiO_2, Fe_2O_3, MnO, Na_2O, K_2O, etc.) was about 6%. The tested slag components content covers most of the iron and steel enterprises in China.

3. Parameters to represent the components

BF slag is a multicomponent mixture, it is essential to find a parameter to synthetically represent the varying components. Generally, the BF slag mainly consists of acid oxide (SiO_2), basic oxide (CaO, MgO) and amphoteric oxide (Al_2O_3). Moreover, an acid usually acts as an oxide ion (O^{2-}) acceptor, whereas, the base acts as an oxide ion donor. Therefore, the acid, basic and amphoteric characteristics can be reflected by the oxides to form acids and bases in the slag melts [27]. Fig. 1 illustrates the simplified drawing of the BF slag melt structure. One can see that, the structure of SiO_2 is a three-dimensional array with each Si^{4+} surrounded by four bridging oxygen (O) arranged tetrahedrally and acts as the network former. By contrast, the network modifiers (Ca^{2+}, Mg^{2+}, etc.) tend to break up silicate network and depolymerize the melt by forming non-bridging oxygen (NBO, O^-). Moreover, the amphoteric oxides (Al_2O_3) play dual roles as network formers or network modifiers depending on the BF slag basicity. Specially, in the basic BF slag Al^{3+} can fit into the polymeric chain of SiO_2 but need to maintain charge balance. That means, a Na^+, K^+ or half of a Ca^{2+} setting near the Al^{3+} is essential.

At present, the number of O^- to O ratio (NBO/T), the optical basicity (Λ) and the corrected optical basicity (Λ_{corr}) are the main parameters to represent the structure of the melting BF slag [28]. Specifically, the NBO/T is a measure of the depolymerization of the slag. However, it failed to differentiate the effects of different cations on the silicate structure. That is, for the BF slag with a same NBO/T the content of main component is various. By contrast, the optical basicity is used to