Decomposition behavior of limestone in early converter slag

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ABSTRACT

Better understanding the decomposition and dissolution behaviors of limestone under steelmaking condition is essential to evaluate the possibility of directly using limestone instead of lime in converter. In this paper, the decomposition behavior of limestone in early converter slag including the decomposition kinetics and microstructure of the produced lime layer were studied, and the effects of slag temperature and stirring speed introduced to the slag bath were examined. Kinetic analysis based both on shrinking core model and dimensionless chemical-heat transfer number (N_{CH}) showed that the limestone decomposition at 1300–1400 °C was a mixed control of chemical reaction and heat conduction through the lime layer. Slag temperature has a significant influence on the decomposition process while the stirring speed plays a minor role when a critical stirring intensity is reached. The obtained effective thermal conductivity varied from 0.21 to 2.51 W m^{-1} K^{-1} and the chemical reaction rate constant ranged between 7.9×10^{-4} and 6.3×10^{-3} m s^{-1}. The produced lime layer has less grain size and apparent porosity than the calcined one. Besides, smaller limestone particle and more heat supply to the converter bath are recommended to accelerate the limestone decomposition in early converter slag.

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1. Introduction

It is well known that lime plays a significant role in slagging during steelmaking process, but directly using limestone instead of lime as slagging material in converter steelmaking process has been paid great attention with the demand for lower production cost and emission reduction in steelmaking industries. Although there are still some debates [1–6] about the decomposition and dissolution behaviors of limestone under the condition of converter steelmaking, many industrial trials [7–11] on limestone slagging mode have been conducted in China.

Compared to the conventional lime steelmaking mode, adding limestone directly into the converter [12,13] is thought to be favorable for energy conservation and emission reduction because both the decomposition and dissolution reactions of limestone would take place in converter, and thus CO_2 emission and energy waste such as the sensible heat of higher-temperature lime could be reduced. Furthermore, the significant amounts of CO_2 generated by limestone decomposition are supposed to play as oxidant for the oxidation reactions in liquid iron bath, leading to the possible reduction of oxygen consumption during converter blowing process [14].

Since an efficient steelmaking process requires rapid assimilation of lime by molten slag, the high-quality lime with high reactivity and porosity is required. As for the limestone calcination in shaft or rotary kiln, the calcined lime with fine crystal grain is considered to be porous

at the early stage, but the lime activity would decrease due to the further grain recrystallization and sintering reaction at high temperature for several hours [15–17]. Therefore, an ideal situation is that the freshly generated CaO is exposed to the surrounding slag immediately to promote a fast dissolution. In the limestone steelmaking mode, the limestone is speculated to decompose to the lime quickly at steelmaking temperature and then the produced lime would dissolve into the molten slag easily due to its high activity [18]. However, the reported results [1] conducted in converter slag at 1600 °C showed that the decomposition reaction controlled by heat transfer was slow and a dense CaO layer would greatly hinder the dissolution into the slag. In addition, the local temperature drop in converter bath caused by the intensive endothermic reaction of limestone decomposition may result in a slower slagging rate [19]. Therefore, more careful considerations should be given to the decomposition and dissolution behaviors of limestone under converter steelmaking condition.

Over the years, thermal decomposition of limestone has been the subject of intensive study and the decomposition rate at 900–1200 °C was found to be controlled by chemical reaction and (or) heat and mass transfer [20–22]. However, there was less study reported on the limestone decomposition at steelmaking temperature. Deng et al. [1] investigated the limestone decomposition in converter slag at 1600 °C and concluded that the decomposition reaction controlled by heat transfer was slow and the produced CaO layer was very dense at the surface. In considering the fact that the temperature ranges from 1300 °C to 1400 °C at the early stage of converter steelmaking process, the decomposition evolution of limestone is supposed to be different from that at 1600 °C or those under the calcination conditions. Moreover, the

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microstructure of the lime decomposed from limestone at 1300–1400 °C, including crystal size and porosity, would also differ from the reported results at 1600 °C, which would further affect the dissolution rate of the freshly produced lime into converter slag. Therefore, the decomposition behavior of limestone at the initial slag-making stage needs to be examined carefully.

In the present work, the kinetics of limestone decomposition in early converter slag was studied and the effects of slag temperature and stirring speed to the slag bath were carefully examined. Furthermore, the microstructure characteristic of the produced lime layer was also investigated. The motivation of this paper is to provide more scientific evidences for better understanding the limestone evolution under the converter steelmaking condition.

2. Experimental

2.1. Preparation of raw materials

Raw limestone lumps were cut into the cubic shape samples in the size of $10 \times 10 \times 10$ mm. CaO powder used for the synthesized slag was prepared by calcining the reagent grade $CaCO_3$ powder at 900 °C for 24 h. Wustite (FeO_x) was synthesized by sintering the equimolar mixture of reagent grade Fe_3O_4 and electrolytic iron powder in an iron crucible at 1200 °C under $CO-CO_2$ atmosphere ($CO/CO_2 = 1$) for 24 h. Thereafter, the early converter slag (synthesized slag) was prepared by mixing CaO, FeO_x and reagent grade SiO_2 powders thoroughly, and then the mixture was pressed into a tablet and charged into a platinum crucible for the decomposition experiment. The composition of the synthesized slag was 21.7 mass% CaO, 43.5 mass% SiO_2, and 34.8 mass% FeO_x, and its melting temperature was confirmed to be about 1190 °C [23]. The composition and CaO/SiO_2 ratio of the synthesized slag were chosen based on a slag formation route with high iron oxide.

2.2. Experimental setup and procedure

Fig. 1 presents the schematic of the experimental apparatus. A vertical electric furnace with $MoSi_2$ heater and alumina reaction tube was employed. The platinum crucible (outer diameter: 50 mm, inner diameter: 45 mm, height: 70 mm) was placed in the constant temperature zone (about 200 mm in length) of the reaction tube. The slag

Fig. 1. Experimental apparatus.

temperature was controlled by a PtRh30-PtRh6 thermocouple located at the bottom of the crucible. Based on the stirring energy density supplied for unit weight liquid during basic oxygen furnace (BOF) process, a corundum rod with the rotating speed range of 100–200 rpm (100, 150, 200 rpm) was used to stir the molten slag during the reaction process. Moreover, other decomposition experiments at 0 and 50 rpm stirring speeds were also carried out to investigate the effect of stirring on the decomposition process.

About eighty grams of the synthesized slag were charged into the crucible and then heated up to the desired temperature, namely, 1300 °C, 1350 °C and 1400 °C respectively. High purity argon gas was introduced from the bottom of the reaction tube and led out from the top. After the slag was melted completely, the prepared limestone sample was inserted into the molten slag to react for different time. Here, the reaction time was defined as the one that the limestone sample was kept in the slag. After reacting for 30 to 180 s, the limestone sample was taken out rapidly and quenched in liquid nitrogen.

The quenched sample was cut along the longitudinal section. The dimensions of the residual limestone were measured by light microscopic and the sample microstructure was observed by scanning electron microscopy (SEM) equipped with energy-dispersive spectroscopy (EDS). In addition, due to the difficulties encountered in measuring the porosity of the produced lime by means of mercury porosimetry, the apparent porosity was determined based on the image analysis and processing method. Firstly, an appropriate threshold value of grey scale was obtained by segmenting the SEM image and counting the grey-level distribution. Then the pores in the SEM image were distinguished from background with the appropriate threshold value. The area percentage (P_A) of the pores in the view fields could be obtained by analyzing and tracking the boundary morphology of all the pores in the two dimension image. Finally, the apparent porosity (volumic porosity, P_V) was semi-quantitatively determined according to Eq. (1). In this work, the apparent porosity was the mean value based on the measured results of five different view fields for the same limestone sample.

$$P_V = (P_A/(1-P_A))^{3/2} \tag{1}$$

3. Results and discussion

3.1. Shape and microstructure of limestone decomposing in early converter slag

Fig. 2 presents the cross sections of the samples decomposed in the slag at 1350 °C for different decomposition time. According to the EDS analysis results, the dark grey zone is confirmed to be the undecomposed limestone whereas the surrounding light grey part is the decomposed lime. It is observed that the limestone sample nearly keeps its original cubic shape during the decomposing process, and on the other hand, the undecomposed limestone core is basically in a spherical shape and diminishes in size gradually with decomposing time. The boundary between the residual limestone and lime layer is very clear. In addition, although no explosion of limestone cube was observed, some cracks across the sample were found as a result of greater pressure gradient caused probably by CO_2 generation.

The microstructures of limestone samples decomposing at different slag temperatures for 180 s are shown in Fig. 3. Fig. 3(a) and (c) show the SEM images of the $CaCO_3$ and CaO coexisting zone at 1300 °C and 1350 °C respectively, and it can be found that fine CaO grains grow around the $CaCO_3$ grains. Moreover, no coexisting zone of $CaCO_3$ and CaO at 1400 °C for 180 s is observed because the complete decomposition time of limestone sample at 1400 °C is about 160 s. Fig. 3(b), (d) and (e) present the CaO zone at 1300 °C, 1350 °C and 1400 °C respectively. The grain size of the produced CaO is about 0.63–0.82 μm at 1300 °C, while those are 0.74–0.75 μm at 1350 °C and 0.66–0.84 μm at 1400 °C respectively. No remar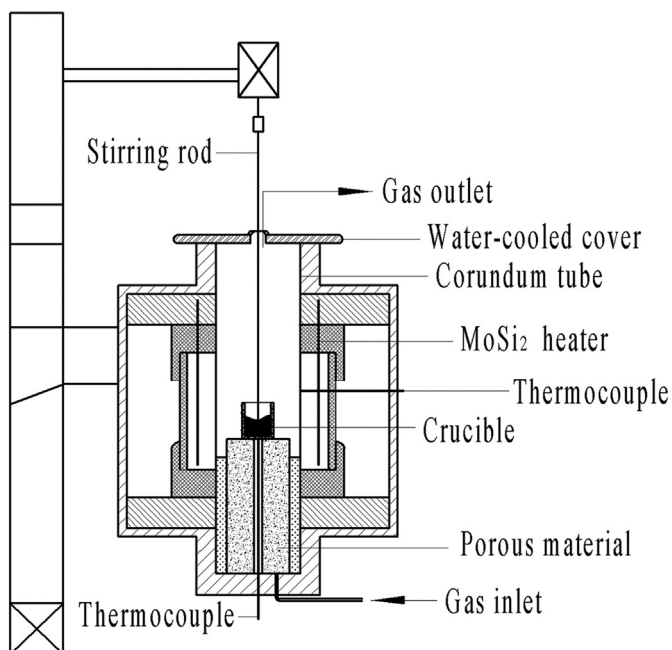kable effect of slag temperature on