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Influence of isothermal temperature and cooling rates on crystallization characteristics of a synthetic coal slag

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HIGHLIGHTS

- An *in-situ* observation was performed to record the crystallization process of a synthetic coal slag.
- Temperature Time Transformation (TTT) and Continuous Cooling Transformation (CCT) diagrams of the slag were constructed.
- With decreasing temperature or increasing cooling rates, the crystals became finer and smaller.
- Based on the classic JMA equation, the crystallization kinetics and mechanism were determined.

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ABSTRACT

In slagging gasifiers, the crystallization ratio and crystal morphology are of great importance to fluidity of slag. Although increasing attention has been paid to the influence of crystallization on viscosity, few studies have investigated crystallization kinetics in slag melts due to challenges associated with high temperature and experimental complexity. In order to gain an understanding of crystallization characteristics, an *in-situ* observation Single Hot Thermocouple Technique (SHTT) system was set up and direct observation of the crystallization process was conducted. After completely melting, the slag would form a film as a result of its surface tension on the tip of the thermocouple. When the slag reached a certain degree of undercooling, crystals would precipitate from the homogenous melt. The crystallization ratio was quantitatively determined by taking advantage of the crystal color difference from the surroundings. A synthetic slag was produced from five oxides, with composition 38.4SiO_2–14.8Al_2O_3–20.8CaO–19.1Fe_2O_3–6.9MgO, which is modeled on a real Chinese coal ash slag with low liquidus temperature and distinct crystallization characteristics. The crystallization characteristics of this synthetic slag were studied under isothermal temperatures and continuous cooling rates. Temperature Time Transformation (TTT) and Continuous Cooling Transformation (CCT) diagrams of the slag were constructed and a fundamental understanding of crystallization influenced by temperature and cooling rates was obtained. With decreasing temperature or increasing cooling rates, the crystals became finer and smaller. At lower temperatures with high degrees of undercooling the incubation time was shortened and the crystallization ratio increased. The influence of cooling rate was not significant until it exceeded 80 °C/min. Then the growth of crystals was greatly suppressed by high cooling rates, even appearing glassy when it surpassed the critical cooling rate. Based on the classic JMA equation, the crystallization kinetics and mechanism were determined. The Avrami parameter n indicates that at temperatures higher than 1200 °C, interfacial reaction mainly controlled the crystallization process, while at lower temperatures, diffusion was dominant. The crystals formed in different temperature regions may be different phases, which can also be predicted by Factsage Software, but needs further validation.

1. Introduction

During high temperature gasification of coal, minerals in the ash form a molten slag layer along the sidewalls of gasification chamber. It is important to understand and control the fluidity of this slag to ensure proper operation of the gasifier. Slagging gasifiers typically operate at temperatures between 1325 and 1600 °C, and crystallization of some phases in the slag is possible in this temperature range. Crystals can change the solid–liquid ratio and liquid composition, which in turn affects slag viscosity. The typical feature of crystalline slag is a rapid rise in viscosity with decreasing

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temperature, which is associated with the temperature of critical viscosity (T_{cv}) [1–3]. If the fluidity of the slag is not good enough, it will cause slag blockage of the reactor exit, and may even force shut down of gasifier. In addition, crystallized phases on the surface or within pores of the reactor sidewalls can influence properties such as thermodynamic stability and thermal conductivity. Crystalline phases may also contribute to excessive wear of refractory walls or excessive heat loss through water-cooled walls.

During operation of a high temperature gasifier, complex metastable conditions are locally created inside the gasifier as fresh slag is continuously deposited on the wall and flows down. Predictions of crystallization dynamics in slags are essential to understand the flow characteristics of slag. Despite increasing attention on crystals in coal slags, the effects of factors such as temperature and cooling rate [4–6] on crystallization behavior have not been extensively studied. Several researchers [5,11] have investigated the influence of quenching temperature on crystallization of coal slags through semi-quantitative analysis of XRD to determine the volume of crystals. But more quantitative methods developed for study of other types of slags with similar composition can also be applied. DTA or DSC is a useful method to study crystallization characteristics and has been widely applied to other kinds of slag under continuous cooling rates [7–10]. But both DSC and the quenching method are limited in that they do not allow direct observation of the crystallization process. Nakano et al. have performed valuable *in-situ* research related to coal slags, which has improved the understanding of crystallization of coal-petcoke slag with V_2O_5 using a Confocal Scanning Laser Microscope (CSLM) [12,13]. Based on their results, they created a Temperature Time Transformation (TTT) diagram for the coal-petcoke mixture, which provides a more fundamental understanding of transformation process. Another useful diagram to provide information of crystallization affected by cooling rates is the Continuous Cooling Transformation (CCT) diagram [14,15] constructed for blast furnace slag. The information in TTT and CCT diagrams reveals the influence of temperature and cooling rates on crystallization for a specific slag.

In the study reported here, we used a special *in-situ* Single Hot Thermocouple Technique (SHTT), which has been successfully applied for crystallization studies with mold slag or blast furnace slag [16–19] to construct the TTT and CCT diagrams. We used this technique to explore the influence of temperature and cooling rates on morphology of crystals for a synthetic coal slag. The crystallization ratio was subsequently determined, which provided insight into the kinetics and mechanism of crystallization.

2. Experimental

2.1. Synthetic slag samples

Coal ash comprises many different metals, mostly in the form of oxides. Since there are impurities and complex phases in real coal ash, various investigators have attempted to simplify the system by using surrogate materials [20,21]. We prepared synthetic slag from five pure oxides which comprise more than 95% components in real coal ash. Five analytical reagents were blended to create synthetic coal ash with the composition $38.4SiO_2$–$14.8Al_2O_3$–$20.8CaO$–$19.1Fe_2O_3$–$6.9MgO$. The reagents were mixed with pure ethyl alcohol and dried at 100 °C for more than 10 h. The dried slag was then ground in an agate mortar to less than 200 μm, achieving better homogeneity. The composition of slag was chosen to represent a real Chinese slag, which was selected for its low melting point and obvious crystallization peak during Differential Scanning Calorimetry (DSC). Factsage 6.3 with two databases, FToxid and FactPS, was used to predict the solid phases in an inert Ar atmosphere. Fig. 1 is the cumulative graph of predictions using the "Equilib" module from 1000 °C to 1500 °C with a 20 °C interval from which we can determine that the liquidus temperature of this synthetic slag is less than 1400 °C.

2.2. Experimental procedures

2.2.1. Differential scanning calorimetry

Preliminary experiments were performed in advance to select a slag composition with strong crystallization characteristics. The sample was measured for its heat release during continuous cooling period in Mettler Toledo TGA/DSC. No more than 20 mg of synthetic slag sample was placed in a Pt crucible, which was then heated up to 1500 °C and held for 20 min under Ar atmosphere with a 100 ml/min flow rate. After the sample completely melted, it was cooled at 10 °C/min to 800 °C. If crystals precipitated, the resulting heat release would display an exothermic peak on the curve.

2.2.2. Single hot thermocouple experiments

The SHT technique is an established experimental procedure that combines the hot thermocouple technique with video observation and image analysis to reveal useful information such as morphologies and solidified fractions directly. Fig. 2 shows the schematic of the apparatus which includes the hot thermocouple and controller, the observation system and computer data acquisition system. The hot thermocouple with 1 mm diameter welded into a circle or U shape is located below the microscope. The thermocouple controller can simultaneously measure temperature while heating a thermocouple. The computer has an image capturing system that records the change of sample through a CCD camera and software that displays experimental conditions such as temperature and time. This system allows direct observation of the crystallization process and can achieve a high cooling rate up to 100 °C/s.

During the experiments, about 10 mg of slag was melted at 1500 °C for 60 s to eliminate bubbles, and a homogeneous film formed on the tip of the thermocouple due to surface tension. A glass lid was placed on top to construct a closed space to reduce the influence of gas flowing across the film. The sample could be cooled to specified temperatures at different cooling rates to produce a CCT diagram. To construct the TTT diagram, the melting slag was rapidly cooled at 100 °C/s to keep a glassy state and then maintained at a constant temperature for 300 s to observe the transformation process. The temperature profiles set in the experiments are shown in Fig. 3.

2.2.3. Calculation of extent of crystallization and crystallization kinetics

Images were analyzed by a computer program to quantitatively evaluate the volume fraction of crystals. The program is based on

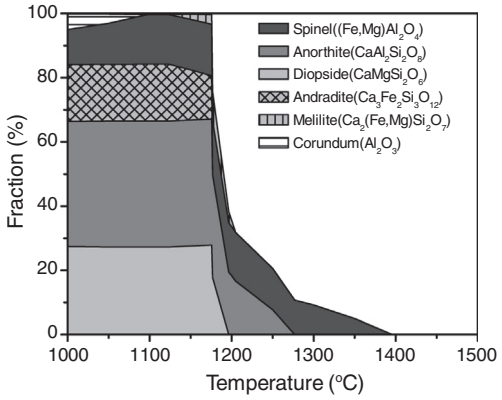

Fig. 1. Factsage predictions of crystalline phase formation of the synthetic slag.