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Crystallization characteristics of a coal slag and influence of crystals on the sharp increase of viscosity

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HIGHLIGHTS

- A "C" shape TTT diagram of a real coal slag was constructed.
- Compositions can change after a long time heat treatment with the elements Si, Na, K, S lost.
- The crystallized spinel distributed in the slag with irregular shape and formed a network resulting in the sharp increase of the viscosity.

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ABSTRACT

In entrained flow gasifiers, crystallization inside the liquid slag can cause an increase of the slag viscosity, affecting flow along the wall and resulting in operational challenges. In the study reported here, a real Chinese ash was investigated for its crystallization behavior as well as the viscosity. Differential Scanning Calorimetry (DSC) and the Single Hot Thermocouple Technique (SHTT) were combined to measure the crystallization temperature and observe the crystallization process, constructing the temperature-time transformation (TTT) diagram. The ash was heated and then quenched to determine the crystalline phases. Unlike the synthetic slag mixed with oxides, the compositions of real ash had some variations after the long time heat treatment, which may attribute to the reducing minerals in the ash. Under inert atmosphere, gehlenite and spinel were the main crystals in cooling process. While under reduced atmosphere, the amount of crystals decreased especially gehlenite. Spinel was widely distributed inside the slag with irregular shape forming a network which caused the sharp increase of viscosity. The temperature of critical viscosity (T_{cv}) was around 1310 °C corresponding to the spinel proportion calculated about 20%.

1. Introduction

In the entrained flow gasifier, after the fuel was gasified and burned out, the ash would form a molten slag layer along the wall. And crystallization inside the slag is a problem that should not be ignored which can cause significant change of viscosity. The crystallization process can be influenced by the chemical compositions as well as conditions such as temperature and cooling rates. In our former study, the influence of conditions and components such as Si, Al, Ca, Fe has been investigated through synthetic slags [1,2]. We have got a general understanding of the crystallization process. However, the real coal ash contains various minerals such as quarz, metakaolinite and other lower amounts of K and Na. During the heating process, the minerals and oxides can decompose and react with each other forming new minerals [3,4]. There may contain some inactive minerals such as quarz or boehmite in the ash which change the effective components for crystallization [4]. Whether the real slag has the same features with the synthetic slag needs deeper investigation. Some researchers investigated the influence of temperature, residence time as well as heat treatment on crystalline phases and proportion [5,6]. But little study involves in the in-situ observation of the crystallization process of coal ashes.

In addition, the temperature of critical viscosity (T_{cv}) is an important criterion which indicates an abrupt change in the viscosity–temperature curve. It is assumed that T_{cv} marks the division between crystal-affected viscosity and no crystal influence viscosity. Hoy found that the drifted crystals had stronger influence than the stationary and when the solid proportion reached 50%, the slag

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displayed as a non-Newtonian fluid [7]. Vargas reviewed former conclusions as the crystal volume fractions in the range 25–55% could cause sharp rheological changes and for irregular shapes the limit may be as low as 5% [8]. However, Song et al. [9] found the T_{cv} has a linear relationship with liquidus temperature (T_{liq}) while Kong et al. [10] regarded the T_{cv} has a direct relationship with the rate of solid formation rather than the absolute proportion. So in this study, a real coal ash was investigated for its crystallization characteristics to get the TTT diagram as well as the influence of crystals on the sharp increase of viscosity.

2. Experiments

2.1. Slag samples

The representative Chinese coal, Kuangou coal from Xinjiang Province of China was used in the experiment. It was firstly crashed and milled to less than 200 μm and then completely incinerated in a muffle oven of which the procedure was set as rising to 500 °C within 30 min and maintaining for another 30 min, then to 815 ± 10 °C and keeping for 1 h. Weight the final mass twice to make sure that the coal was completely burned out. Chemical compositions of the ash were analyzed by X-ray fluorescence (XRF) spectroscopy shown in Table 1.

The viscosity of the coal ash was measured by the HAAKE viscometer in Chinese Coal Research Institute according to the standard test procedure for the viscosity of coal ash DL/T 660-2007. The temperature was firstly heated to 1500 °C at 10 °C/min and kept for 5 min. Then the motor of axis was started and the viscosity data was obtained every 10 °C interval from 1460 °C to the lowest temperature at which the rotor could hardly rotate. The data was measured three times at each temperature point and got the arithmetic average mean value. The atmosphere was kept under weak reducing atmosphere 60/40 CO_2/CO. The viscosity curve is shown in Fig. 1. It can be derived of the T_{cv} as 1315 ± 10 °C.

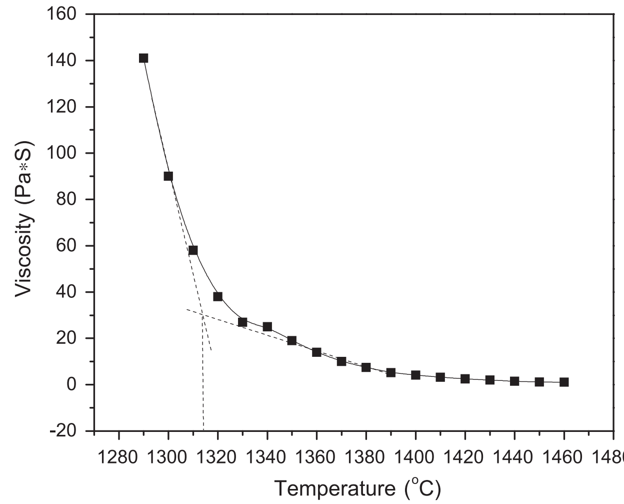

Fig. 1. The viscosity–temperature curve of Kuangou slag.

2.2. Experimental methods

2.2.1. Differential scanning calorimetry

Mettler Toledo TGA/DSC 1 was used to acquire the DSC signal. For each experiment, a sample of approximately 20 mg was placed in a Pt crucible with an identical crucible as reference. The samples were heated up to 1500 °C under 100 ml/min Ar and kept molten for 10 min. Then they were cooled to 800 °C at 10 °C/min to find the crystallization peak.

2.2.2. Single hot thermocouple technique

The single hot thermocouple technique can achieve a high cooling rate up to 100 °C/s, which can keep the sample in a glassy state when cooling. Thus the isothermal crystallization process can be studied by in-situ observation. The slag was firstly melted and then cooled under different temperatures between 1000 °C and 1400 °C. To construct the TTT diagram, the melting slag was rapidly cooled at 100 °C/s to keep a glass state and then kept at constant given temperature for 300 s to see the transformation process. Details of this method as well as the temperature profiles can be found in our previous article [14] which had been used to investigate the crystallization characteristics of synthetic slags.

2.2.3. Water-quenching method

Water-quenching method is a way to solidify the structure in melting slag at high temperature and then study the quenching slag at room temperature, which is common in the phase diagram investigation. The solidification was achieved in a high temperature furnace up to 1600 °C which has been described in our former study [2]. It can quench the samples at desired temperature and time very quickly in case of phases change during cooling. Kuangou ash placed in a 99 porcelain crucible was heated up to 1500 °C and kept for 40 min and then cooled at 10 °C/min to desired temperature. In case of the reaction of ash with alumina crucible wall, a 0.3 mm molybdenum flat was put inside the crucible which could reduce the overflow of slag along the wall and gathered more products. The atmosphere can be switched freely between N_2 and 60/40 CO/CO_2. In this experiment, as the sharp increase of viscosity occurs at round 1300 °C, the quenching temperature was set at 1300 °C to determine the crystalline phases both under N_2 and reducing atmosphere 60/40 CO_2/CO. The quenched samples were crashed and grinded to less than 200 μm which were prepared for XRD analysis.

2.2.4. Thermodynamic equilibrium calculations

The thermodynamic computer package FactSage has been used in other studies to make predictions of multiphase equilibria, liquidus temperature and the proportion of liquid and solid phases for a coal ash system [11,12]. In our study, FactSage was used to predict the equilibrium phases from 800 to 1500 °C with a 20 °C interval. Phase formation data for the primary oxides and their combinations were selected from the FToxid and FactPS databases. The results were used as a reference and compared with the quenching products.

Table 1
Analysis of the original ash by XRF.

XRF analysis (%)	SiO_2	Al_2O_3	CaO	[a]Fe_2O_3	MgO	TiO_2	Na_2O	K_2O	SO_3	Si/Al	Si + Al
	27.77	21.97	19.13	15.77	2.02	0.62	2.68	2.02	6.44	1.26	49.47
Melting temperatures (°C)	DT	ST	HT	FT							
	1167	1180	1200	1240							

[a] Iron is expressed in the form of iron oxide.