Applied Clay Science xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Applied Clay Science

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

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In situ high temperature X-ray diffraction study on high strength aluminous porcelain insulator with the Al_2O_3-SiO_2-K2O-Na_2O system

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ARTICLE INFO

Article history:
Received 27 February 2016
Received in revised form 16 July 2016
Accepted 16 July 2016
Available online xxxx

Keywords:
In situ high temperature
XRD
Porcelain insulator
Mineral
Reaction

ABSTRACT

The high strength aluminous porcelain insulator with a mineral composition of kaolinite, corundum, microcline, quartz, small amounts of albite and anatase was investigated by in situ high temperature XRD (HTXRD) from 25 °C to 1300 °C. The amount change and reaction of minerals contained in the porcelain insulator were presented vividly. The full process occurred in successive stages: 1) kaolinite decomposed into amorphous metakaolinite in the temperature range of 500–600 °C; 2) metakaolinite kept amorphous form up to about 1000 °C; 3) at about 1000 °C, amorphous metakaolinite generated primary mullite; 4) after bout 1200 °C, microcline began to melt, forming an alkaline liquid phase which facilitated the growth of primary mullite into secondary mullite; 5) the alkaline liquid phase could etch β-quartz, resulting in the reflection intensity of β-quartz decreasing; 6) corundum was very stable in the whole heating process.

1. Introduction

Kaolin, composed mainly by aluminosilicate, is an essential raw material in the ceramic industry (De Aza et al., 2014; Dondi et al., 2014). It has diverse applications such as sanitary ware, building ceramics, refractory ceramics and porcelain insulator (Lee et al., 2008; Ngun et al., 2011; De Aza et al., 2014). Among the applications mentioned, porcelain insulator possesses the highest mechanical strength, and its manufacture process is complicated (Liebermann, 2003). Porcelain insulators, before put into application, need to pass about 20 standard property tests (e.g. electromechanical failure load test, flash test and power frequency sparking test), which are strict to guarantee safety.

Insulators, as indispensible elements, are widely used on power transmission and distribution network. They have two major functions: fastening mechanically and insulating electrically the active components of electric network (Liebermann and Schulle, 2002). As an eligible insulator, it is required to possess the properties such as high resistivity, high dielectric strength, low loss factor, superior mechanical strength, excellent in radiating heat and insulating components even in humid and corrosive condition (Liebermann, 2002; Amigó et al., 2005; Piva et al., 2013). According to the material composition, insulators could be divided into three main kinds of insulators, namely porcelain insulator, composite insulator and glass insulator.

Porcelain insulator, having been put into application more than 160 years since 1850 when insulators were introduced in the construction of power network by Werner Von Siemens (Liebermann, 2003; Islam, 2004; Meng et al., 2012; Meng et al., 2014), is most widely used among the three kinds of insulators. Porcelain insulator possesses several outstanding properties simultaneously (i.e. high mechanical strength, high resistance and corrosive resistance), which could not be realized by other materials (Meng et al., 2012; Meng et al., 2014). Even so, the glass insulator also occupies a significant market share and is widely accepted by many countries and areas in recent years.

The properties of insulator are closely related to a few major factors: the constituent phases resulting from high temperature reaction involving the raw materials used; the microstructure of the body; the degree of densification and the sintering process (Liebermann, 2003).

Although the sintering process of porcelain insulator has been studied for a long time in the porcelain insulator industry, there still remain some details which are interesting but not well presented or understood for the restriction of experimental equipment and method. It is still meaningful to investigate the sintering process of porcelain insulator.

The aim of this work is to present the high temperature behavior of minerals contained in the porcelain body as well as reactions happened between different minerals by in situ high temperature x-ray diffraction (HTXRD) vividly. The in situ HTXRD is a significant technology to investigate reaction and phase conversion upon high temperature. It makes that available to monitor the short-lived phase during heating. Particularly, we want to detail the decomposition of kaolinite to metakaolinite,

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http://dx.doi.org/10.1016/j.clay.2016.07.014
0169-1317/

the crystallization of mullite from amorphous metakaolinite and the growth of secondary mullite from kaolinite relics with the isolines 3D view function of XRD analytical software HighScore. It is really an interesting method that can give readers a visualized sight about both phase composition at each temperature and the variation tendency of reflection intensity with temperature smoothly (i.e. each phase's amount variation trend). As for the HTXRD isolines 3D view, it is a three dimensional surface image. Three axes of the image correspond to intensity, 2theta and temperature or time, respectively.

2. Experiment and methodology

2.1. Specimens

Industrial raw materials taken from Bijie Highland Porcelain Insulator Company (Guizhou province, China) were used. Specimens with different mineral composition were prepared. Specimen 1 is the green body of 420 kN-level high strength porcelain insulator taken from Bijie Highland Porcelain Insulator Company. This formula has been put into industrial application successfully and is of high mechanical property. The mineral composition of specimen 1 determined by XRD analysis is: kaolinite, corundum, microcline, quartz and small amounts of albite and anatase. The chemical composition of specimen 1 is shown in Table 1. Specimen 2 is natural kaolin exploited from Mijiaping (Guizhou province, China) by Bijie Highland Porcelain Insulator Company. It is mainly composed of kaolinite and small amounts of quartz and anatase. Specimen 2 was used as one of the raw materials of specimen 1. The chemical composition of specimen 2 is shown in Table 1.

2.2. HTXRD experiment

The HTXRD data was collected on a Panalytical multifunction X-ray diffractometer (model: Empyrean), equipped with an Anton Paar high temperature accessory (APHTK-16N) and a 3D PIXcel detector. The heating process was divided into many continuous parts from ambient temperature to 1300 °C. The heating speed was 20 °C per minute. The diffraction patterns were recorded every 50 °C or 100 °C and at temperature points interested. About 26 XRD patterns were recorded for each sample. The total firing time in the Anton Paar chamber was about 300 min.

The measurement was done according to the following steps. Firstly, specimens were crushed and finely ground with a pestle in an agate mortar. Secondly, the ground powder was blended with some water and stirred so that it could form an suspension. Thirdly, the suspension of specimen was spread on a rectangle platinum film to form a uniform layer with a size of 2 cm (length) × 1 cm (width) × 0.01 cm (thickness). Fourthly, the platinum holder was put in the Anton Paar high temperature accessory. Finally, one could start the measure process.

The HTXRD measurements were performed at diverse temperature points (ambient pressure), in the 2θ range of 5–65°, in the mode of continuous scanning with 0.013°in step size and a counting time of 25 s per step. Working voltage and current were 40 kV and 40 mA, respectively. Before collecting diffraction pattern at each given temperature point, the temperature was kept for a few minutes to ensure temperature uniformity.

2.3. Scanning electron microscopy observation (SEM)

The specimens undergoing HTXRD analysis were scraped from platinum film. Then the specimens were etched with a 10% (volume) HF solution for 60 s and dried later. Finally the specimens were coated with a carbon layer for crystal phase observation. The experiments were done on a scanning electron microscope (model: JSM-6490LV, Japan).

2.4. DSC-TG experiment

The DSC-TG experiment was done on a TG-DTA analyzer (model: NETZSCH STA 449F3) in the temperature range of 40–1200 °C with a heating rate of 20 °C per minute (air atmosphere).

2.5. Transmission electron microscope (TEM) observation

The specimens undergoing HTXRD analysis were scraped from platinum film for TEM observation. The experiment was done on a transmission electron microscope (model: TecnaiG2F20S-TWIN TMP).

3. Results and discussion

3.1. Decomposition of kaolinite

The HTXRD isolines 3D view of specimen 1 and specimen 2 are presented in Fig. 1. It shows that all minerals remained stable when heating from ambient temperature to 500 °C. The water absorbed was vented out which was shown on the HDXRD patterns by the decreasing of background intensity.

The reflection intensity of kaolinite remained the same almost before 500 °C, which means that kaolinite did not decompose in this temperature range. The 001 and 002 reflections are strong reflections of kaolinite. In the temperature range of 500–600 °C, the intensity of 001 and 002 reflections sharply decreased as a result of kaolinite decomposing into metakaolinite with the reaction (Brindley and Nakahira, 1958; Chakraborty and Ghosh, 1978; Chakraborty, 2003; Chen et al., 2000; Ptáček et al., 2012; Teklay et al., 2015): $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ (kaolinite) → $Al_2O_3 \cdot 2SiO_2$ (metakaolinite) + $2H_2O$ (gas), which was testified by an endothermal peak on the DSC curve and a mass reducing slope on the TG curve (Fig. 2). The gaseous water molecular (H_2O) could easily leave the reaction interface, i.e., the interval between the silica tetrahedron sheet and the alumina octahedron sheet in the crystal of kaolinite, which could facilitated the equilibrium of the reaction moving to the right. After 600 °C, the intensity of background increased which was shown by the changing of background color (Fig. 1). The cause may be metakaolinite is an amorphous phase but it retained some of structure characteristics of kaolinite. So it is short-range ordered to some extent. The results were also corresponding with the study of De Aza et al. on kaolinite by time-resolved powder neutron diffraction (De Aza et al., 2014), in which, activation energies of kaolinite decomposition, mullite nucleation and growth were calculated.

Kulbicki and Grim (Kulbicki and Grim, 1959; Grim and Kulbicki, 1961; Wahl and Grim, 2012) first studied the phase transformation of clay minerals such as kaolinite and montmorillonite with the in situ high temperature XRD method. The decomposition temperature interval of kaolinite observed by them was corresponding with our result,

Table 1
Chemical compositions (mass%) of specimens.

	Al_2O_3	SiO_2	K_2O	TiO_2	Fe_2O_3	Na_2O	CaO	MgO	Ablation ratio
Specimen 1	45.30	45.10	2.85	1.75	0.81	0.74	0.43	0.35	3.5
Specimen 2	38.22	45.92	0.21	1.55	0.53	0.75	0.21	0.25	12.38

Please cite this article as: Meng, Y., et al., In situ high temperature X-ray diffraction study on high strength aluminous porcelain insulator with the Al2O3-SiO2-K2O-Na2O syste..., Appl. Clay Sci. (2016), http://dx.doi.org/10.1016/j.clay.2016.07.014