Applied Clay Science 143 (2017) 199–204

Contents lists available at ScienceDirect

Applied Clay Science

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

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Novel ceramics prepared from inferior clay rich in CaO and Fe_2O_3: Properties, crystalline phases evolution and densification process

Feng Jiang[a,b], Yu Li[a,b,*], Lihua Zhao[a,b], Daqiang Cang[a,b]

[a] State Key Laboratory of Advanced Metallurgy, University of Science and Technology Beijing, Beijing 100083, China
[b] School of Metallurgy and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, China

ARTICLE INFO

Keywords:
Inferior clay
Calcium oxide
Iron oxide
Novel ceramics

ABSTRACT

Inferior clay rich in CaO and Fe_2O_3 is a typical clay with huge reserves in southwest of China, which cannot be used in traditional aluminosilicate system ceramics. To efficiently utilize the inferior clay, a method of preparing novel ceramics containing CaO and Fe_2O_3 was put forward. In this study, effects of inferior clay proportion on properties, CaO on evolution of crystalline phases and Fe_2O_3 on densification process were analyzed by XRF, XRD, TG-DTA and SEM-EDS combined with physical properties tests. The results showed that addition of inferior clay (from 20 to 70 wt%) significantly affected sintering temperature (from 1190 to 1130 °C). High activity CaO decomposed by carbonate transformed into anorthite and diopside at low temperature. Fe_2O_3 promoted generation of low-temperature liquid phase, which facilitated densification process. The fired ceramics (60 wt% inferior clay) sintered at 1130 °C exhibited excellent properties with water absorption of 0.05%, linear shrinkage of 6.8% and flexural strength of 70 MPa. This batch was applied into an industrial experiment and 1160 m^2 qualified ceramics (ISO 10545-4:2004) were fabricated.

1. Introduction

Inferior clay rich in CaO and Fe_2O_3 cannot be efficiently used in the manufacturing of traditional aluminosilicate system ceramics due to its composition characteristics. The raw materials of the system were ternary mixtures of clay, feldspar and quartz filler (Tarvornpanich et al., 2008b). During the sintering process, kaolinite or other clay minerals underwent dehydroxylation and formed semiamorphous meta-kaolinite between 450 and 600 °C. At 950 °C, meta-kaolinite recrystallized with loss of amorphous silica and formed Al–Si–spinel, followed by formation of mullite above 1050 °C (Tarvornpanich et al., 2008a; Andrini et al., 2016). This was attributed to the feature of the system that clay mineral phase reacted with itself and finally formed mullite as main crystalline phase. CaO and Fe_2O_3, as impurities in SiO_2–Al_2O_3–K_2O (Na_2O) system ceramics, were strictly restricted to less than 3 and 0.8 wt%, respectively (Zhao et al., 2014). Excessive CaO content led to narrowing of the firing range, even resulted in deformation of ceramic body due to low viscosity of glassy phase at high temperature (Dai et al., 2010). Similarly, Fe_2O_3 can also cause ceramic body deformation, especially combining with alkali or alkali-earth in the feldspar (Roy et al., 2010). Therefore, it is difficult to utilize inferior clay rich in CaO and Fe_2O_3 in the traditional system ceramics.

Faced with fierce market competition, it was quite essential for ceramic industry to efficiently utilize these low quality materials (Ji et al., 2016; Martinez-Martinez et al., 2016). Recently, extensive researches have been devoted to the fabrication of ceramics from solid waste containing CaO or Fe_2O_3. Influence of different CaO source in production of anorthite ceramic was earlier investigated (Kurama and Ozel, 2009). The results showed that main crystalline phases were all transformed into anorthite. Based on previous study, recycled paper processing residues, mainly composed of calcium carbonate, were reused as additives to fabricate ceramics (Sutcu and Akkurt, 2010). The porous ceramics were successfully fabricated with 30–40 wt% paper processing residues and contained anorthite as major phase. In a recent study, pyroxene ceramics were prepared from steel slag with high CaO and Fe_2O_3 content (Zhao et al., 2014). The novel ceramic exhibited excellent physical properties, especially the flexural strength of 143 MPa, which was attributed to its newly formed pyroxene group minerals. These studies demonstrated that it was feasible to reuse solid waste with high CaO and Fe_2O_3 content as raw materials of ceramics. However, ceramics fabricated in above mentioned studies were all prepared inevitably from high grade clay. Limited attention was paid to inferior clay, which occupied a large proportion among raw materials of ceramics.

The purpose of this study was to fabricate CaO–MgO–SiO_2–Al_2O_3 (Fe_2O_3) novel ceramics from inferior clay rich in CaO and Fe_2O_3. The

* Corresponding author at: 30 Xueyuan Road, Haidian District, Beijing 100083, China.
E-mail address: leeuu00@sina.com (Y. Li).

http://dx.doi.org/10.1016/j.clay.2017.03.026
Received 28 July 2016; Received in revised form 17 March 2017; Accepted 18 March 2017
0169-1317/

effect of inferior clay proportion on properties of the ceramics, CaO on evolution of the crystalline phases and Fe_2O_3 on densification process were mainly emphasized on.

2. Experimental procedure

2.1. Raw materials

The raw materials used in this study were inferior clay, bauxite tailings and quartz. These raw materials were all obtained from Gui Zhou province of China.

2.2. Sample preparation

Batch (300 g) was mixed and wet ground (with 300 mL water) in a pot mill for 20 min to meet proportion of particles with size greater than 20 μm as less than 10%. The slurry was dried at 105 °C for 12 h, granulated with 6–10% moisture and sieved through 20 mesh. Samples with dimension of 100 mm × 50 mm × 7 mm were hydraulically compacted by uniaxial pressing at 25 MPa in room temperature. The shaped samples were dried at 105 °C for 12 h. Then, the dried samples were fired at the heating rate of 5 °C/min and holding period of 180 min. Finally, the fired samples were subjected to physical tests such as water absorption, linear shrinkage and flexural strength.

2.3. Characterization of raw materials

Chemical composition of raw materials was determined by using a sequential X-ray fluorescence spectrometer with maximum power of 60 KV and 140 mA, and scan speed at 300 °/min. Mineralogical composition was studied by using an X-ray diffractometer working at 40 kV and 40 mA with Ni-filtered CuKα radiation (wavelength = 1.5406 Å). The 2θ range was from 10 to 100°, step size at 2°, scan speed at 20°/min and counting time at 240 s. Thermal behavior was determined by using a Netzsch STA 409 simultaneous analyzer in flowing air. The heating rate was 10 °C/min, holding time for 30 min and cooling rate at 20 °C/min. Microstructure of ceramics was observed by scanning electron microscope using an EVO18 Special Edition at 25 kV.

2.4. Characterization of ceramics

Water absorption was determined using fired (105 °C for 12 h) and water saturated (soaking for 45 min at vacuum of 9.8 MPa) samples with a CXK-A type ceramic water absorption vacuum device according to standard (ASTM C373-14, 1988). Linear shrinkage was obtained by measuring length of samples before and after sintering using a caliper with a precision of ± 0.01 mm according to standard (ASTM C326, 1997). Flexural strength was measured by a three-point flexural method with a digital display ceramic tiles anti-break testing machine according to the standard procedure (ISO 10545-4: 2004).

3. Results and discussion

3.1. Analysis of raw materials

Chemical compositions of raw materials are listed in Table 1. Besides SiO_2 (54.90 wt%) and Al_2O_3 (13.26 wt%), the inferior clay had relatively more content of CaO (16.87 wt%) and Fe_2O_3 (6.09 wt%). Bauxite tailings showed high amount of SiO_2 (21.6 wt%), Al_2O_3 (50.39 wt%) and CaO (13.03 wt%). Quartz was composed of SiO_2.

XRD patterns of inferior clay and bauxite tailings are presented in Fig. 1(a). Quartz, calcite, dolomite, illite and enstatite ferroan were identified as the major mineral phases of inferior clay. The main mineral phases of bauxite tailings were kaolinite, diaspore, cronstedtite and kilchoanite. Quartz consisted of nearly quartz mineral phase.

Fig. 1(b) exhibits thermal behavior of inferior clay with six endothermic peaks in DTA curve. Weak peaks at 115 and 187 °C were probably due to removal of weakly bound water or water present in interlayers of minerals (Mahmoudi et al., 2017, 2016; Semiz, 2017). Peaks at 528 and 567 °C could be assigned to separation of crystallization water (de Almeida Azzi et al., 2016; Stevenson and Gurnick, 2016) and transformation of quartz (Knapek et al., 2016), respectively. A significant peak at 738 °C could be attributed to decomposition of dolomite and calcite (Cultrone et al., 2001; Liu et al., 2016). The peak at 1159 °C might be caused by the melting of inferior clay. TG curve indicated that these changes were responsible for the mass loss of about 15 wt%.

Table 1
Chemical composition of inferior clay, bauxite tailings, quartz (wt%).

Raw materials	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	K_2O	Others
Inferior clay	54.90	13.26	16.87	3.79	6.09	3.09	1.92
Bauxite tailings	21.60	50.39	13.03	2.79	5.18	2.72	4.28
Quartz	99.40	0.08	0.11	0.03	0.25	0.01	0.08

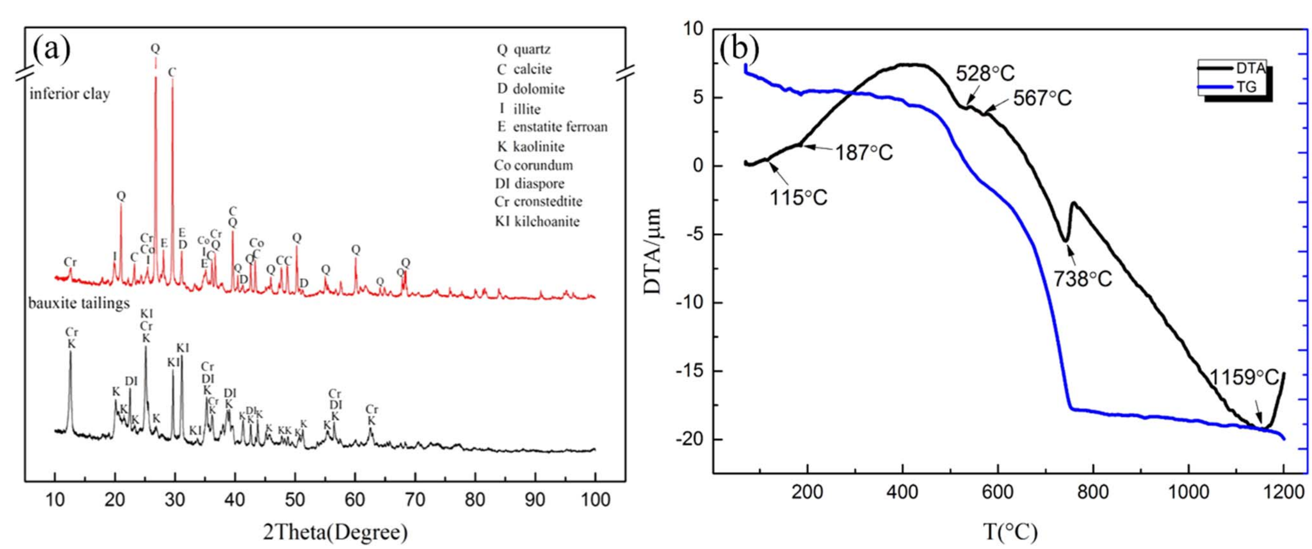

Fig. 1. (a) XRD patterns of raw materials, (b) TG-DTA analysis of inferior clay.