Research paper

A kaolinitic clay from Yantai (China): Improvement of properties and microstructure

Xiangming Li *, Mingjun Gao

School of Environment and Materials Engineering, Yantai University, Yantai, Shandong 264005, PR China

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ABSTRACT

The properties and microstructure of a kaolinitic clay were improved by sintering at 1085–1095 °C with addition of cinder powder and calcium sulfate. Both sintering temperature and the additive content have great effect on the properties and microstructure of the clay. The clay sintered with 15–20 wt% additive at 1085–1095 °C possesses a high open porosity of 34.2–38.1%, flexural strength of 10.8–14.8 MPa, low volume shrinkage of 2.4–6.2%, tailored microstructure and well-connected open pores, which is considered suitable for manufacturing irrigation pitchers and units for water seepage and filtration.

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1. Introduction

In the past two decades, ceramics with high open porosity, good mechanical properties and tailored microstructure have attracted much attention because of their expanding technological applications, such as separation materials (Kitaoka et al., 2004; Cheow et al., 2008), catalyst supports (Naik et al., 2012; Newnham et al., 2012), and gas filters and implantable bio-ceramics (Yoon et al., 2007, 2008). And, the most attention have been focusing on preparing advanced porous ceramics, such as alumina (Li et al., 2013a,b; Potoczek, 2008), silicon nitride (Li et al., 2012a,b, 2013a,b) and silicon carbide (Li et al., 2010), for structural or functional applications in some specialty environments.

Recently, porous ceramics have found a new application in arid region for water-saving irrigation because of their good water permeability and filtration functions (Bainbridge, 2001; Siyal et al., 2013; Siyal and Skaggs, 2009). In water-saving irrigation, advanced porous ceramics are expensive and superfluous, while porous clay meets the low cost requirement of agricultural production (Bainbridge, 2001; Siyal et al., 2013; Siyal and Skaggs, 2009). There is an increasing demand for porous clay products in water-saving irrigation, but the products prepared by existing techniques show unsatisfactory properties due to their large volume shrinkage and deformation (Monteiro and Vieira, 2005; Souza and Holanda, 2004). For example, a porous clay sintered from clay body with 5 wt% oily waste addition has a flexural strength of 12.1 MPa and open porosity of 23.6%, which meets the performance requirement of irrigation pitchers and units for water seepage and

filtration, but the high volume shrinkage of 26.9% seriously reduces the ratio of finished irrigation products (Monteiro and Vieira, 2005).

As revealed by our research, the properties of porous clay could be obviously improved by sintering a clay body with a certain amount of cinder powder and calcium sulfate ($CaSO_4$). In this paper, porous clay is prepared by sintering clay body which is cold-pressed from clay powder with addition of cinder powder and $CaSO_4$. The effect of sintering temperature and additive content on the composition, flexural strength, volume shrinkage, open porosity and microstructure of the porous clay is investigated, and the suitable sintering temperature and additive content are discussed and determined.

2. Experimental

2.1. Preparation process and theoretical basis

The raw kaolinitic clay was from Yantai city (China) (geographical coordinates: 37°24′45.86″ N; 121°08′08.27″ W). The cinder collected from boiler room was washed and dried at 90 °C for 10 h, and then ball-ground into powder using a planetary ball grinder at a high speed (rotation speed of 360 r/min, revolution speed of 400 r/min). The cinder powder was passed through a 60-mesh sieve, and then proportionally mixed with $CaSO_4$ (analytically pure). The obtained mixture was used as additive and added in clay powder at levels of 5, 10, 15, 20 and 25 wt% respectively. The new obtained mixture was ball-ground in the planetary ball grinder for 5 h at a low speed (rotation speed of 180 r/min, revolution speed of 200 r/min). The obtained powder blend was spread on a vibrating screen and sprayed with distilled water at the same time of sieving. After water-spraying, the moisture content of

* Corresponding author.
  E-mail address: li_xiangming@yahoo.com (X. Li).

powder blend is controlled at about 6–8 wt%, and the powder blend was cold–pressed into clay body at 10 MPa using a 30 mm deep × 50 mm diameter circular steel die.

Fig. 1 shows the XRD pattern of raw kaolinitic clay. As can be seen, the clay is composed of a large amount of quartz and kaolinite, a small amount of hematite and calcite and a very little amount of unknown component. In order to make clear the effect of cinder powder and $CaSO_4$ on the properties of porous clay, the clay powder was washed using diluted hydrochloric acid for removing the microconstituent as much as possible. The composition of clay powder after acid pickling was characterized in an inductive coupled plasma–optical emission spectrometer (ICP–OES, Optima 8000, Perkin–Elmer, USA). As shown in Table 1, the clay powder is composed of 59.3 wt% of SiO_2, 27.6 wt% of Al_2O_3, 1.7 wt% of TiO_2 and 11.4 wt% of others. Since no peak of Al_2O_3 of crystalline phase was detected in Fig. 1, the Al_2O_3 in Table 1 is actually as the Al_2O_3 of chemical component.

Fig. 2 compares the XRD patterns of original cinder powder and the cinder powder heat–treated in air for 5 h at 700 and 1000 °C respectively. As shown in Fig. 2–a, the origin cinder powder is composed of a large amount of quartz, amorphous phase and a small amount of mayenite ($Ca_{12}Al_{14}O_{33}$) and mullite ($Al_6Si_2O_{13}$). As shown in Fig. 2–b, after heat–treating in air for 5 h at 700 °C, the crystal phase in cinder powder remained almost unchanged with an obvious reduction of amorphous phase, and the weight of cinder powder decreased by about 19.3%. As shown in Fig. 2–c, after further heat–treating in air for 5 h at 1000 °C, the height of quartz peaks increased much with a complete disappearance of amorphous phase, and the weight of cinder powder remained unchanged. As known from above result, the amorphous phase is composed of about 19.3 wt% carbon and an amount of silica.

The $CaSO_4$ in the mixture plays two key roles in the whole preparation process. During cold–pressing, $CaSO_4$ increases the strength of clay body and makes the clay body demould easy. During sintering, the decomposing–derived CaO from $CaSO_4$ will react with the amorphous silica and Al_2O_3 of chemical component in clay body to produce anorthite ($CaAl_2Si_2O_8$), which is the key reason strengthening the bonding necks among clay grains and raising the flexural strength of porous clay (Mukherjee and Das, 2013; Wu et al., 2013; Saucedo et al., 2012).

Eqs. (1) and (2) show the decomposition reactions of $CaSO_4$ in air and in carbon–reducing atmosphere respectively.
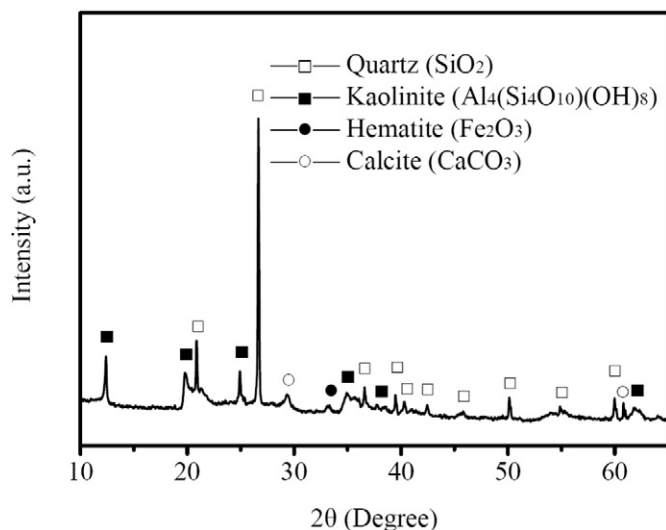
$$CaSO_4 \rightarrow CaO + SO_2 + 1/2 O_2 \tag{1}$$

$$CaSO_4 + 1/2 C \rightarrow CaO + 1/2 CO_2 + SO_2 \tag{2}$$

Table 1
Composition of clay powder after acid pickling.

Composition	SiO_2	Al_2O_3	TiO_2	Others
Content (wt%)	59.3	27.6	1.7	11.4

Calculated by using Factsage Thermodynamics Software (Thermfact/CRCT and GTT–Technologies, Canada and Germany), the variation of Gibbs free energy (ΔG) of above two reactions is expressed as a function of temperature. As shown in Fig. 2, $\Delta G_T^0(1)$ decreases from 205.9 to −11.3 kJ/mol as temperature rises from 800 to 1700 °C, and $\Delta G_T^0(2)$-decreases from 7.5 to −119.1 kJ/mol as temperature rises from 800 to 1300 °C. The result shown in Fig. 3 demonstrates that $CaSO_4$ decomposes hardly unless temperature rises to higher than 1650 °C in air but decomposes easily when temperature rises to 850 °C in carbon–reducing atmosphere. Incidentally, the large amount of carbon in cinder powder provides enough carbon source of Eq. (2).

Calculating according to the content of carbon in cinder powder and the mole ratio between $CaSO_4$ and carbon in Eq. (2), the weight ratio between $CaSO_4$ and cinder powder in clay body is controlled at 2:1. As suggested by the result of our preliminary experiment, the suitable preparation for porous clay is sintering the clay body in air for 2 h at temperature in the range of 1050–1105 °C, and the clay body should be protected in nitrogen during temperature rising process. For the convenience of following discussion, the porous clay sintered from the clay body with additive content of (m) wt% at temperature of (n) °C is named as Clay–(m, n).

2.2. Characterization and tests

The phase analyses were conducted by X–ray diffraction (XRD, X'Pert Pro, Philips, Netherlands). The flexural strength (σ) was evaluated via the three–point bending test with a support distance of 30 mm and a loading speed of 0.5 mm/min. The volume shrinkage was calculated with the measurement of dimensions of the samples. The open porosity was measured by Archimedes method. The microstructure was observed by scanning electron microscopy (SEM, S–4800, Hitachi, Japan).
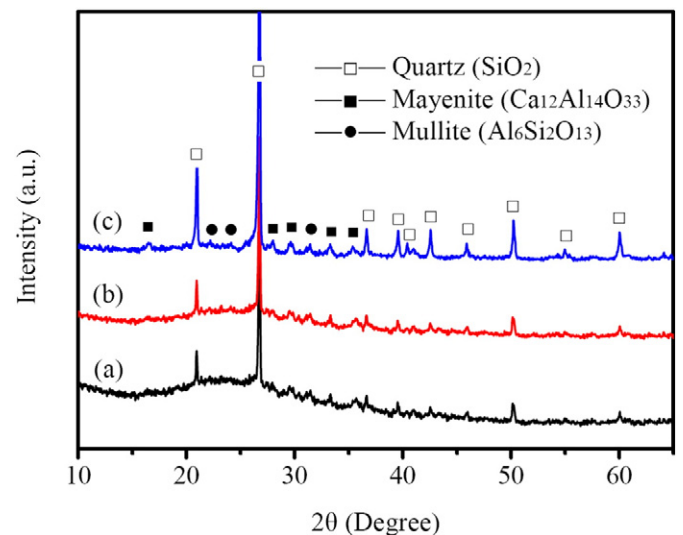
Fig. 1. XRD pattern of raw kaolinitic clay powder.

Fig. 2. XRD patterns of original cinder powder (a) and the cinder powder heat–treated in air for 5 h at 700 (b) and 1000 °C (c) respectively.