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Research paper

The properties of Southern Thailand clay-based porous ceramics fabricated from different pore size templates

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ABSTRACT

Open cell porous ceramics were produced by low-cost polymeric sponge method using natural clays (Surat Thani clay and Ranong clay) from Southern Thailand and alumina powder as raw materials. Open-cell polyurethane sponges with different pore sizes were used as templates for ceramic slurries. Batch formulations of the samples were formed into green bodies and fired at 1150 and 1200 °C at controlled firing rates. The properties studied include solid content, linear shrinkage, porosity, average pore size, pore size distribution, phase composition, phase morphology and compressive strength. This study found that the composition and pore size of sponge template strongly affected the physical properties and mechanical strength of the synthesized porous ceramics. It was found that porous ceramics could be produced from all ceramic compositions without internal cracking and distortion of the bulk structures. Surat Thani clay acted as a source of ball clay giving a better densification and shrinkage after sintering whereas Ranong clay, which is kaolinitic clay gave a better strength due to the presence of mullite as a major phase after firing at 1200 °C. The interlocking structure of the needle-like mullite phase could add to the evidence for higher compressive strength in the compositions containing higher relative ratio of Ranong clay to Surat Thani clay.

1. Introduction

Porous ceramic is a class of materials with high porosity. Porous ceramics are important in many industrial applications due to several unique properties such as relatively low mass, low fractional density, low thermal conductivity, resistance to chemical attack, resistance to high temperature and thermal cycling, high specific surface area and good permeability (Brezny and Green, 1993; Nettleship, 1996; Sepulveda, 1997; Sepulveda and Binner, 1999; Luyten et al., 2009). They are used and being considered for a wide range of technological and advanced engineering applications such as filters, lightweight sandwich structural panels, catalyst supports, heat exchanger, bone tissue engineering, absorbent and membranes (Nettleship, 1996; Schmidt et al., 2001; Scheffler and Colombo, 2005; Studart et al., 2006; Taslicukur et al., 2007). Applications are also rapidly growing and of great importance in the fields of environmental areas (Huang and Gibson, 1995). The most common applications for open-cell porous ceramics are molten metal filters, diesel engine exhaust filters, industrial hot gas filters and grease filter for kitchens (Chen et al., 1998; Colombo, 2002). The open cells are interconnected, which allows fluid to pass through the porous ceramic with a relatively low pressure drop (Powell and Evans, 1995; Rice, 1996). During the last few years, great efforts have been devoted for the researches on innovative processing technologies of porous ceramics, resulting in better control of the porous structures and substantial improvements of the ceramic properties. Improvements in processing methods and innovation are required because of the increasing specific demands on properties of such materials (Luyten et al., 2009; Colombo and Bernardo, 2003). Porous or cellular ceramics with three-dimensional network of struts can be processed by various methods which include foaming method by bubble generation into slurry or at a green state during a specific thermal treatment, gel-casting of foam, aerogel, sol–gel methods, pyrolysis of various organic additives and polymeric sponge method (Saggio-Woyansky et al., 1992; Montanaro et al., 1998; Schmidt et al., 2001; Konopka et al., 2004; Rambo et al., 2006). These processing routes employ raw materials of various natures and lead to porous ceramics with a variety of morphologies, pore sizes and properties for specific industrial applications.

The polymeric sponge method relies on the replica templates in order to produce highly porous ceramics having interconnected large pores and sufficiently strong struts without cracks. It can give ceramic bodies with porosity ranging from 70 to more than 90% of the total volume. The process involves impregnation of open-cell polymeric foam with ceramic slurry containing particles and appropriate binders followed by burning-out of the organic portion through sintering

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process of the ceramic skeleton which yields a replica of ceramic foam from the original polymeric foam (Peng et al., 2000a,b; Han et al., 2002). The attractive feature of this method lies in the easy control of pore size by choosing different sponge templates, which will determine the pore size of ceramic foam after sintering. Many steps must be optimized to make a foam product with desired performances for example the characteristics of polymer sponge template such as density, pore size, pore size distribution, pore morphology, the formulation of ceramic slurry, the viscosity of the slurry, and the thermal process: consisting of drying, and burning out of organic components and sintering of ceramic body (Brown and Green, 1994; Lee and Rainforth, 1994; Costa Oliveira et al., 2006; Wen et al., 2008). In case of open cells, fluid can penetrate and is a very important factor for the filter with the property of separation–filtration.

The nature of raw materials significantly affects the properties of porous ceramic bodies. Thailand has large deposits of clay minerals such as deposits found in the southern regions that are high-grade aluminosilicate based clay minerals. The growing demand for porous ceramics in industries led to the application of high quality low cost clay based materials. Kaolin (Ranong clay) with little plasticity, and ball clay (Surat Thani clay) with high plasticity were rich resources of aluminosilicate based clays and therefore had been utilized in this study. Kaolin and ball clay that are used in this study were supplied locally for high grade ceramic products. According to the preliminary test, ball clay and kaolin densified well above 1100 °C and 1150 °C, respectively. The densification however, also depends on several factors such as associated minerals and impurities in clays, heating rate, holding time, and sintering atmosphere. Sintering temperatures of 1150 and 1200 °C were chosen in this study to represent the sintering characteristics around the temperature range mentioned above. Lecomte-Nana et al. (2011) mentioned in their work that between 1150 and 1200 °C, large shrinkage in clay-based ceramics occurred probably resulting from the densification of the sample by a viscous flow mechanism in relation with the formation of a liquid as predicted by the SiO_2–Al_2O_3–K_2O phase diagram. At 1200 °C mullite and corundum coexisted in a stable matrix, exhibiting good thermal and chemical stabilities particularly regarding thermal cycles.

The aims of this study were to fabricate porous ceramics via polymeric sponge method using synthesized flexible polyurethane foams as replica templates with particular emphasis on the processing–microstructure–property relations. Three different average pore sizes of 600 μm, 950 μm and 1300 μm, all with uniform normal distribution, were prepared. The raw materials utilized were ball clay (Surat Thani clay), kaolin (Ranong clay) and alumina powder. There are only a few investigations dealing with clay-based porous ceramics and it was of our interest to study the effect of varying the ratio of kaolin (Ranong clay) to ball clay (Surat Thani clay) on the physical and mechanical properties of porous ceramics. The amount of alumina powder was kept at 10 wt.% in all ceramic compositions with the expectation of reducing the shrinkage and increasing strength of the fired samples. The relationships between ceramic composition, firing conditions and the resulting properties were discussed in this paper to demonstrate the feasibility of fabricating porous ceramics from these clay deposits.

2. Materials and characterization

2.1. Sample preparation

The raw materials: alumina powder, Surat Thani clay and Ranong clay were supplied by Ajax Finechem and Cernic Intl, Bangkok. The moisture contents were less than 2.5% for all of the powders. The characteristics of such powders are shown in Table 1 and the ceramic compositions are shown in Table 2. The appropriate amount of the powders were precisely weighed according to Table 2 and then the ball milled in distilled water using high-grade alumina milling balls of 8 mm diameter. Ball milling was carried out in a HDPE bottle at 80 rpm for 24 h to obtain thick aqueous slurry. In addition, polyvinyl alcohol (PVA) was added as a binder with a concentration of 1.0 wt.% excess into a slurry which provided strength to the ceramic structure after drying and prevented collapse during burning out of the organic portion. All the slurry compositions were controlled at a specific gravity of 1.50 for consistency by adjusting the amount of added water during ball milling.

Flexible polyurethane sponges with three different average pore sizes of 600 μm, 950 μm and 1300 μm were prepared. Sponge templates were cut into dimensions of 20 mm × 20 mm × 20 mm for solid content, porosity and compressive strength measurement and 80 mm × 25 mm × 20 mm for linear shrinkage measurement. The sponges were then dipped into the ceramic slurry for 30 s followed by squeezing for a few times in order to fill the open pores. Subsequently, the impregnated sponges were taken out and excess suspensions were squeezed out by pressing the impregnated sponges with two parallel plates to a constant gap. Since the sponges were flexible they can be pressed easily. The gap between the two parallel plates was set at about 5 mm when compressed from the 20 mm thickness side. The applied pressure was carried out by hands therefore error in pressure may have existed. The sponges containing suspensions were dried in air at room temperature (30–35 °C) for 48 h to remove water and the solid contents in samples were measured and averaged. The sintering consisted of slow heating rate at 2 °C/min to 700 °C and kept for 1 h for the pyrolysis (burning out) of polymeric sponge without collapsing the ceramic structure and to avoid the build-up of pressure within the coated struts. The subsequent stage was firing with a heating rate of 3 °C/min and soaking for 30 min at maximum temperature of 1150 and 1200 °C. Then the furnace was naturally cooled to room temperature to give interconnected porous structures. For each ceramic composition at least ten good samples were fabricated for obtaining averaged results.

3. Characterization

3.1. Composition of raw materials

Raw materials were characterized for composition using an analytical instrument X-ray Fluorescence Spectrometer (XRF), Bruker AXS S4, Germany. Pioneer Spectra Plus software of the Bruker was used for data analysis. Loss on ignition (LOI) was also measured at 1000 °C. LOI is defined as the weight loss during heating of clay due to

Table 1
Composition and properties of raw materials (LOL = loss on ignition at 1000 °C).

Raw material	d_{50} (μm)	Moisture content (%)	Chemical composition (wt.%)								
			SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	LOI
Surat Thani clay (ball clay)	8.2	1.60–2.15	56.35	34.05	4.17	0.75	0.73	0.12	2.45	1.25	N/A
Ranong clay (kaolin)	10.8	1.50–2.25	48.23	40.42	0.51	0.24	0.07	0.05	0.82	0.08	8.62
Alumina	14.6	0.58–0.90	0.01	99.7	0.04	–	0.06	0.03	0.05	–	–

Note: LOI test was not performed for ball clay therefore data is not available.