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ScienceDirect

Ceramics International 41 (2015) 14263–14269

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Concentration dependent pore morphological tuning of kaolin clay foams using sodium dodecyl sulfate as foaming agent

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Received 2 June 2015; received in revised form 9 July 2015; accepted 9 July 2015
Available online 15 July 2015

Abstract

Microstructural tailoring of kaolin foams was successfully performed from kaolin clay mineral by surfactant assisted foaming technique using the anionic surfactant sodium dodecyl sulfate (SDS). The foams were prepared via frothing of aqueous kaolin suspension with SDS solutions of different concentration and the stability of the foam was improved by insitu polymerization of methylol-urea to urea formaldehyde resin. Furthermore, the effect of surfactant concentration on slurry foaming characteristics and the corresponding change in the pore morphology of the dried foams were investigated. The result showed that the pore size, pore volume and interconnectivity changed with the increased amount of SDS. In addition, the role of SDS micellar stability on the frothing capacity and the analogous modification in the microstructure of final sintered foam were explained by a possible mechanism based on the variation of micellar stability with concentration.

Keywords: Ceramics; Microporous materials; Microstructure

1. Introduction

The requirement for porous ceramic materials (PCM) with application-oriented pore morphology in various industrial and medical sectors such as catalytic supports, scaffolds, filters, bone tissue engineering, etc. lead to the intense research in tailoring of the microstructure of PCM [1–6]. In fact, the microstructural features like pore size, porosity, interconnectivity, etc. are the decisive parameters for the various functional properties of PCM such that highly interconnected pore structures and hierarchical pore size distribution is desired for catalytic applications [7] whereas low connectivity and high porosity are the requisites for thermal insulation panels for aerospace applications [8,9]. Although there are many viable processing techniques available which lead to distinct pore morphology [1,10], the direct foaming method offers a simple and inexpensive way to produce PCM, which involves the incorporation of air bubble into the ceramic slurry by agitation [11]. The pore characteristics can be easily modified by controlling the size and stability of the air bubble.

Surfactant assisted foaming techniques have been investigated for the past few decades since they are capable of being adsorbed at the foam interface, thereby stabilizing the air bubble. The foaming capability of surfactant was observed above the critical micelle concentration (CMC) as the micelle formed above the CMC acts as a reservoir to supply surfactant molecules to the foam interface [1,12,13]. However, surfactant adsorption at the foam interface is completely reversible [14] and hence, foam consolidation is an unavoidable step for surfactant assisted foaming techniques using different foam setting mechanisms such as “insitu” polymer blowing method [15,16], sol–gel phase transition [17] insitu polymerization techniques [1,18,19], gelation techniques, etc. [20,21].The final pore morphology of the material depends on the balance between bubble disproportionation and the kinetics of the setting mechanism.

Polymer based direct foaming method was developed to produce strong and machinable porous ceramics with a wider chemical composition range. Further sintering of the foam will burn-off the fugitive polymer binder resulting in a highly

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http://dx.doi.org/10.1016/j.ceramint.2015.07.056
0272-8842/

interconnected porous network. Binner et al. [22] successfully used "insitu" free radical polymerization of acrylamide monomer for the setting of ceramic foams. The production of environmentally hazardous gas evolved during burn-off of acrylamide gave way to the development of environmental friendly gelation techniques. However, the setting reactions of these alternative setting agents are considerably slower than the polymerization reaction. Polymerization of methylol urea to the urea-formaldehyde resin (UF) has been used as a setting mechanism for the fabrication of dense ceramic materials by gel casting method. The advantages observed with UF binder are the low pyrolysis temperature, pyrolysis products of low molecular weight, complete binder removal, and endothermic decomposition procedure which can be performed under isothermal conditions [23,24].

Many investigations were conducted on the influence of micelle structure on the foaming capacity of surfactant. Though micelle supply molecules to the foam interface, stable micelle does not enhance the flux of surfactant molecules to the newly created interface [25]. The micelle size, structure and stability are crucial parameters that influence the foaming capacity of surfactant [26,27]. However, the influence of these factors on the microstructure of the final porous body was not investigated as per our knowledge. In this present work, we developed a method for the microstructural tailoring of porous kaolin clay using different concentrations of an anionic surfactant sodium dodecyl sulfate. Moreover, the porous body exhibited a higher concentration of mullite phase after sintering to 1350 °C, which remarkably increased the strength of the foam. Besides, the foamability and foam stability attained at different concentrations were compared in terms of the pore size, pore distribution and interconnectivity pores on the processed kaolin foams, and a possible mechanism has been discussed.

2. Materials and methods

2.1. Materials

The materials used were kaolin clay mineral (BCK, aps ~2 μm, pH 6.8, English Indian Clay), sodium polyacrylate (SPA), (Accumer (40%)), for the dispersion of clay slurry, and sodium dodecyl sulfate (SDS), (AR Grade, SD fine chemicals, India), an anionic surfactant for foam stabilization. The monomer methylol-urea used for the foam setting was prepared from formalin and urea (SD Fine Chemicals, India) by the method reported elsewhere [28].

2.2. Fabrication of porous kaolin material

Aqueous clay suspensions (50 wt% or 28.8 vol%) for foaming were prepared by dispersing the particles in deionized water with 0.3 wt% (w.r.t. clay) of SPA and ball milled for 24 h using clay balls. Processing methods for porous kaolin can be described in three steps viz., (a) frothing of aqueous solution of SDS with varying concentration (0.3–6 wt%) by magnetic stirring at 900 rpm for 1 h, (b) the addition of well dispersed clay slurry (10 ml) to the frothed SDS solution while magnetic stirring is continued for another 1 h for the homogenization of the air bubbles, and (c) addition of the setting agent (12 wt% w.r.t. clay) which is the partially polymerized methylol urea (MU) solution. The polymerization of methylol urea (MU) solution was initiated separately by adding the requisite amount of urea in acidic medium (pH~2) until a milky solution was obtained, and this foam stabilizer was added immediately. Further polymerization lead to thick clay foam. The whole stirring process was done in the plastic mold and removed after drying at ambient temperature for 24 h. It was further heat treated at 120 °C in an air oven for 6 h so that the low density urea formaldehyde resin gets cross-linked and forms a high density polymer and gives strength to the green body.

The strength of the processed green body was further enhanced by the sintering process, in which the green body was heated continuously to 350 °C at a heating rate of 1 °C/min and held for 1 h for the complete binder removal, then to 1350 °C at a heating rate of 10 °C/min and sintered for 3 h. The different samples processed are represented as SDS-*X*, where *X* represents the SDS concentration.

The physical parameters like density, total porosity (P_t), closed porosity (P_c), and open porosity (P_o) of the sintered samples were determined by water penetration method based on Archimedes principle by the following equation [29]:

$$\text{Density,}\quad d_b = \frac{m1}{m3-m2} \times d_w$$

$$\text{Open porosity,}\quad P_o = \frac{m3-m1}{m3-m2} \times 100$$

$$\text{Total porosity } P_t = \frac{dt-db}{dt} \times 100$$

$$\text{Closed porosity } P_c = P_t - P_o$$

where $m1$ is the mass of the dried sample, $m2$ is the apparent mass of the saturated sample weight in liquid, $m3$ is the mass of the saturated sample weighed in air, d_t is the density of the solid, determined according to EN 993-2 (or calculated from the composition), d_w is the density of the fluid for buoyancy, d_b is the bulk density of the sample.

The XRD analysis of sintered and green kaolin foams were carried out by PANalytical Instrument, thermal analysis of green kaolin foam was performed by Hitachi High-Tech STA 7200 instrument. Pore size and interconnectivity were analyzed by Mercury Intrusion Porosimeter (Quantachrome Poremaster for Window) and the microstructural features of the porous body by SEM (JEOL Scanning electron microscopy).

3. Results and discussion

The foamability and foam stability at different SDS concentrations (0.3–8 wt%) were characterized by measuring the foam volume after 1 h of magnetic stirring at 900 rpm and at different idle times after the foaming process as shown in Fig. 1a and b respectively. The analysis revealed that good foamability, and a