Preparation and properties of nanostructured ceramic foam from kaolinite

Petr Ptáček [a],*, Karel Lang [b], František Šoukal [a], Tomáš Opravil [a], Lukáš Tvrdík [b], Radek Novotný [a]

[a] Brno University of Technology, Faculty of Chemistry, Centre for Materials Research CZ.1.05/2.1.00/01.0012, Purkyňova 464/118, Brno, CZ-612 00, Czech Republic
[b] P-D Refractories CZ, Nádražní 218, Velké Opatovice, CZ-679 63 Czech Republic

A B S T R A C T

The effective method for preparation and stabilization of nanostructured ceramic foam from kaolinite is described in this work. The technique is based on the redistribution of particles from original kaolinite aggregates and on the formation of solid framework of aqueous foams stabilized by surfactants. This process is spontaneous and highly effective as the surface energy of the system decreases and provides the driving force for rearrangement of solid phase in foam. The stability of these structures is time-limited, as water flowing from the bubble walls reduces their thickness. Therefore the structure of foam must be stabilized by the materials absorbing water physically or by formation of hydrates. The following high-temperature treatment provides solid foam prepared by sintering and having certain mechanical strength. The foams of bubble walls thickness within the nanometers scale can be prepared by this method hence the thickness of wall is considerably smaller than the median of particle size of original kaolinite.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Foams can be defined as dispersion systems based on the bubble gas phase, usually air, dispersed in continuous matrix of liquid (*aqueous and non-aqueous liquid foams*) or solid (*solid foams*), e.g. pumice as well as steel, glass and concrete foams. The diameter of bubbles is usually of several millimeters, but the spherical shape is not common as the weight of foam causes the mutual deformation and the formation of irregular polyhedral cells. The structure of foams is often compared to honeycombs. The bubble walls always include the same angle of 120°, thus maximum four bubbles can be in contact at one point. Such structure provides foam with certain mechanical strength and elasticity [1–4].

Liquid foams are usually prepared by mechanical dispersion of gas in liquid in the presence of surfactant. These compounds reduce the surface tension due to the formation of films on the interface as they contain both the hydrophobic and the hydrophilic groups. Foams are then always formed under dynamic conditions so the equilibrium of adsorption of surfactant is usually not achieved. The applied kind and concentration of surfactant determine the time-stability and the structure of foam. Higher viscosity of surface layer, its flexibility and hydration of polar groups of surfactant decelerate flowing of water from bubble walls and thus are factors which contribute to the time-stability of foams. This fact may have significant influence on the magnitude of forces stabilizing foam and foam films [3,5–9].

The research on the structure, behavior and properties of foams is motivated by both, the preparation of foams and the prevention from undesirable formation of foam. For the technical application (usually filters, carriers of catalysts, biomaterials and thermal insulating materials [4,10]) such factors as stability, specific surface and porosity of foams are important. Foams were also used in wide range of industrial processes e.g. flotation [11]. As for the time-stability of foams, the control of bubble size and the preparation of monodisperse foams are intensively studied [12]. The structure and the processes of coarsening and drainage of foams [13] and its dynamics are also affected by fine particles [14–18].

The paper deals with the technique of preparation of nanostructured ceramic foam from kaolinite where the formation of kaolinite framework is driven by decreasing surface energy of the system and provides mechanical support to the foam structure. The stabilization of foam by diatomaceous earth significantly increases the time-stability. The structure and properties of foam as well as the processes occurring during the stabilization and further thermal treatment were investigated.

2. Experimental

2.1. Preparation of foam

Kaolin with the content of kaolinite (Sedlec Ia, produced by Sedlecký kaolin) of 92% was used to prepare the solid framework of aqueous foam stabilized by anionic surfactant of a sulfate-type. The diatomaceous earth (Holland) and high-alumina cement (AC, Secar 52, Lafarge) were used for the stabilization of the foamed system.
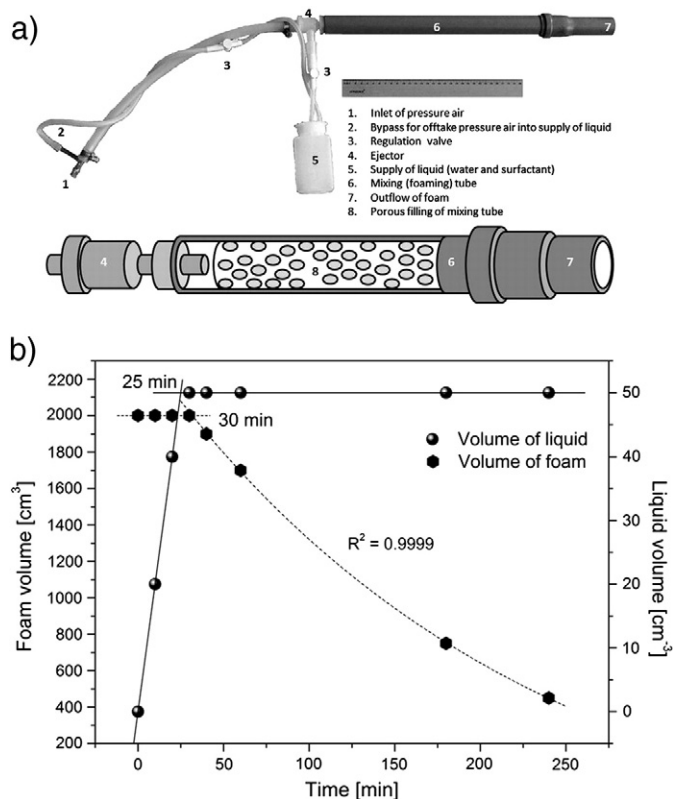
Fig. 1. Foam producing device (a) and the time-stability of foam (b).

Foam was prepared using the equipment shown in Fig. 1(a). The usage of mixture of surfactant and water with the mass ratio of 1:22 enables to prepare foam of the volume density of $30 - 50 \ kg \times m^{-3}$ (depending on the applied working air pressure in the mixing tube). The time stability of foam is given in Fig. 1(b). While the volume of foam stays almost unchanged within the first 30 min, the volume of water on the bottom of column reaches a maximum value of 50 ml. After this period, the volume of foam decreases exponentially with time.

The composition of the system and some properties of the components of foam are given in Table 1. The median of particle size (x_{50}) of kaolinite, diatomaceous earth and alumina cement was investigated by particle size analyzer Helos (Sympatec). The pour density (PD) was assessed according to national standard ČSN 727018.

The preparation of foam is schematically shown in Fig. 2. Setting of alumina cement provides the mechanical performance for the manipulation with raw foam before thermal treatment. In order to avoid undesirable effect of surfactant on the hydration process, AC was firstly mixed with water. Within the induction period when the hydration has just begun but its rate was very small, kaolin and next separately prepared water foam were stirred into the AC mixture. While AC stabilizes foamed system via water consumption for the formation of hydration products, diatomaceous earth absorbs the water physically.

Foam achieves long-term stability by the addition of diatomaceous earth or other matter of high porosity which can adsorbs water. The foamed and stabilized kaolinite slurry was inserted into the mould. Setting of cement provides mechanical strength sufficient for the manipulation during following thermal treatment — drying at 110 °C and firing with heating rate 2 °C min^{-1} up to temperature of 1250 °C under static air kiln atmosphere.

2.2. Foam properties and thermal treatment

The structure and the properties of foam were investigated by scanning electron microscopy (SEM) using field emission microscope Jeol JSM-7600F. High temperature X-ray diffraction analysis (HT-XRD, X'pert Empyrean, PANanalytical) with high temperature chamber HTK 16 (Anton Paar) and simultaneous TG-DTA and EGA were used to investigate the changes in the phase composition during high temperature treatment. Effluent gas analysis (EGA) was performed with TG-DTA Q600 (TA Instruments) connected with measuring cell of infrared spectrometer iS10 (Thermo Scientific) via stain-less steel capillary heated to the temperature of 200 °C. Specific surface area (SSA) of foam was measured by BET (Chembet 3000, Quantachrome instruments).

The apparent density and porosity of foam after thermal treatment to temperature of 1250 °C were assessed by the evacuation method and the hydrostatic weighting and the pycnometric measurements were used for the determination of the true density. The thermal conductivity at ordinary temperature was measured by TCi (C-Therm) analyzer without the contact agent.

The behavior during sintering was investigated by the horizontal type heating microscope EM 201 (Leitz). The cylinder shaped specimen of the diameter and the height of 3 mm was heated with heating rate of 5 °C min^{-1} up to the temperature of 1600 °C under static air. The pictures of specimen were collected by CCD camera with the step of 25 °C and used to determine the temperature of the point of sintering (SP).

3. Results and discussion

Fig. 3 shows that the particles originating from the large aggregates of kaolinite (a) are redistributed near to the surface of liquid phase to form a solid framework of raw foam that makes a solid replica of the original water-surfactant foam added to the slurry of kaolin and alumina cement. The process leads to the formation of bubbles with wall thickness lesser than the size of aggregates of kaolinite in the applied kaolin (b).

Fig. 4 shows the morphology of foam after thermal treatment. The walls of cells in foam form an angle of ~120° (a). Despite structural rearrangement and roughening of foam during the setting of AC and the thermal treatment, the thickness of wall of foam cells is maintained in nanometers scale (b). The dimensions considerably smaller than the diameter of particle size in original kaolinite (Table 1) prove the structure rearrangement of kaolinite aggregates during the preparation of foam.

The processes during the thermal transformation of stabilized kaolinite foam into ceramic foam were studied by high-temperature X-ray diffraction analysis (Fig. 5).

Initial sample consists of kaolinite, muscovite, quartz and calcite. The presence of surfactant leads to the formation of nordstrandite instead of expected gibbsite during the hydration of alumina cement. The dehydroxylation causes the diffraction lines of nordstrandite and kaolinite to disappear at 275 °C and 575 °C, respectively. The transformation of low quartz to high quartz takes place at 575 °C. Lime is formed by thermal decomposition of calcite at 675 °C. These diffraction lines gradually disappear from the temperature of 1025 °C due the formation of gehlenite followed by anorthite (1250 °C). The diffraction lines of illite are present up to the temperature of 1025 °C. Mullite and cristobalite are formed at the temperatures higher than 1175 °C.

The results of TG-DTA and EGA performed on stabilized foam are shown in Fig. 6(a) and (b). Small endothermic peak at 63 °C is related

Table 1
The composition of foamed system and properties of foam constituents.

Component	Kaolin [% wt.]	Diatomaceous earth [% wt.]	Alumina cement [% wt.]	Water [% wt.]	Stabilized foam [dm^3]
Content	39.7	1.0	2.6	56.7	10
x_{50} [μm]	4.3 ± 0,1	10.4 ± 0.3	9.3 ± 0.1	–	–
PD [kg m^3]	476 ± 12	305 ± 10	1054 ± 6	–	–