

Novel glass ceramic foams materials based on red mud

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Abstract

Glass ceramic foams were prepared using red mud and fly ash with added CaCO_3 as foaming agents. The aim of the present work was to investigate the possibility of adding red mud, an alkaline leaching waste, in the raw material for the preparation of glass ceramic foams. The results of mineralogical analyses as well as the microscopic examination showed that the use of the red mud affect the mineralogical characteristics and structures of the as produced foams. The influence of amount of red mud on the bulk density and compressive strength of samples was further evaluated. The experimental results showed that relatively low bulk density foams ($0.33\text{--}0.41\text{ g/cm}^3$) could be obtained by using low sintering temperature ($760\text{--}840\text{ }^\circ\text{C}$) when the red mud/fly ash ratio does not exceed 40:60. The reduction of sintering temperature or, above all, the reduction of the holding time, was found to limit the coalescence and significantly improve the compressive strength of the foams ($0.33\text{--}2.74\text{ MPa}$).

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1. Introduction

Glass ceramic foams are porous materials filled with small uniform pores, which are closed or inter-communicating. The specific structure of glass ceramic foams determined that this sort of materials has many properties including low density, low thermal conductivity, high surface area, good thermal shock resistance, high specific strength, etc. [1]. Hence, glass ceramic foams represent a highly valuable material for thermal and acoustic insulation, since they possess a generally higher mechanical, chemical and thermal stability than the polymeric foams currently employed [2]. For instance, in the case of a fire, polymeric foams are known to be largely damaged with the evolution of potentially toxic gases, while glass ceramic foams, on the contrary, are un-inflammable due to their inorganic nature [3,4]. Dating back to 1930s, the process of forming the glass ceramic foams is to introduce the gases into the molten raw materials [5]. This method has not been taken nowadays. By far the simplest technique for producing porous

ceramics is based on powder sintering with the incorporation of foaming agents, which is also the method employed in the present investigation. Incorporation of foaming agents generates porosity by emitting gas during reaction at elevated temperatures [6]. During sintering, the foaming may be caused by an oxidation effect, which is typical for C-based “foaming agents”, namely C (graphite, carbon black, coal, etc.) and SiC, or by a decomposition process of minerals like carbonates (Na_2CO_3 , CaCO_3 , MgCO_3 , etc.) or sulfates (CaSO_4 , i.e. gypsum) [2].

Ongoing concern over the disposal of solid wastes from the residues of power generation and the processing and manufacturing industries has led to a tremendous amount of work investigating the feasibility of recycling these wastes over the last decades. Glass ceramic foams represent an interesting application for solid wastes from an economic and environmental point of view. Various methods have been used to produce glass foams from a wide range of industrial wastes. Various solid wastes have been used including coal ash [6,7], fly ash [8–10], metallurgical slag [11] and other specific sediment from reservoir [12].

Red mud or bauxite tailings produced during alkali leaching of bauxite have continued to be one of the prime concerns

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of aluminum/alumina industry from the point of view of resource conservation and protection of the environment [13]. Red mud characterizes to be of high alkalinity. Alkaline solution and red mud slurry usually seep from the red mud landfill site or pipelines into ground or underground water, having the risk of contamination of natural resources and living organisms. Generally, 1–1.5 t of red mud will be produced with each ton of alumina production. It is estimated that nearly 90 million ton of red mud is produced annually worldwide. Presently in China alone nearly 15 million ton is generated every year, making the country as one of the largest producer of red mud [14]. Over the last few decades, efforts have been directed towards finding cost effective and compatible solutions for waste minimization and utilization. Specific innovations pertaining to utilization of these wastes highlighted in the paper include metal recovery from red mud, applications in the treatment of wastewater [15–19] and as additive to plastic or ceramic materials (bricks, tiles) [20–22].

As mentioned above, much work has been carried out in recent years to reuse the red mud. Sometimes, because of the complexity of red mud, preproduction refinements, which may complicate and increase the cost of a recycling process, are needed in order to yield a waste material that is worth recycling into a new useful material with a certain function. On the other hand, if pores in a material can be exploited to achieve a certain property, e.g. sound or thermal insulation, porous materials become a viable option for reusing red mud without a (usually costly) refining step.

The present paper aims at studying the feasibility to reuse red mud in the production of glass ceramic foams. In the present study, calcium carbonate (CaCO_3) was used to produce glass ceramic foams. During the heating process the carbonate ions decomposed to generate CO_2 gas as the softened glass phase forms, and the gas is then enclosed by the glassy phase, producing a porous structure in the sintered samples in the end. Relationship has been examined between red mud addition and resulting pore morphology and mechanical properties of foams produced from selected mixtures of red mud and fly ash.

2. Experimental procedure

2.1. Materials

Red mud used in this paper had a chemical composition (wt%) of 21.03% SiO_2 , 26.49% Al_2O_3 , 27.36% Fe_2O_3 , 2.27% CaO , 10.02% Na_2O , and 1.53% TiO_2 . Cullet of fly ash had a chemical composition (wt%) of 48.31% SiO_2 , 36.99% Al_2O_3 , 4.66% Fe_2O_3 , 2.26% CaO , 0.80% MgO , 0.31% Na_2O , 0.98% K_2O and 1.41% TiO_2 . The particle size of the red mud and the fly ash was mainly in the range of 1–10 μm and 10–40 μm , respectively. Six samples comprising red mud and fly ash

with red mud/fly ash (R/F) ratios R10F90, R20F80, R30F70, R40F60, R50F50 and R60F40 were prepared. The total mass percentage of red mud and fly ash mixtures is 60%. $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (30 wt%) is introduced as the flux agent to lower the softening point of compounds and make the composition be close to formation range of glass [10]. CaCO_3 (5 wt%) and Na_3PO_4 (5 wt%) are chosen as foaming agent and foaming stabilizer, respectively.

2.2. Processing

Batches were obtained by dry mixing the components in a ball mill for 2 h. Uniaxial pressing was conducted at 20 MPa in a laboratory press, and cylindrical pellets of 25 mm in diameter and 6 mm thick were obtained. The specimens were then fired in air, in an electric laboratory furnace with a heating rate of 15 $^\circ\text{C}/\text{min}$. Each sintering experiment was carried out in duplicate at different maximum temperatures in the range 760–840 $^\circ\text{C}$, and with different holding times (5–30 min), to evaluate the effect of these parameters on the characteristics of the glass ceramic foams. Natural convection inside the furnace was used for cooling.

2.3. Characterization techniques

The bulk density of materials was determined by measuring the weight and the dimensions of the produced materials. The obtained foams were subjected to compression tests by using an UTS machine, with a crosshead speed of 1 mm/min, employing samples of about 10 mm $\times$ 10 mm $\times$ 10 mm, cut from larger specimens. Five different samples of each composition were tested.

The morphology of the foams was investigated by optical microscope and scanning electron microscope. Samples in powder form were subjected to X-ray diffraction analysis to investigate the crystalline phases (XRD, D/max-rA, Japan Rigaku), by using Cu Ka radiation (0.154056 nm), with the scanning rate 8 $^\circ/\text{min}$ and the scanning range 5 $^\circ$ –80 $^\circ$ at room temperature.

3. Results and discussion

3.1. Influence of red mud content

Fig. 1 shows the appearances of the foam glasses with different red mud/fly ash ratios at the temperature of 780 $^\circ\text{C}$ for 30 min. The volume first increases with increasing addition of red mud; however when the red mud/fly ash becomes more than R40/60, the volume begins to shrink and the surface becomes less smooth. Pellets with red mud/fly ash ratio R10F90, R20F30,



Fig. 1. Side view of pellets comprising red mud and fly ash sintered at 780 $^\circ\text{C}$. (A) R10F90; (B) R20F80; (C) R30F70; (D) R40F60; (E) R50F50; and (F) R60F40.

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