

Processing of low-density alumina foam

Prasanta Jana, V. Ganesan*

Materials Chemistry Division, Indira Gandhi Centre for Atomic Research, Kalpakkam 603102, Tamil Nadu, India

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Abstract

A novel method for synthesizing low-density alumina foam has been developed. The alumina foam with 98.5% porosity was synthesized by an unconventional route from an aqueous aluminum nitrate–sucrose solution. The resin formed by heating this solution underwent foaming and set into solid green foam, which was sintered at 1873 K. The thermogram of the green foam showed mass loss in four stages. The foam exhibited interconnected porous network with window size in the range 103–226 and 167–311 μm for foams sintered at 1223 and 1873 K, respectively. The alumina foam sintered at 1223 K exhibited gamma phase and that sintered at 1873 K exhibited alpha phase.

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1. Introduction

Alumina in various forms has important industrial applications. Alumina powder is widely applied in catalytic processes owing to its chemical strength and thermal stability in a wide temperature range. The major applications of alumina are in refractory, ceramic, polishing and abrasive material industries. Cooper and Taylor¹ reported use of alumina as getter material for ^{137}Cs in sodium. Alumina ceramics with porous network, namely the alumina foams, have important applications in thermal insulation, molten metal filtration, diesel engine exhaust filtration, catalytic support and industrial hot gas filtration. It also finds applications in health and medical fields such as bio-ceramics in hip replacements and drug delivery.^{2–6} Kosmulski et al.⁷ reported complete filling of porous alumina with ionic liquids such as 1-alkyl-3-methylimidazolium tetrafluoroborates, hexafluorophosphates, trifluoromethanesulfonate and bis(trifluoromethylsulfonyl) imides which can be utilized to produce solid electrolytes for batteries and fuel cell applications. Bose et al.⁸ studied an improved procedure for producing ceramic scaffolds as bio-ceramic materials with controlled porosity. The authors concluded that porous alumina scaffolds both pure and hydroxyapatite coated form

can potentially provide a non-toxic surface for bone bonding.

Alumina also finds application as base material for gas and liquid purification. We envisage application of alumina foam doped with C and Ni, as radionuclide trapping material for purification of sodium in fast reactor primary circuits free of fission and activated corrosion products such as ^{137}Cs , ^{134}Cs , ^{54}Mn and ^{60}Co .

Generally, alumina foams are synthesized by impregnation or electrospraying of alumina slurry, prepared by ball milling, on polymeric replica. Jayasinghe and Edirisinghe⁹ synthesized alumina foam with 96% porosity by carbonizing alumina dispersed polyurethane foam prepared by electrospraying alumina–ethanol slurry on polyurethane foam. Han et al.¹⁰ reported preparation of alumina foam with 86% porosity combining the sponge method and the pore former technique. They reported synthesis of alumina foam from alumina slurry prepared by ball milling 95% alumina and 5% additives together, followed by addition of aqueous solution of 5% polyvinyl alcohol (PVA) and impregnated in polymeric sponge. Prabhakaran et al.¹¹ prepared alumina foam with 93.5–96.7% porosity from a mixture of alumina, aluminum nitrate and sucrose solution. In this method, aluminum slurry, prepared by ball milling, and a dark viscous resin of aqueous aluminium nitrate–sucrose solution, prepared by heating on a hot plate, were mixed together to obtain a green foam, which on sintering at 1873 K in air yielded alumina foam. Dhara and Bhargava¹² reported a simple

* Corresponding author. Tel.: +91 44 27480219; fax: +91 44 27480065.
E-mail address: ganesh@igcar.gov.in (V. Ganesan).

direct casting route to ceramic foam (95% porosity) from alumina slurry, prepared by ball milling alumina with ovalbumin (freshly extracted egg white) and Darvan 821A as a dispersant.

Although combustion synthesis is a well-known technique, use of combustion technique for synthesis for alumina foam is not popular. Most of the earlier works report synthesis of alumina foam using alumina slurry as a precursor. The well-dispersed alumina slurry is prepared by ball milling. The slurry is electrosprayed or impregnated on polymer matrix followed by heating in air to get replica of that polymeric matrix. In this communication, we report a novel synthesis of alumina foam with 98.5% porosity from aqueous aluminum nitrate–sucrose solution without use of alumina slurry as a precursor material. Since aluminum nitrate and sucrose are water soluble, this process does not demand impregnation or electrospraying techniques as in other reported processes. The process reported in this work is very simple to synthesize alumina foam.

2. Experimental

An aqueous solution containing 25 g of sucrose in 150 mL of distilled water with 10 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was prepared in a Teflon beaker. The pH of prepared solution is 3.5. The solution was slowly concentrated by heating at 383 K on a hot plate with constant stirring (100 rpm), till it turned into a dark viscous resin. After a while, the resin started foaming and upon continuous heating at 383 K in an air oven over a period of 24 h yielded dry foam. The green foam thus obtained was cut into regular shapes and heated in a furnace at a heating rate of 100 K/h up to 1873 K in air with 5 h of soak time to obtain sintered alumina foam.

Since the synthesized alumina foams could be shaped, their bulk densities were readily calculated from their weights and volumes. The bulk densities of alumina foam sintered at 1223 and 1873 K were 0.03 and 0.06 g/cc, respectively. The porosity (P) of the foam was calculated using the equation:

$$P = \frac{100(\rho_t - \rho_b)}{\rho_t}$$

where ρ_t is the theoretical density and ρ_b is the bulk density of the material.^{10,11} Foams sintered at 1223 and 1873 K were in γ -alumina and α -alumina phases, with theoretical densities of 3.71 and 3.98 g/cc, respectively. The calculated porosities of alumina foams sintered at 1223 and 1873 K were 99% and 98.5%, respectively.

The thermal stability of green foam was studied at a constant heating rate of 10 K/min up to 1473 K both in air and in argon atmosphere. A high temperature thermogravimetric analyzer (TGA, SETSYS 16/18 Evolution, Setaram, France) with a resolution of 1 μg was employed. For evolved gas analysis, a quadrupole mass spectrometer (Pfeiffer Vacuum, Germany) was used. The green foam in fine powder form was loaded in an alumina crucible and connected to the microbalance of TGA.

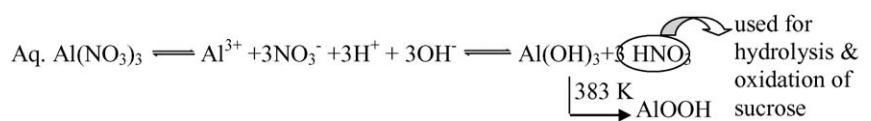
The carrier gas (air and argon) was passed over the sample at a rate of 20 mL/min throughout the experiment.

The microstructure of the alumina foams was obtained using scanning electron microscope (SEM, Philips, XL30, The Netherlands). In scanning electron microscopy, high-energy electrons interact with the specimen and the collected secondary and backscattered electrons are utilized for imaging. Since the alumina foams are electrically non-conducting, they were coated with gold–palladium alloy using a sputter coater (VG Microtech, UK) prior to examination by SEM.

The room temperature X-ray diffractograms of powdered green foam and alumina foams sintered at 1223 and 1873 K were recorded using X-ray diffractometer (Philips X'pert system, The Netherlands) with Cu K α radiation ($\lambda = 0.15406 \text{ nm}$). The crystallite size was calculated using Scherer's formula.

3. Results and discussion

Owing to high degree of dissociation, $\text{Al}(\text{NO}_3)_3$ in water is present mostly as constituent ions namely Al^{3+} , NO_3^- , H^+ and OH^- . It is known that sucrose in acidic aqueous medium undergoes hydrolysis to form glucose and fructose. Upon heating, the glucose and fructose are further oxidized to a mixture of hydroxy carboxylic acids such as gluconic, saccharic, glycolic and tartaric acids. Upon heating the solution further, the hydroxy carboxylic acids undergo polymerization and condensation to form a resin, which after a while forms a solid foam.¹³ The foaming of the resin was accomplished by the evolution of NO_x gas generated by the decomposition of $\text{Al}(\text{NO}_3)_3$. This was also corroborated by the fact that sucrose did not undergo foaming in the absence of $\text{Al}(\text{NO}_3)_3$ or HNO_3 when heated at 383 K. $\text{Al}(\text{NO}_3)_3$ in presence of sucrose is decomposed to form AlOOH at 383 K, because the acidic part (HNO_3) of aqueous sucrose– $\text{Al}(\text{NO}_3)_3$ solution is used to hydrolyze and oxidize the sucrose as indicated below.^{11,13}



In this synthesis procedure of alumina foam, sucrose– $\text{Al}(\text{NO}_3)_3$ solution upon heating with constant stirring formed a viscous resin containing AlOOH with the undecomposed $\text{Al}(\text{NO}_3)_3$ dispersed in the resin. After several hours of heating at 383 K, the resin formed solid green foam. The green foam was sintered up to 1873 K. The alumina foams exhibited densities of 0.03 and 0.06 g/cc and porosities of 99% and 98.5% after sintering at 1223 and 1873 K, respectively. The sintered foam exhibited good mechanical strength for handling as indicated in the trial runs in liquid sodium for radionuclide trap studies.

Thermal stability of green foam was studied both in air and in argon atmosphere up to 1473 K. The mass loss of the green foam was noticed up to 910 K after which no mass loss was observed. In air atmosphere, the green foam showed 92% mass loss in four stages (stage-I: 300–440 K, stage-II: 440–516 K, stage-III: 516–700 K and stage-IV: 700–910 K) as shown in Fig. 1. Stage-I

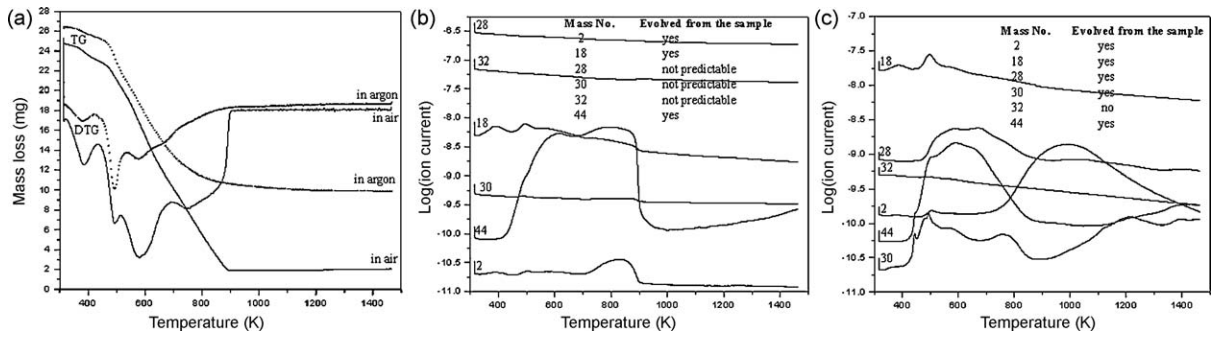


Fig. 1. Thermal study of alumina foam: (a) thermal decomposition pattern of green foam in air and in argon, (b) concentrations of evolved gas from green foam in air and (c) concentrations of evolved gas from green foam in argon as measured from respective ion currents as function of temperature.

was due to removal of adsorbed moisture from the green foam. Stages II–IV were due to decomposition of other compounds present in the green foam. It is seen from the evolved gas spectrum that almost all gases started evolving at nearly the same temperature although the rate of evolution of different gases vary with different temperatures as indicated in stages (II–IV). Owing to this, it was difficult to resolve the processes taking place in the individual stages II–IV. In argon atmosphere, the green foam showed 62% mass loss in three stages (stage-I: 300–423 K, stage-II: 423–583 K and stage-III: 583–910 K). From the evolved gas analysis, both in air and in argon atmosphere, it was concluded that the gases which evolved from the green foam were H₂, H₂O, CO, NO and CO₂.

Fig. 2 shows secondary electron images of (a) alumina foam sintered at 1223 K, (b) alumina foam sintered at 1873 K, (c) solid bridge of alumina foam cage structure and (d) grains in solid bridge.

The alumina foam sintered at 1223 K showed elliptical shaped windows that were held by hexagonal edges with 103–226 μm window size. The alumina foam sintered at 1873 K showed elliptical shaped windows that were held by distorted hexagonal edges with 167–311 μm window size. It indicated an increase in window size with increasing sintering temperature, in spite of the decrease in overall volume of the foams. But from the density measurements, it was concluded that the density was found to increase with increase in sintering temperature. Generally with increase in sintering temperature, the window size is expected to decrease leading to a decrease in volume and hence an increase in density. But, in the present case, the window size increase was due to the breaking of weak edges of alumina foam to form bigger windows, still resulting an overall decrease in total volume. Fig. 3 shows the energy dispersive X-ray (EDX) spectra of (a) green foam and (b) alumina foam sintered at 1873 K. Fig. 3(a) shows three peaks. The first peak is corresponding to C (0.277 keV). Second is due to O (0.525 keV)

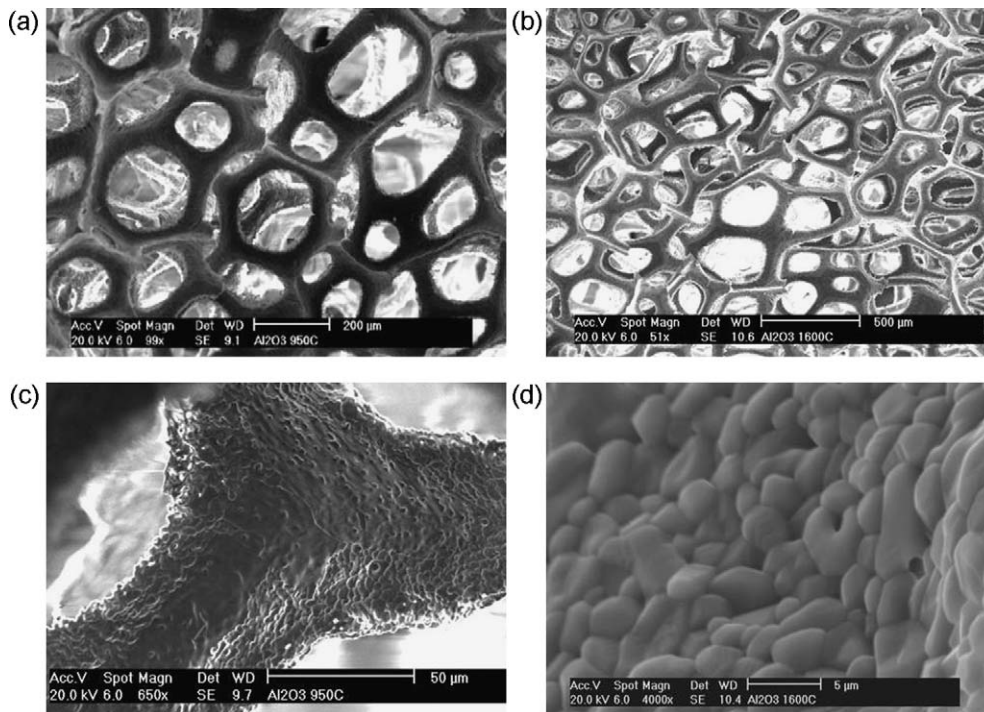


Fig. 2. Secondary electron images of: (a) alumina foam sintered at 1223 K, (b) alumina foam sintered at 1873 K, (c) solid bridge of alumina foam cage structure and (d) grains in solid bridge.

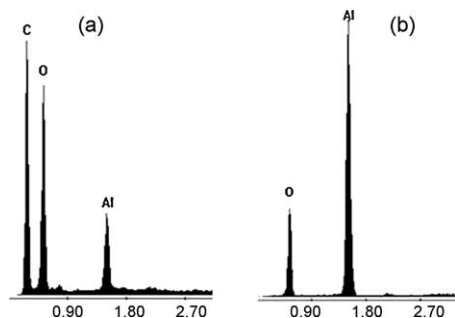


Fig. 3. EDX spectra of: (a) green foam and (b) alumina foam sintered at 1873 K.

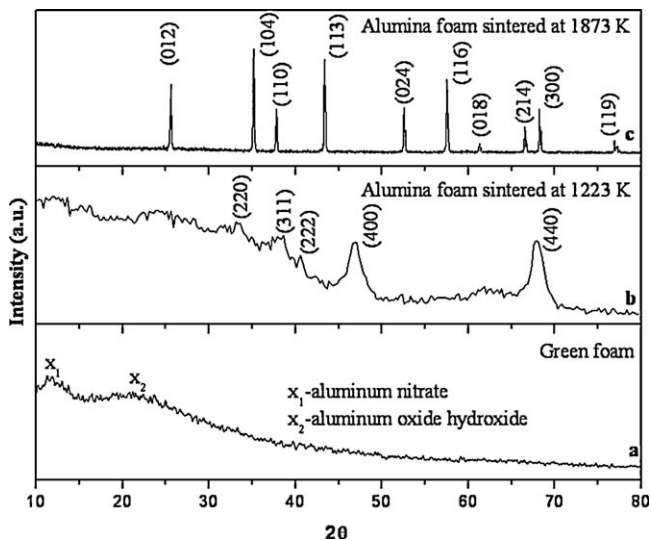


Fig. 4. XRD pattern of: (a) green foam, (b) alumina foam sintered at 1223 K and (c) alumina foam sintered at 1873 K.

and third be due to Al (1.486 keV). In case of Fig. 3(b) peak corresponding to C is vanished and only two peaks are observed due to O and Al. This indicated that all the carbon impurity was removed from the alumina foam making the foam high pure.

Alumina exists in a variety of metastable structures including γ , η , δ , θ , κ and χ -phases, as well as its stable α -phase.^{14,15} Fig. 4 shows the typical XRD patterns of the green foam and foams sintered at 1223 and 1873 K. From the XRD patterns, it is clear that the alumina foam sintered at 1223 K is in γ -alumina phase with cubic crystal system (JCPDS file no. 29-0063) and that sintered at 1873 K is in α -alumina phase with rhombohedral crystal system (JCPDS file no. 81-1667). The green foam (383 K) is amorphous in nature as shown in Fig. 4(a). It is also evident from Fig. 4(a) that AlOOH and undecomposed $\text{Al}(\text{NO}_3)_3$ are dispersed in the green foam. As the green foam is carbonized at very low temperature (383 K), no sharp peaks are visible in the XRD pattern. The crystallite size of alumina foam sintered at 1223 K was 6 nm and that sintered at 1873 K was 61 nm.

4. Summary

A novel method for synthesis of very low-density alumina foam was developed through aqueous aluminum nitrate–sucrose solution route without employing electrospinning or impreg-

nation (on polymeric replica) technique. The alumina foams sintered at 1223 and 1873 K exhibited densities of 0.03 and 0.06 g/cc with porosities of 99% and 98.5%, respectively. The mass loss of the green foam was noticed up to 910 K, which reached a plateau through. The green foam exhibited 92% and 62% mass loss in air and in argon atmosphere, respectively. From the evolved gas analysis of the green foam, it was concluded that the gases that evolved were H_2 , H_2O , CO , NO and CO_2 . The alumina foam sintered at 1223 K showed near circular windows of 103–226 μm that were held by hexagonal edges. The alumina foam sintered at 1873 K showed elliptical shaped windows of 167–311 μm that were held by distorted hexagonal edges. EDX spectra indicated that the synthesized alumina foam (1873 K) is free from carbon impurity. From the XRD patterns, it was clear that the alumina foam sintered at 1223 K was in γ -alumina phase with cubic crystal system and that sintered at 1873 K was in α -alumina phase with rhombohedral crystal system. The crystallite size of alumina foam sintered at 1223 K was 6 nm and that sintered at 1873 K was 61 nm.

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