

Fabrication of High-Strength Alumina Composite Foams Through Gel-Casting

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ABSTRACT

A water-soluble gelatin combined with polyethylene microspheres was developed to prepare alumina composite foam. Gelatin was used as the gelling agent and polyethylene was used as the pore making template. On the other hand, kaolin was used to provide green strength and CuO was applied to decrease the required temperature as a sinter aid. Alumina bodies need elevate temperature for sintering, thus increasing the process cost. This process could be carried out at 1000 °C, therefore, it is more appropriate compared to previous studies. The effect of CuO amounts on the open porosity, water adsorption, and density as well as on the mechanical strength of the sintered foams was evaluated. The resulting samples, with relative densities between 0.97 and 1.16 g/cm³, and compressive strength between 1.4–5.5 MPa, comprised microstructures of semi-spherical pores. The phase component of the samples consist ~60% alumina, 11–15 % CuAl₂O₄, and 24–27 % Al₂SiO₅. The degree of crystallinity measured in the range of 66–83%. These changes are related to the CuO/Al₂O₃ ratio. On the other hand, gelatin and polyethylene as the gelling agent and pore template were used successfully in gel-casting process.

1. Introduction

Alumina is a widely used and cost effective ceramic material due to its exclusive characteristics such as high hardness, low thermal expansion coefficient, high refractoriness, outstanding thermal shock resistance, relatively high thermal conductivity, and electrical insulation [1]. Therefore, it finds a large number of applications not only in powder form but also in bulk configuration. Alumina powder is used as filler, catalyst, purification agent, abrasive, etc. [2]. Dense alumina bodies are applied in several industrial usages such as grinding balls, ceramic rollers, thermocouple tubes, seal rings and so on [3]. The other beneficial forms of alumina bodies are the porous components finding fundamental

applications such as: (i) cellular and conventional insulating bricks [4], (ii) electronics equipment including fuel cell scaffolds [5], batteries [6], (iii) filter, (iv) biomedicine [7], etc.

The feasibility of the preparation of porous ceramic bodies has been investigated, illustrating three main methods: (1) using polymeric foam to replicate ceramic materials, (2) emulsion templating, and (3) addition of a foaming agent to ceramic powder suspensions. The first method is based on coating polymeric foam with a ceramic slip. Firing the obtained product leads to burnout the organic part and to achieve the ceramic foam. The second method consists of the covering of hollow particles with a ceramic suspension (stabilizing gas bubbles).

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After that, the obtained particles are poured in a mold and packed together in the presence of the ceramic suspension. This process can be accomplished by blowing gas. The third technique includes a foaming agent, which is added to a ceramic suspension, casted in a mold, and then set by using a gelling agent [8].

There are several reports in the ceramic foam preparation field using the above method and/or methods, which are similar [9-13]. The researchers tried to improve the characteristics of the prepared foam by adjusting the shaping parameters, the additives amount, the kinds of materials, and also by using a combined method. In this study, a combination of two different techniques, the second and the third one, has been used to prepare alumina composite foam. For this reason, alumina powder as the main component was used. The sintering temperature of this material is relatively high; therefore, a sinter aid should be added. CuO was selected for this aim and the influences of Al₂O₃/CuO ratio on phase component, microstructure, physical properties, and mechanical behavior of the as-prepared foam bodies were studied.

2. Materials and methods

Alumina powder (99.7 %, G grade, Fibroma, India), kaolin (WBB, England), CuO (Labsynth, Brazil), sodium metasilicate (Na₂SiO₃, MS Jain group, Germany), Polyethylene microsphere (d=0.93 g/cm³, <100 μm, Clariant Italia SPA, Italy), and Gelatin (BE, Spain) were used as the raw materials. Alumina was used as the main component of the foam body. The preparation method was combined of gel-casting and emulsion templating. Polyethylene microsphere and gelatin were applied as air-bubble template and gelling agent, respectively. Although gelatin provides the green strength of the casted bodies, it acts after setting. Kaolin was added to the mixture to provide the green strength before gelatin setting. Sodium metasilicate was added as deflocculant in the kaolin containing mixture. CuO was used as a sinter aid to decrease the sintering temperature. The preparation procedure consists of four steps; suspension preparation, casting, drying, and sintering.

Three different suspensions were prepared according to Table 1. Alumina, kaolin, and CuO powders, water, and sodium metasilicate were poured in a rapid mill with alumina balls and

mixed for 30 min. Then, polyethylene was added to the as-prepared suspension and manually mixed. Finally, gelatin powder was solved in hot water and added to the suspension.

Cartonplast box with dimensions of 5×5×5 cm³ was used as the mold and the casting was accomplished under vibration to facilitate de-airing. It was relaxed for a day at 4 °C to set the gelling agent and then the shaped samples were de-molded. The drying process is very important in this procedure, because any remaining moisture in the bulk samples leads to distortion or destruction of the samples. The freeze-dryer (Christ, Germany) was used to achieve the aim. For this reason, the de-molded samples were frozen for 3 h at -20 °C, and then transferred to a freeze-dryer and treated for 48 h. After that, the samples were relaxed for 2 weeks to remove the moisture completely. The sintering process was accomplished at 1000 °C for 5 h with the heating rate of 5 °C/min.

The phase components of the samples were characterized by X-ray diffractometer (Xpert, Philips). The crystallite sizes of the specimens were calculated from the broadening of the XRD peaks using the Williamson-Hall method [14] according to equation (1).

$$B \cos \theta = 0.9 \frac{\lambda}{d} + \eta \sin \theta \quad (1)$$

Where d , θ , λ , η and B are crystallite size, diffraction angle, wavelength of the X-ray ($\lambda_{\text{Cu}}=1.540598 \text{ \AA}$), lattice strain, and the peak full width at half maximum (FWHM), respectively. Thus, when “ $B \cdot \cos \theta$ ” is plotted against “ $\sin \theta$ ” (for the main peaks of each XRD pattern), a straight line is obtained with the slope as lattice strain (η). The degree of crystallinity of the samples was quantitatively evaluated. In this method, ‘sum of net area’ / ‘sum of total area’ in PANalytical X’Pert High Score software was the criterion for the degrees of crystallinity. To calibrate the results, the backgrounds of peaks were determined by considering 100 % crystallinity for the commercial Al₂O₃ powder. The mass fractions of the identified phases were calculated by the matrix flushing model [15] using values of the scale factor (SF) and reference intensity ratio (RIR) values from the X’Pert software database. These methods were used elsewhere [16-19].

The microstructure was recorded by scanning electron microscopy (SEM, VEGA, TESCAN-LMU, Czech Republic). Simultaneous thermal

analysis (STA) of the dried samples was done under argon atmosphere at 1000 °C by a Netzsch system (409 PC Luxx, Netzsch, Germany). The compressive strength (CS) and elastic modulus (EM) of the samples were evaluated by three-point bending test (Gotech, Taiwan), according to ASTM C-133-97. The apparent porosity (AP), water absorption (WA), and bulk density (BD) were measured based on ASTM C-20-92. It should be mentioned that all of the compressive strength, apparent porosity, water absorption, and bulk density measurements were performed in triplicate and the actual results were calculated as the average values and the error bars are presented on the graphs. The follow diagram of the mentioned process is represented in Figure 1.

Table1. Chemicals amount for slurries preparation

Sample	A	B	C
Alumina (g)	74.7	72.4	70.1
CuO (g)	20.7	22.9	25.1
Kaolin (g)	66.1		
Polyethylene (g)	3		
Gelatin (g)	18		
Water (g)	115		

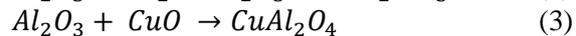
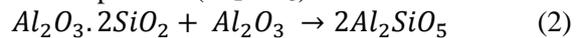
3. Results and Discussion

3.1. Phase component

Figure 2 shows the XRD patterns of the samples. After the firing process at relatively low temperature (1000 °C), the changes in the crystalline phase component of the as-synthesized bodies are due to the decomposition of kaolin, reaction between CuO and Al₂O₃, and amorphous phase formation. As the starting materials were similar with different amounts, the phase components are similar, including Al₂O₃ [Ref. Code: 71-1126], CuAl₂O₄ [Ref. Code: 73-1958], and Al₂SiO₅ [Ref. Code: 3-0513]. The phases amount depends on how much CuO is added to the mixture.

Semi-quantitative phase components and the degree of crystallinity are represented in Table 2. Sample A (containing the maximum amount of Al₂O₃ and the minimum amount of CuO) retains a high degree of crystallinity. On the other hand, the highest amounts of Al₂SiO₅ and the lowest amounts of CuAl₂O₄ have been

observed in this sample. It appears that the relatively low CuO content is responsible for the limiting the reaction between Al₂O₃ and CuO to form CuAl₂O₄, since this reaction leads to the appearance of a Eutectic line at 900 °C [20]. The crystallinity is dependent on the CuO amounts; therefore, this parameter reaches to the highest value in this sample. In samples B and C, increase in CuO and decrease in Al₂O₃ lead to the decrease in crystallinity and Al₂SiO₅ amounts and the increase in the CuAl₂O₄ amounts. More Cu amount facilitates reaction (3); therefore, reaction (2) cannot proceed well and its product (Al₂SiO₅) amount decreases.



The dominate phase of the samples is Alumina with more than 60 % of the phase component.

3.2. Microstructure

Figure 3 shows the photograph of the dried (part A) and sintered (part B) foam bodies, illustrating the skin layer on the surface. This layer on the surface can be removed before sintering, whereas the sintered bodies had sufficient strength for handling. The cellular structure and the cells cannot be seen in this figure due to their tiny dimensions.

Figure 4 shows the SEM images of the as-prepared samples. The microporous structures are observed for all samples. The interior walls of holes in sample A are not smooth, whereas the holes shapes in sample C are very regular. This phenomenon can be related to the degree of crystallinity. The existence of adequate amounts of liquid phase during sintering leads to form the strong walls, so they perfectly retain their structure. It should be mentioned that there are two kinds of holes in samples: semi-circular holes with a size of ~50 μm, and irregular-shaped holes with a size of <10 μm. The first type is probably originated from polyethylene microspheres. The particles size of this powder was about 40–80 μm. The calcination process causes the burnout of micro-balls and their traces are remained as holes. The second type of holes is originated from any organic materials present in the material such as gelatin, and also the structural water of kaolin.

A careful observation of the SEM graphs reveals the presence of some 10-50 μm particles; in

accordance with the particle size of G-grade alumina, they could correspond to Al_2O_3 particles which were identified by XRD. Since the sintering temperature was relatively low for alumina powder, no particles size change can occur. On the other hand, SEM images show the samples to contain a large amount of $<1 \mu\text{m}$ particles, related to the as-prepared phases

(CuAl_2O_4 and Al_2SiO_5 , see Figure 2). These tiny particles mostly sintered together surrounding the holes and Al_2O_3 particles. This phenomenon is dominated in sample C, related to the increased liquid phase amount elevated by the CuO powder.

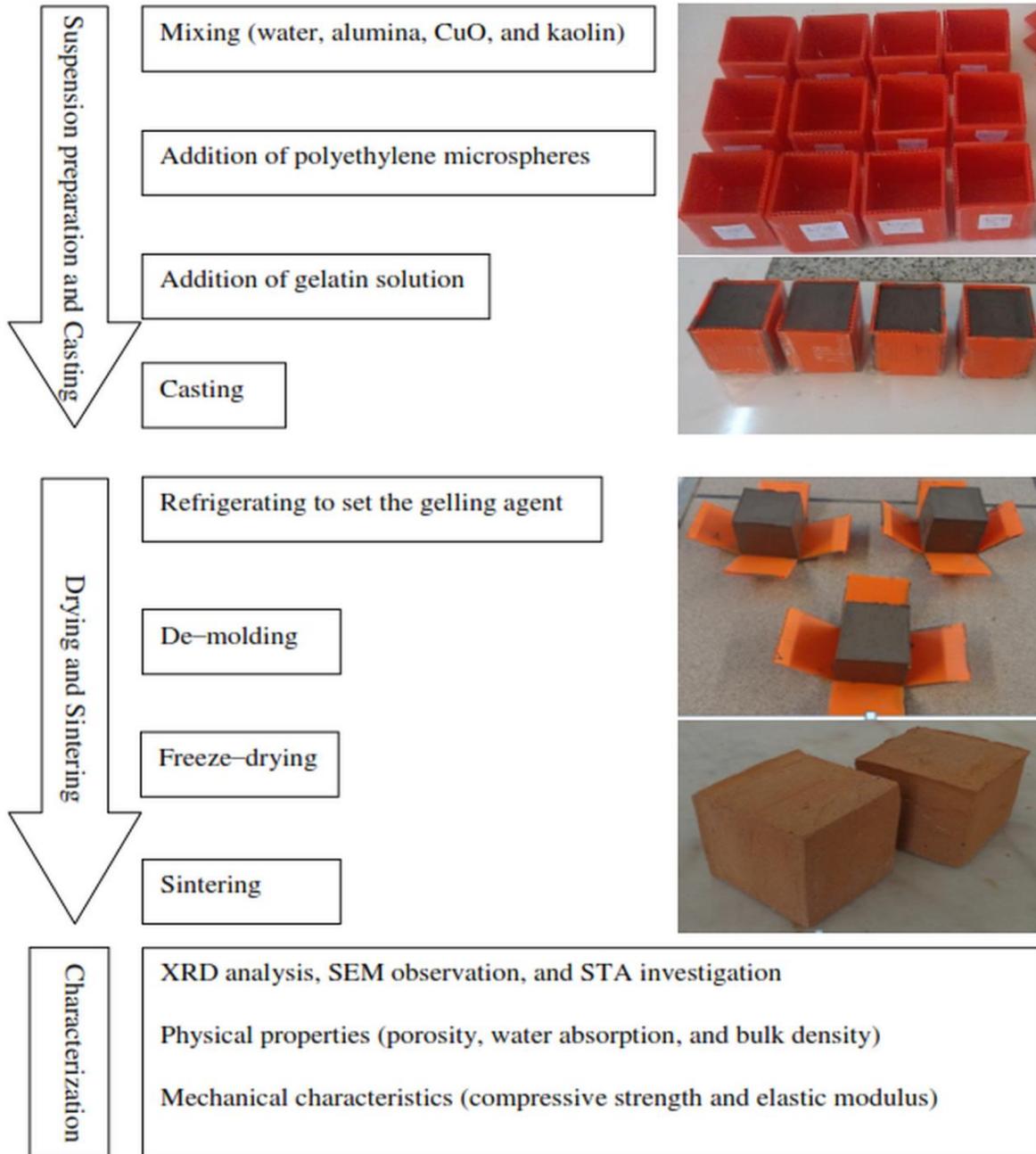


Fig. 1. Follow diagram of the gel-casting process

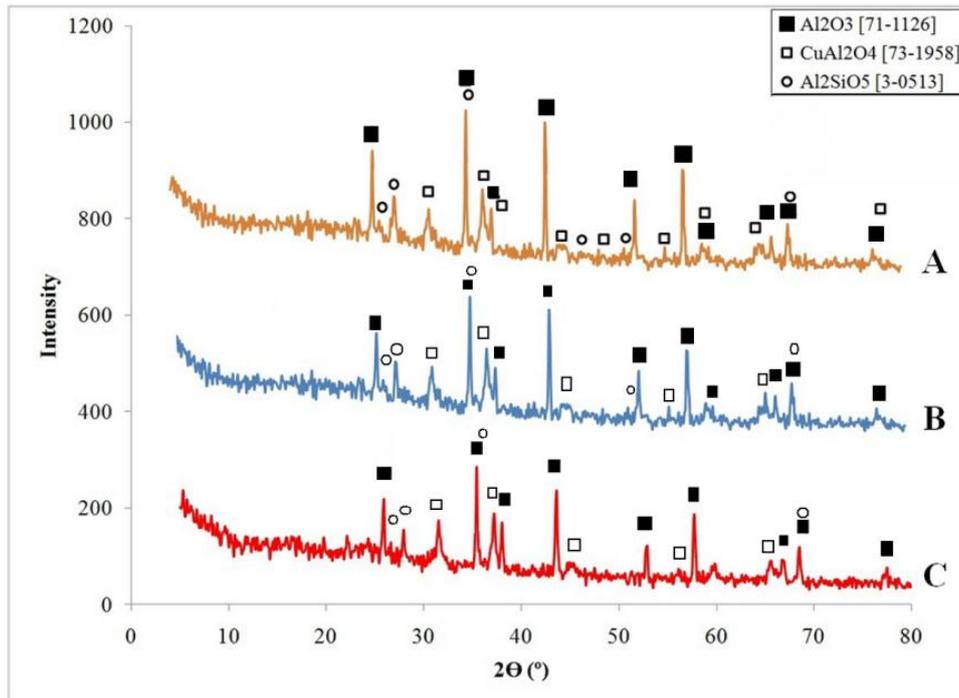


Fig. 2. XRD patterns of the as-prepared alumina foam bodies

Table 2. The amounts of Al_2O_3 , CuAl_2O_4 , Al_2SiO_5 and crystallinity of the 3 samples.

Sample	A	B	C
Al_2O_3 (%)	61.6	61.2	60.8
CuAl_2O_4 (%)	11.6	13.4	15.2
Al_2SiO_5 (%)	26.6	25.2	23.8
Degree of crystallinity (%)	83	75	66

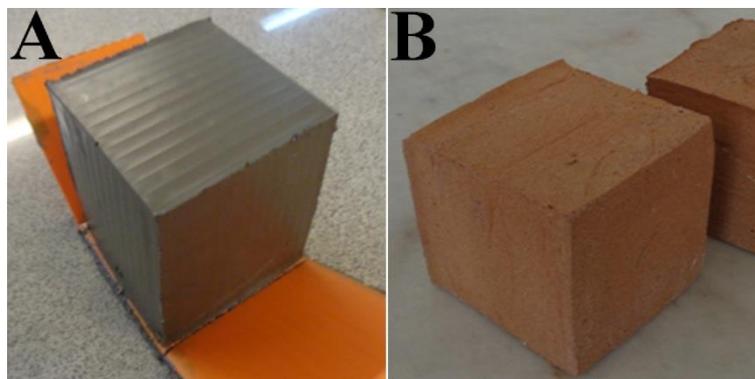


Fig. 3. Photograph of the dried and sintered ceramic foam showing skin layer on surface

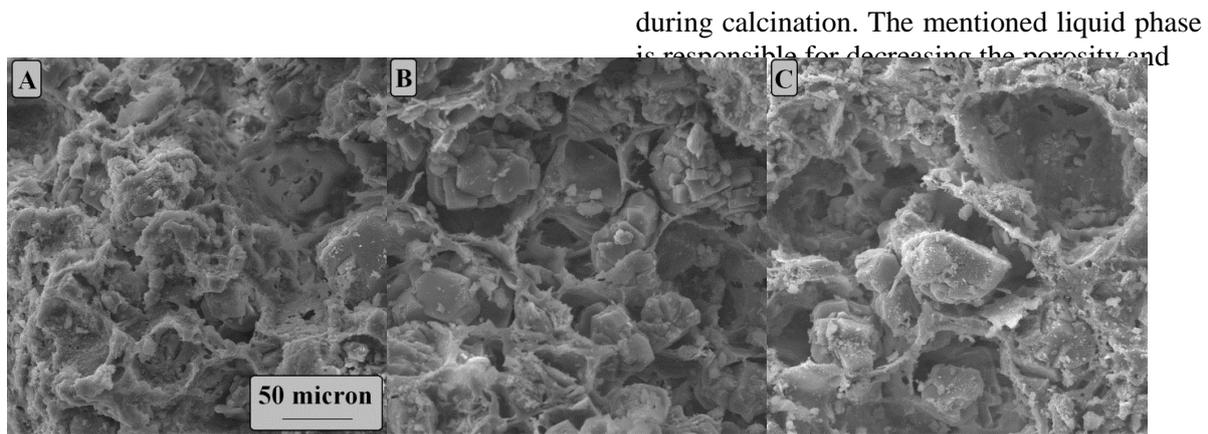


Fig. 4. SEM images of the as-prepared alumina foam bodies

3.3. Physical and mechanical characterization

Table 3 and Figure 5 present AP, WA, and BD values of the samples. As can be seen, AP and WA decreased with the increase in the CuO amount. By increasing the temperature of CuO/Al₂O₃ mixture, a liquid phase can be formed at >900 °C [20]. The liquid phase fills the porosities, decreases AP and WA, and consequently increases BD. The more CuO amount is added, the more liquid phase can be formed in the sample, and then the more decrease can be observed in AP and WA values (see Figure 5). The influence of these changes on the mechanical properties of the samples should be considered. Table 4 and Figure 6 present the CS and EM values of the samples. As can be seen, the strength of the samples increased by increasing the CuO amount. This phenomenon is related to the formation of conjugations between alumina particles. The CuO containing liquid phase is considered as the sintering agent and makes conjugates between Al₂O₃ particles. The more CuO is added to the mixture, the more increase in strength can be achieved. On the other hand, EM of the samples exerts a similar behavior. The XRD results in Table 2 confirm this exertion. By increasing the CuO amount, the amounts of CuAl₂O₄ increased and the crystallinity decreases. This shows that CuO and Al₂O₃ react with each other and form a new phase on the particles surfaces, forming a bond and increasing the strength. On the other hand, any decrease in crystallinity means that the amorphous phase content increases. This can be related to the formation of a liquid phase

increasing the total density.

The mechanical properties of a foam are related to the influences of the open porosity as well as particle size and pore dimension [21]. SEM images show this relationship in the samples. The pore size decreased in samples; A>B>C, and the porosity shapes become regular by increasing CuO amounts; C>B>A. The microscopic observations confirm the physical and mechanical evaluations.

The main reason for the application of foam-like ceramics is their mechanical properties such as strength. The porosity amount and mechanical strength are in reverse trend; therefore, the optimum amounts should be determined. Comparison between samples A and B shows that their porosity difference is about 5%, whereas this value for B and C is about 16%. On the other hand, the CS value increased about 57% in sample B compared to A, whereas this value increased about 27% in sample C compared to B. This shows that the condition for sample B is more appropriate than that for sample C.

3.4. Burn-out behaviors

The STA analysis (TGA, DTA, and dTG) of the dried body (sample B as the best one) is illustrated in Figure 7. The main weight loss is related to the temperature range of 200–600 °C (see TGA curve in Figure 7–A). This event occurred at 300 and ~500 °C (see dTG curve in Figure 7–A), corresponding to two exothermic peaks at this temperature range (oval region in Figure 7–B). The weight loss of this sample was about 25 wt. %, relating to the burnout of

gelatin, polyethylene, and structural water of kaolin. Endothermic dehydration of kaolin to form kaolinite begins at 200–300 °C and transformation of kaolinite to disordered metakaolin occurs at 550–600 °C [22]. Figure 7–B shows that these events occurred at 296 and 600 °C. Therefore, the exothermic peak at 450 °C refers to the burning of organic materials [23]. Considering sample B, it is revealed that its dried body contains 40, 12.5, 36, 1.6, and 9.9 wt. % of alumina, CuO, kaolin, polyethylene, and gelatin, respectively. The theoretical mass loss corresponding to the decomposition of organic component and kaolin is measured to be about

20 %. This difference is probably related to the present water in the dried sample, which is conjugated to gelatin [24].

As can be seen, the burn–out range is wide, facilitating the de-binding step. Meanwhile, the presence of numerous capillary channels and open porosities in the green body of the samples is the other agent that helps the organic materials to escape during heating. It seems that a heating rate of 5 °C/min, which was used in this study, is appropriate for removing the released gas without cracks.

Table 3. Apparent porosity, water absorption, and bulk density of alumina foams

Sample	Apparent Porosity (%)				Water Absorption (%)				Bulk Density (g/cm ³)			
	I	II	III	AP	I	II	III	WA	I	II	III	BD
A	66	67	67	66.7	67	68	68	67.7	0.99	0.97	0.98	0.98
B	64	63	63	63.3	63	62	62	62.3	1.01	1.03	0.97	1.00
C	54	53	52	53.0	44	46	45	45.0	1.16	1.14	1.15	1.15

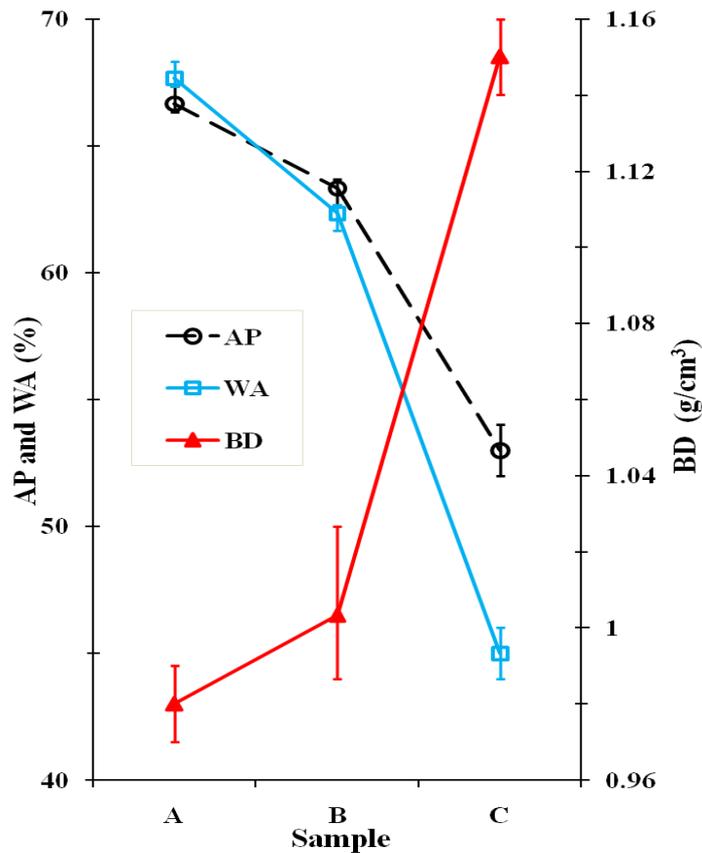


Fig. 5. AP, WA, and BD values of the as–prepared alumina foam bodies

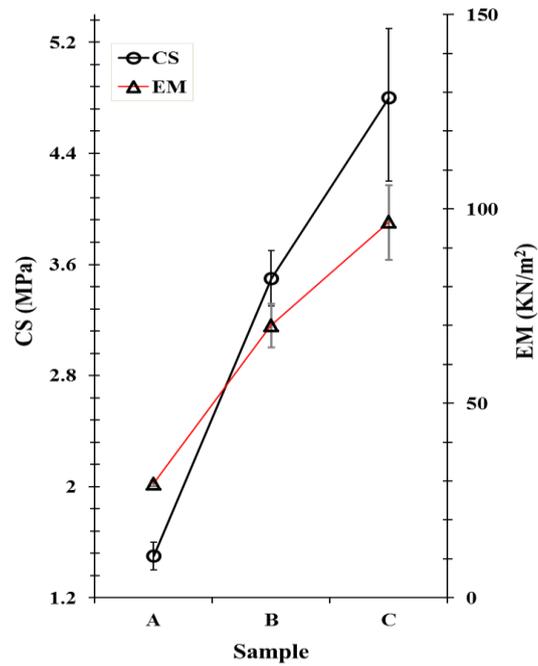


Fig. 6. CS and EM values of the as-prepared alumina foam bodies

Table 4. Compressive strength and elastic modulus of alumina foams.

Sample	Compressive Strength (MPa)				Elastic Modulus (KN/m ²)			
	I	II	III	CS	I	II	III	EM
A	1.5	1.6	1.4	1.5	28.5	30.1	29.4	29.3
B	3.3	3.7	3.5	3.5	64.5	75.7	70.0	70.1
C	5.4	4.7	4.3	4.8	106.2	87	96.5	96.6

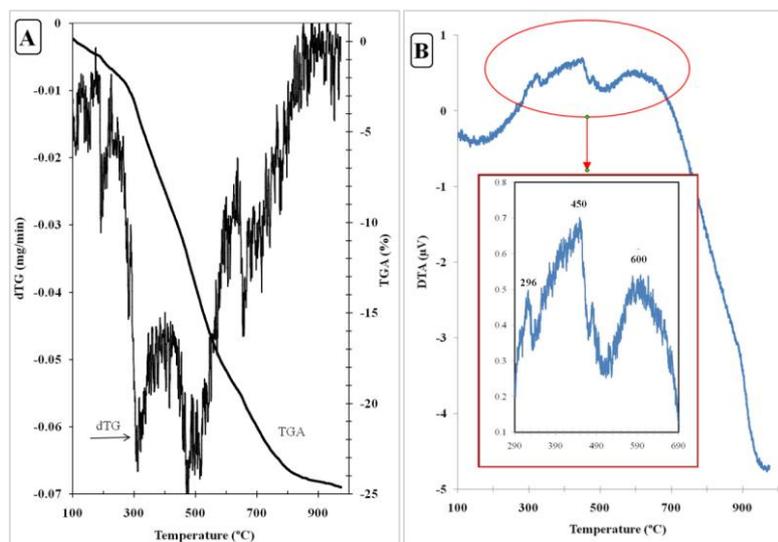


Fig. 7. The STA analysis of the as-prepared alumina foam bodies

4. Conclusions

Alumina composite foam prepared by the sintering temperature of 1000 °C showed density in the range of 0.97–1.16 g/cm³, apparent porosity in the range of 52–67 %, and compressive strength in the range of 1.4–5.4 MPa. CuO with 10–15 wt.% plays an essential role to decrease the required temperature by forming Al₂O₃/CuO eutectic mixture with a melting point of < 900 °C. The formation of CuAl₂O₄ on alumina particles leads to create ceramic bonding between them and increases the strength. On the other hand, a liquid phase can be formed during sintering and leads to stabilize the pores, which were formed by removing the organic compounds. As porosity and mechanical characteristics are in a reverse trend, the optimum Cu amounts were estimated about 12 wt. % (sample B), with a density of 1.00 g/cm³, a porosity of 63.3 %, and a strength of 3.5 MPa.

Gelatin as a non-toxic material was used as the gelling agent to provide the green strength. This organic material burns out during firing and makes some irregular-shape porosity. Polyethylene microspheres were applied as the pores creation template. This material is responsible for regular-shape holes in the as-synthesized samples. A combination of two foam-making techniques, i.e. emulsion templating and addition of a foaming agent, was used. In this way, the aim of current study named “fabrication of high-strength alumina composite foams” could be achieved.

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