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In situ mullite foam fabrication using microwave energy

S. Akpinar[a,*], I.M. Kusoglu[b], O. Ertugrul[b], K. Onel[b]

[a] Afyon Kocatepe University, Department of Material Science and Engineering, Afyonkarahisar, Turkey
[b] Dokuz Eylul University, Department of Metallurgical and Materials Engineering, Izmir, Turkey

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Abstract

In situ mullite ceramic foams were fabricated using polymeric sponge replication method from ceramic slurry containing alpha alumina and kaolin mixtures. Ceramic preforms were processed using microwave energy and conventional heating. The sintered foam samples were characterized by SEM and XRD observations, density measurements and compression tests in order to observe the effect of two different sintering techniques on the structure and properties. It was found that the microwave processing was completed in a shorter burning out and sintering cycle and produced structures having higher mullite transformation ratio and fine grains.

Keywords: Microwave assisted sintering; Mullite; Ceramic foam; Rheology; In situ

1. Introduction

Ceramic foams are porous materials with large voids of the size ranging from 10 μm to 5 mm.[1,2] Ceramic foams with interconnected open pore structure, in particular mullite reticulate ceramics are used in applications, which include filters for high pressure and high-temperature gas flow, filters for diesel exhaust emissions, substrates for catalytic reactions and fused metal filtering.[3] Due to low thermal-expansion coefficient and good thermal-shock resistance as well as excellent mechanical and chemical stability at elevated temperatures, the development of porous mullite ($3Al_2O_3{\cdot}2SiO_2$) ceramics has received considerable interest in recent years.[4]

The most common route for producing reticulated porous ceramics (RPCs) is the replication method.[1,5,6] This method is based on the impregnation of a polymer sponge with a ceramic suspension or precursor solution in order to produce a macroporous ceramic exhibiting the same morphology as the original porous material. In the polymer replica approach, a highly porous polymeric sponge is initially soaked into a ceramic suspension until internal pores are filled in with ceramic material. The impregnated sponge is then passed through rollers to remove the excess suspension and enable the formation of a thin ceramic coating over the struts of the original cellular structure of polymer sponge. At this stage, the slurry has to be sufficiently fluid to be partially removed under the shearing conditions applied by the rollers, but the remaining ceramic wet coating should be viscous enough to avoid dripping. Therefore, ceramic suspensions exhibiting shear-thinning behavior are needed to efficiently coat the polymeric template. The ceramic coated polymeric template is subsequently dried and pyrolysed through careful heating between 300 and 800 °C. Heating rates usually lower than 1 °C/min are required in this step to allow for the gradual decomposition and diffusion of the polymeric material, avoiding the build up of pressure within the coated struts. After removal of the polymeric template, the ceramic coating is finally densified by sintering at temperatures ranging from 1100 to 1700 °C depending on the material.[7]

However, it is difficult to produce porous ceramics with controlled microstructure as the struts of the reticulated structure are often cracked during pyrolysis of the polymeric foam. Many flaws usually remain in the structure, which weakens the structural properties of RPCs, especially the strut flaws reduce the compressive strength of porous ceramics to levels usually lower than the strength theoretically predicted for open cell structures.[8] The most common flaws encountered in the open cell foam materials are longitudinal strut cracks.[9] These cracks may arise from stresses originated from differential drying, thermal expansion mismatch between the polymer and the ceramic coating, and the gas pressure produced by pyrolysis of the polymeric skeleton. It

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[*] Corresponding author. Tel.: +90 272 2281423; fax: +90 272 2281422.
E-mail address: akpinar@aku.edu.tr (S. Akpinar).

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is likely that cracks on the strut surface of the fabricated foams are produced at a temperature near the "melting point" of the polymer, as suggested by Brown and Green.[9,10]

Another possibility is that cracking occurs due to thermal expansion differences between the polymer and ceramic coating at relatively low temperatures. As the polyurethane has a higher thermal expansion coefficient ($\alpha = 100 \times 10^{-6}\,\mathrm{K}^{-1}$) than the ceramic ($\alpha = 4 \times 10^{-6}\,\mathrm{K}^{-1}$), this allows cracks to form at temperatures shortly before "melting", due to either accumulated thermal strains or the large volumetric expansion of the polymer at temperatures approaching the melting point.[10]

To decrease flaws it is necessary to develop improved processing techniques to optimize and control the structure of RPCs.[8] Many attempts have been made to avoid this shortcoming, for instance, improving the wetting of the suspension on the sponge with the help of additives, performing a second impregnation step to fill the cracks in the ceramic struts, and introducing fibers or reactive compounds to enhance the material's integrity.[7]

Heating rate is an important factor in decomposition of polymer sponge which affects the final microstructure and also the strength of the ceramic foam. Most workers applied very slow heating rates, such as 1 °C/min, while burning out the polymer sponge in order to avoid crack formation. However, slow heating rate means very long processing durations. Slow heating rates and long dwell times during sintering promote grain growth. In the case of microwave heating heat is generated by the interaction of microwaves with the ceramic material, volumetric heating takes place, thus very high heating rates are possible. It is therefore possible to process ceramic foams by microwave heating, in a fraction of the time it takes for conventional firing. With short microwave sintering runs, the time for grain growth is diminished. The resulting smaller grains make the microstructure more uniform and increase the strength.[11] In microwave processing energy is directly transferred to the material through interaction of electromagnetic waves with molecules leading to heating. With the use of microwaves for sintering Al_2O_3, ZrO_2, MgO and SiC a dense material of improved microstructure with uniform and finer grains can be obtained in a shorter time as compared with the conventional processes.[12–14]

In the present work it is aimed to produce reticulated in situ mullite ceramics by the polymer sponge process, through the reaction sintering of clay and alumina using a microwave furnace and a conventional electrical furnace. The structure and properties of mullite foams sintered conventionally and by microwave energy have been evaluated. The effect of microwave energy on the decomposition of polymer sponge and sintering of mullite and resultantly on the duration of the complete process has been observed.

2. Experimental work

As porous template starting material, commercial polyurethane sponge having a cell size of approximately 20 ppi (pores per inch) was used to produce mullite foams. In order to quantify thermal behavior of polyurethane sponge, simultaneous thermal analyses (differential thermal analysis, DTA and thermo-gravimetric analysis, TGA) were performed in air at a heating rate of 10 °C/min.

Table 1
Chemical compositions of raw materials.

Composition (wt%)	Kaolin	Alumina	Magnesia	Gibbsite	Bentonite
SiO_2	48.34	0.03	0.97	0.01	67.52
Al_2O_3	36.83	98.50	0.33	64.65	12.78
Fe_2O_3	0.70	0.03	0.48	0.02	0.83
TiO_2	0.04	0.00	0.00	0.00	0.06
CaO	0.08	0.00	1.46	0.00	1.96
K_2O	1.86	0.00	0.00	0.00	2.39
Na_2O	0.04	0.50	0.00	0.30	0.79
MgO	0.28	0.00	96.47	0.00	1.40
Ignition loss	12.14	0.94	0.29	35.02	12.27

For synthesizing mullite phase 41.6 wt% α-Al_2O_3 ($d_{50} = 6.512\,\mu m$ and specific surface area $1.43\,m^2/g$) and 51.4 wt% kaolin ($d_{50} = 9.822\,\mu m$, specific surface area $11.804\,m^2/g$) were used as starting raw materials. Gibbsite and MgO were added to the mixtures in amounts of 5 and 1 wt% respectively as sintering aids. A total amount of 1 wt% sodium carboxymethyl-cellulose (CMC) and bentonite were added to mixture for thickening and improving the rheological behavior of the slurry. The chemical compositions of the starting powders are listed in Table 1.

The slurry was prepared in distilled water and adjusted with 0.8 wt% commercial deflocculant Dolapix CE-64 (Zschimmer and Schwarz, Germany) to achieve a good dispersion of ceramic particles in aqueous solution. For the preparation of slurry, distilled water was first mixed with CMC and Dolapix CE-64 by stirring for 5 min. Kaolin, bentonite and the other ceramic powders were added into solution and mixed for 30 min.

A rheological study has been carried out to optimize the processing of the porous mullite foams by using a rotational stress-controlled rheometer (Bohlin-CVO model rheometer). The measurements were performed at constant temperature (20 °C) using a cone and plate configuration. A pre-shearing was performed at high shear rate ($1000\,s^{-1}$) for 1 min before the measurement followed by an equilibrium time for 30 s to transmit the same rheological history to all tested suspensions. Sweep measurements were then conducted in the shear rates ranging from about 0.1 to $1000\,s^{-1}$.

The polyurethane sponge pieces were firstly immersed in the slurry. Then the impregnated sponge pieces were passed through a set of rotating rollers to remove excess slurry. The distance between the preset rollers was 20% of the sponge thickness. Ceramic coated sponge pieces were dried at room temperature for 24 h.

In conventional sintering process, dried samples were heated to 600 °C at a heating rate of 1 °C/min in order to burnout the sponge accordingly to the results of DTA–TG analysis of the sponge. Subsequently, the samples were heated in conventional furnace to 1500 and 1600 °C at a rate of 5 °C/min and sintered for different durations (2 and 4 h) in air to obtain mullite transformation.

In microwave sintering process, dried samples were placed in a thermally insulated alumina fiber box, in which SiC susceptors were used to absorb microwave energy and heat the specimens. Alumina and clay exhibit low dielectric losses (0.1 ± 0.03 and ≤ 1, respectively) and are difficult to heat in a microwave furnace at room temperature,[12] therefore SiC crucible with a high dielectric loss (300 ± 50) was used as susceptor. The temperature of the samples was monitored using an infrared pyrometer with the circular crosswire focused on the sample surface. The emissivity of the pyrometer (Kleiber 273-LWL) was set to 0.80 in order to measure the exact temperature of samples surface. Samples were heated to 600 °C in 30 min and held for 10 min by applying 320 W of microwave power to burn out the sponge and then heated to 1500 °C in 2 h and held for 2 h in air by applying 960 W of microwave power. The samples were cooled to 300 °C in 3 h after sintering was completed.

The linear shrinkage of samples during the course of sintering was determined using the following equation:

$$\text{Shrinkage} = \frac{l_g - l_p}{l_g} \times 100$$

where l_g is the height of green sample and l_p the height of fired product. The height was measured by sliding gage. Bulk density of the sintered foam samples (ρ_b) was calculated from dimensional measurements and mass of the sintered samples. Solid density (ρ_s) of samples where the mullite formation is highly completed was determined using Micromeritics Accu ρyc II 1340 model gas (helium) pycnometer on crushed sintered foam consisted of the single struts and the broken cell walls. The macrostructures of sintered samples were visually examined and the microstructures were observed by scanning electron microscopy (SEM) (Model JSM–6060 JEOL, Japan). Phase analysis of the sintered samples was conducted by standard powder X-ray diffractometer (RIGAKU, Japan). Compressive strength (σ_c) of the sintered samples with dimensions of 50 mm × 50 mm × 10 mm, was measured using a Shimadzu (Japan) universal testing machine fitted with compression plates, at a cross head speed of 0.5 mm/min.

3. Results and discussion

In the production of ceramic foams by the replica method, in order to achieve a ceramic coating of acceptable characteristics on a polyurethane foam scaffold, the slurry should have the appropriate thixotropic or shear-thinning behavior.[15] The thixotropic behavior of slurry is characterized generally by measuring the thixotropic loop between the ascending and descending parts of the flow curve. In descending part of the curve, the shear stress is lower due to the breaking down the bond chain through the suspension and deflocculating phenomenon. This means that when polymeric sponge is impregnated with ceramic slurry, suspension is fluid enough to enter, fill and uniformly coat sponge web and subsequently regain enough viscosity under static conditions to remain on sponge.[16] Fig. 1 shows the flow curve of the slurry of mullite (with 65 wt% solid) compositions used in the experiments. The curve of mullite slurry shown in Fig. 1 exhibits a distinct thixotropy loop and a characteristic shear-thinning behavior that is required for the present application.

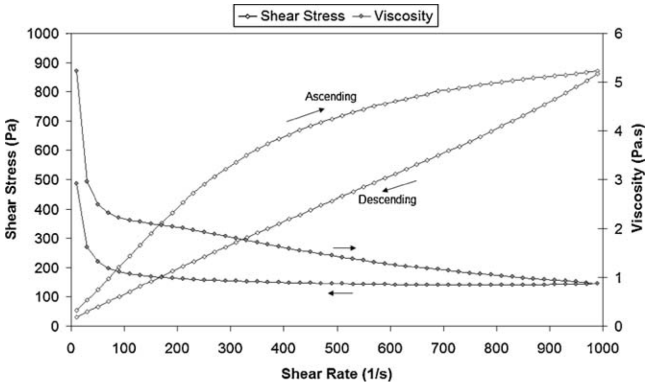

Fig. 1. Flow curve of mullite slurry for 65 wt% solid loading.

The burn out stage of the polymer foam should be carried out carefully using suitable heating rate at the appropriate temperature, otherwise dried ceramic foam structure may become destructed. Therefore thermal behavior of polyurethane sponge was determined by DTA/TG analysis. As seen in Fig. 2, the decomposition of polyurethane sponge takes place in three stages in air. The first stage, which starts at approximately 220 °C and continues up to 350 °C showing a small endothermic signal at about 300 °C which is probably the beginning of decomposition. In the second stage (350–450 °C), a higher intensity exothermic signal is observed at about 400 °C, where weight loss is almost complete due to burn out of the carbon produced by decomposition of the polymer and the generation of gas during the polymer oxidation. There is no significant weight loss in the third stage (450–600 °C), so the major fraction of polymer is burnt out between 220 and 600 °C. These observations are comparable with those of Dressler et al.[17] The decomposition step is very important to prevent the ceramic structure from destruction, due to the high pressure of the generated gas, which deteriorates mechanical properties of ceramic foam. For that reason, a slow heating rate of 1 °C/min was used up to 600 °C for damage free removal of the organics from the ceramic foam bodies in conventional heating process.

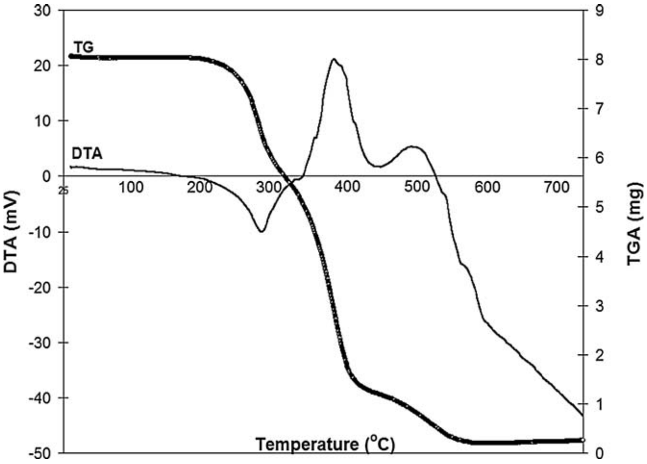

Fig. 2. Differential thermal (DTA) and thermal gravity (TG) curves of the green polyurethane sponge at a heating rate of 10 °C/min.

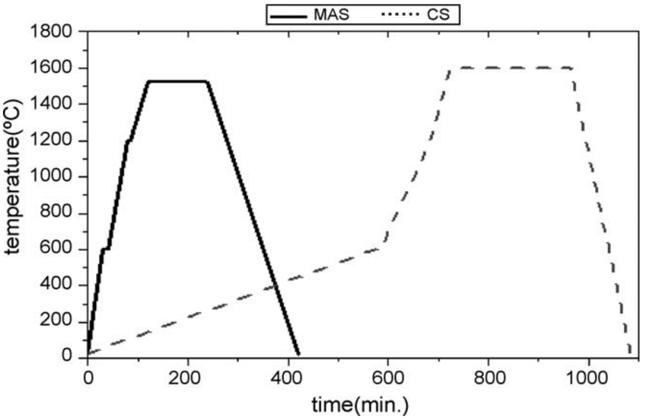

Fig. 3. Typical heating profiles for conventional sintering (CS) and microwave assisted sintering (MAS) processes.

During conventional heating, the burnout stage of the polymer foam takes approximately 10 h as the heating rate is 1 °C/min, on the other hand damage free burnout stage lasts only 40 min in the case of microwave sintering. Due to the nature of microwave heating, increased heating uniformity can be achieved during microwave processing, the polymer organic migrates out through the ceramic coating more uniformly, in contrast to the conventional heating, resulting in faster organic removal. As expected, shorter total process duration was achieved in producing mullite foams by microwave heating than by the conventional processing. Typical heating profiles for both conventional sintering (CS) and microwave assisted sintering (MAS) processes are given in Fig. 3.

The XRD patterns of sintered samples are given in Fig. 4. The pattern of the sample sintered at 1500 °C for 2 h by microwave processing show mainly mullite peaks but there are also corundum peaks of low intensity. The samples sintered conventionally at the same temperature and duration show corundum peaks of higher intensity. This indicates that the ratio of mullite transformation is lower in the case of conventional sintering. In the samples sintered conventionally at 1600 °C for 4 h, the XRD pattern shows mullite peaks and small corundum peaks, similar to those sintered using microwave energy at 1500 °C for 2 h. However lower corundum peak intensities mean that the ratio of mullite formation is higher in the samples sintered using microwave energy.

Table 2
Typical properties of sintered mullite ceramic foams.

Properties	Conventional sintering (1600 °C, 4 h)	Conventional sintering (1500 °C, 2 h)	Microwave assisted sintering (1500 °C, 2 h)
Shrinkage (%)	14.21	10.44	10.86
ρ_b (g/cm^3)	0.51	0.31	0.40
ρ_s (g/cm^3)	3.08	3.12	3.11
ρ_r	0.17	0.10	0.13
σ_c (MPa)	0.26	0.11	0.21

Macro images of sintered foams obtained by conventional processing and microwave processing are given in Fig. 5a and b respectively. It is observed that all the pores are open after dipping, rolling and sintering steps. Struts appear to be dense and all connected to each other. In microwave sintered samples struts look smooth and free of cracks and pores.

The resultant microstructures of the sintered samples are given in Fig. 6, which shows a remarkable difference between the grain sizes of samples having different processing parameters. The samples sintered conventionally have large grains and the highest temperature of sintering (1600 °C) yields structures of largest grain size. It is to be noted that in the conventionally sintered samples untransformed phases coarsen as well as mullite grains. The microstructural observations show that

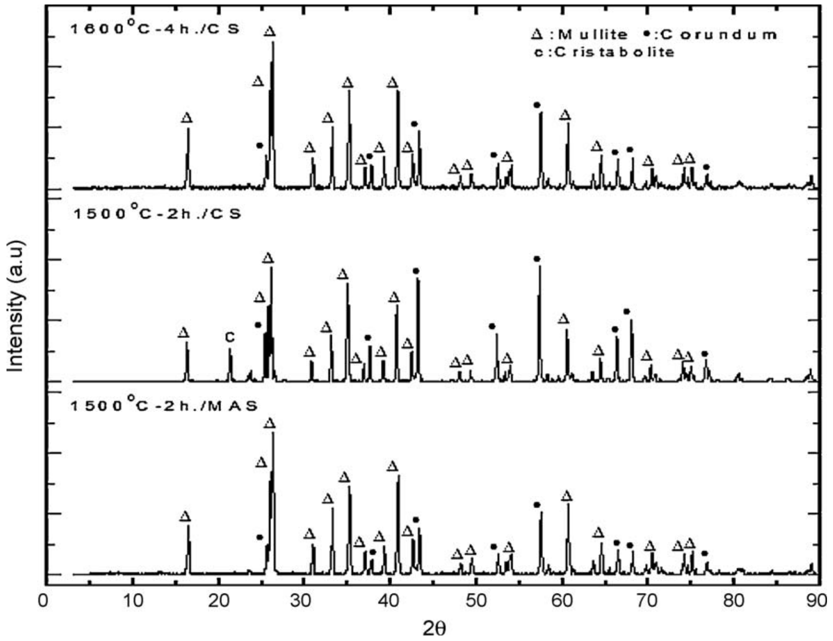

Fig. 4. XRD patterns of the sintered samples obtained through conventional sintering (CS) and microwave assisted sintering (MAS).

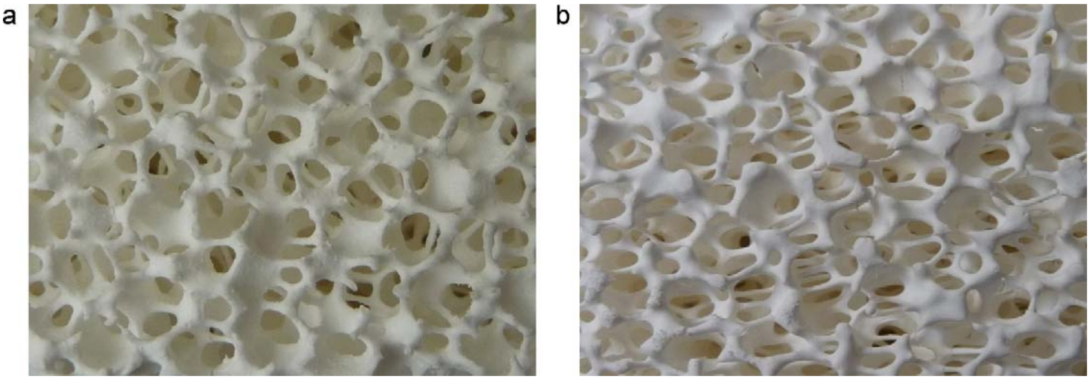

Fig. 5. Macro images of sintered foams obtained by (a) conventionally sintered at 1600 °C for 4 h and (b) microwave sintered at 1500 °C for 2 h.

mullite grains grow more readily in conventionally sintered samples, while the rapid and uniform heating in microwave sintering process facilitates the formation of structures with higher ratio of mullite transformation and smaller grain size.

The typical properties of conventional and microwave assisted sintered foam samples are summarized in Table 2. The observed shrinkage of fired samples occurs as the polyurethane sponge and chemically bound water of kaolin is removed, and the structure is sintered. The shrinkage of microwave sintered sample is 10.86 vol%. However, the shrinkage values of the conventionally sintered samples at 1500 °C for 2 h and at 1600 °C for 4 h are 10.44 and 14.21 vol%, respectively.

The results given in Table 2 show that the samples sintered conventionally at 1600 °C for 4 h exhibit highest shrinkage, bulk density and relative density values, but the lowest value of true density, 3.08 g/cm^3. True densities, measured by gas pycnometer, reveal that foam samples sintered using different methods and parameters have comparable true density values.

The most significant property describing the behavior of porous ceramics is the relative density (ρ_r), which is the ratio of the sample bulk density (ρ_b) to the solid density (ρ_s). There are micromechanical models that relate the solid properties and the foam properties such as the relative density and the cell size and geometry to foam mechanical behavior. The most applicable method to predict the mechanical behavior of cellular ceramics

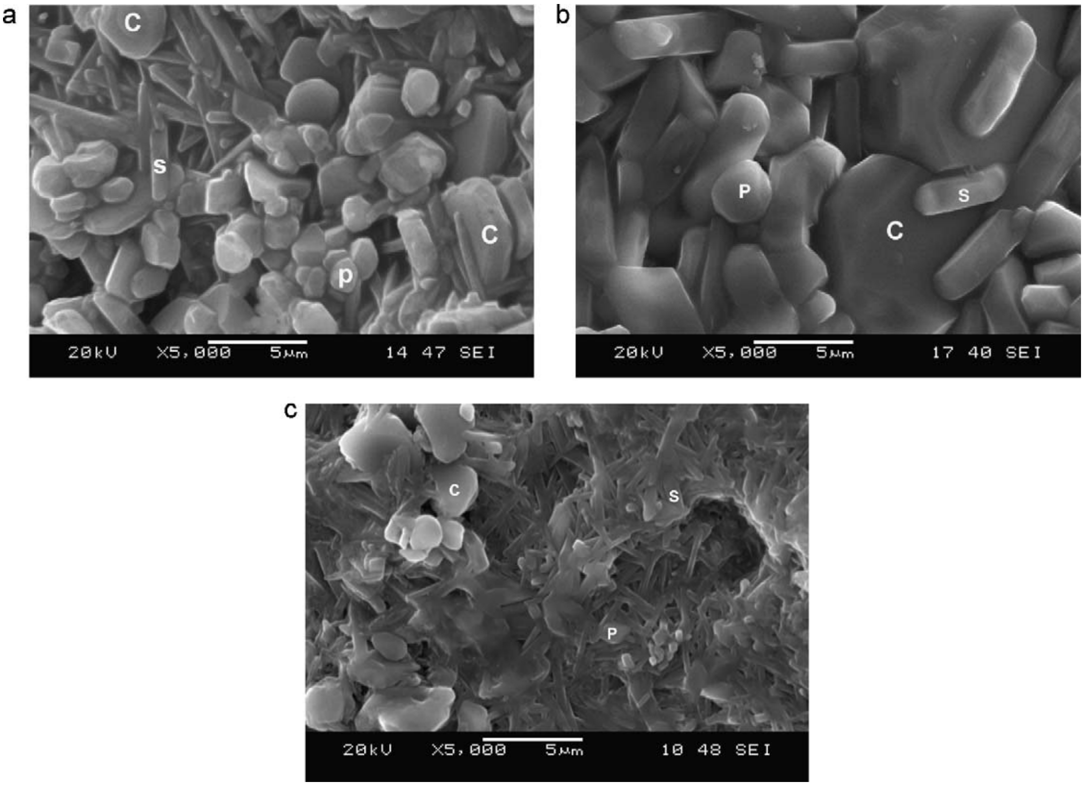

Fig. 6. SEM observation of the grain size and fine porosity of the sintered foams; (a) 1500 °C-2 h/CS, (b) 1600 °C-4 h/CS, (c) 1500 °C-2 h/MAS (P: primer mullite, S: seconder mullite, C: corundum).

is the model that has been published by Gibson and Ashby. They used a simple unit cell and described the failure in structure by the failure of cell struts. Maiti et al. applied the Gibson and Ashby (GA) model to describe the compressive strength of brittle porous materials. The crushing strength of the cellular body (σ_{fs}) via the strut strength and relative density is been expressed by Eq. (1).[16]

$$\sigma_{\mathrm{cr}} = C \cdot \sigma_{\mathrm{fs}} \cdot \left(\frac{\rho}{\rho_{\mathrm{s}}}\right)^{3/2} \tag{1}$$

According to this equation, the samples conventionally sintered at 1600 °C should have the highest compressive strength as they possess the highest relative density (0.17) as given in Table 2. Experimental results confirm this prediction; the samples conventionally sintered at 1600 °C have an average compressive strength value of 0.26 MPa, higher than those sintered at 1500 °C. The samples sintered at 1500 °C, by conventional heating and microwave heating have different relative densities. Microwave processed samples have higher relative density values, and as expected, exhibit higher compressive strength.

4. Conclusions

Reticulated in situ mullite foams are produced using microwave energy and conventional heating. In microwave processing the decomposition of polymer sponge is completed in 40 min, giving undamaged end products, while the duration is 10 h for conventional processing. Total processing duration is approximately 7 h and 17 h for microwave and conventional heating respectively. The sintered foam structures contain mullite and some untransformed corundum phase. Microwave sintering yields higher ratio of mullite transformation and structures of smaller grain size than conventional sintering at the same temperature for the same duration. Compressive strength values of the samples are comparable and can be related to relative density values.

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