



Ceramic Foam Synthesis and Its Modification for Use at High Temperature

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ABSTRACT

Many properties of open-cell ceramic foam prepared by means of the sponge replication method can be controlled by adjusting the viscosity of the ceramic slip with respect to the pore count of the polymer sponge template. Ceramic foam obtained by this method was subsequently coated with various materials, such as urea-formaldehyde and carboxymethylcellulose (CMC), and its structural properties were analysed and interpreted in order to establish its potential applicability as a thermal insulator. Ceramic foams were prepared with different densities by varying the density of the ceramic slurries used (1.1845, 1.2798, 1.3567, 1.54332, 1.6543 and 1.7234 g/cm³). The physical properties of the ceramic foam produced, such as density, were characterised according to ASTM C 271-94, whereas porosity was characterised using the Archimedes method. The foams were analysed with XRD, SEM and FTIR, among other techniques.

Key words: Foam, Ceramic, Isolated temperature, Mullite.

INTRODUCTION

Ceramic foam is currently a very exciting area of research due to its wide applicability. Many of the authors have conducted extensive reviews on the subject. Buciuman¹ mentioned that ceramic foams have been in development for around three decades, and are now used commercially as filters for molten metal and hot gases. In recent years,

however, other applications have also been explored. For instance, the potential for ceramic foams as catalyst carriers, burner heads, or fuel-cell electrodes has gained increasing interest. Ceramic foams can be highly suitable catalytic carriers where a low pressure drop is mandatory. In comparison to honeycomb monoliths, they offer the additional advantages of radial mixing within the body and enhanced mass and heat transfer due to

the turbulence of the flow. Foam carriers exhibit a high contact surface between the gas phase and the solid, and can be manufactured in different geometries, allowing for adjustment of axial or radial flow patterns in the reactor. Pioneering work reported in the field of catalysis with foam carriers concerned the partial oxidation of hydrocarbons¹⁻⁴, catalytic combustion^{5,6}, and the removal of soot from diesel exhaust^{1,7,8}. There are several routes for manufacturing ceramic foams. Among these, the polymer sponge replication method of Schwarzwald and Somers⁹ is most suitable for the fabrication of oxidic, reticulated foams with easily accessible, open cells^{10,11}. This method consists of coating an elastic polymer sponge with open cells with a slip containing the precursors of the ceramic material together with other additives. Coating is achieved by immersing the polymer sponge into the slip, expelling the excess (e.g. by compression), and drying. Subsequently, the green body is exposed to a temperature treatment. In a first stage, the organic skeleton is burned off in air. At temperatures above 1400°C, the particles forming the ceramic replica are sintered.

There are several developments that have been published in the area of the synthesis of ceramic foam and the various uses they may have. Have published a number of routes for ceramic foams according to the final application is required to give. In this work, we have based on already published work¹, we want to enhance the process of ceramic foam synthesis and the study of density, but mainly we wish to explore the use of simple treatments with molecules for establishing whether organic chemical compounds can improve their thermal isolation properties.

EXPERIMENTAL

Foams synthesis

In our research, the procedure used for the synthesis of ceramic foam is based on the publication of Buciuman¹. The ceramic foam carriers were made by means of the polymer foam replication method⁹. Polymer sponges were used (polyester, Koepf AG), with a pore size of the range of 50 ppi,

and cut into pieces of 30-60 mm diameter. Most of the work reported here was carried out with alumina-mullite foams. For the preparation of the respective slip, the ceramic precursors (boehmite, kaolin and silica in a weight ratio of 4.5:3.5:2) were suspended in water containing poly(vinylpyrrolidone) (Luviskol, BASFTM) as an organic binder and Dolapix PC 67 (Zschimmer & Schwarz[®]) as a deflocculant. The mixtures were milled with alumina balls for 45 min. The slip was used to coat polymer sponges of different pore counts with 50 ppi. The various combinations used for the production of the other foam ceramics are summarised in Table 1. The solid content (based on the mixtures) was varied to produce ceramic slurries with densities of 1.1845, 1.2798, 1.3567, 1.54332, 1.6543 and 1.7234 g/cm³, in a distilled water medium¹². Coating was performed by immersing the sponge pieces in the slurry, squeezing them, and passing them through rollers preset at 80% impression to expel the excess slip. The bodies were dried for 24 h at room temperature and heated at 1°C/min to 700°C, and then a further at 10°C/min to the final temperature (1800°C), which was held for 500 min to achieve sintering of the ceramic.

Characterization of foams synthesized

The properties of the ceramic foam produced were characterised according to ASTM C 271-94 and the porosity was characterised using the Archimedes method. The morphological study was performed using a scanning electron microscope (JEOL). Different analysis techniques were used to characterise the synthesised ceramic samples: with CuK α radiation. Powder diffraction data were collected in the 2 θ ranges 4–80° in steps of 0.02° 2 θ , with 1s per step. The operating voltage and current were 40 kV and 45 mA. Photographs of samples were taken with a digital camera (CasioTM, Japan). Scanning Electron Microscopy micrographs were obtained with a Hitachi S-2400 instrument. Nitrogen adsorption isotherms were measured at liquid N₂ temperature (-196 °C) and N₂ pressures ranging from 10⁻⁶ to 1.0 p/p₀ with a Autosorb 3B (Quantachrome, Boynton beach, USA)^{13,14}. The chemistry of the ceramic foam synthesised was characterised by IR spectroscopy (NicoletTM, US.).

Table 1: Vibrations and bending of infrared spectra of ceramic foams

Band No	Synthesised foam A	Foam treated at high temperature B	Carbonated foam coated with carboxymethyl-cellulose C	Carbonated Foam coated with sucrose solution (20% w/w) D	Foam coated with urea-formaldehyde resin 1:1 p/v E
1	466.70 bending Si-O 555.41 "Rocking" movement	466.63 bending Si-O 555.41 "Rocking" movement	474.41 bending Si-O 555.41 "Rocking" movement	466.70 bending Si-O 555.41 "Rocking" movement	470.55 bending Si-O 555.41 "Rocking" movement
2	R ₂ SiH ₂ Vibrations Si-O-Al, Si-O-Si	Vibrations Si-O-Al, Si-O-Si	R ₂ SiH ₂ Vibrations Si-O-Al, Si-O-Si	Movement R ₂ SiH ₂ Vibrations Si-O-Al, Si-O-Si	Si-O-Al, Si-O-Si
3	900.61 "Scissors" movement R ₂ SiH ₂ movement (R alkyl) Stretch Si-O-Al	900.61 Flexes out of plane C=C "Scissors" movement R ₂ SiH ₂ movement (R alkyl) Stretch Si-O-Al	—	900.61 Flexes out of plane C=C "Scissors" movement R ₂ SiH ₂ movement (R alkyl) Stretch Si-O-Al	900.61 Flexes out of plane C=C "Scissors" movement R ₂ SiH ₂ movement (R alkyl) Stretch Si-O-Al
4	1180.24 Asymmetric stretch Si-O-Si,Al	1180.24 Stretch C-O Asymmetric stretch Si-O-Si,Al	1180.24 Stretch C-O Asymmetric stretch Si-O-Si,Al	Stretch Si-O-Al 1180.24 Stretch C-O Asymmetric stretch Si-O-Si,Al	1191.81 Stretch C-O Asymmetric stretch Si-O-Si,Al
5	-	1645.01 Vibrations H-OH	1645.01 Vibrations H-OH	1645.01 Vibrations H-OH	1645.01 Vibrations H-OH
6	2940.96 Stretch C-H Symmetrical aliphatic	—	—	2940.96 Stretch C-H Symmetrical aliphatic	-
7	3446.23 Stretch O-H associated, intermolecular hydrogen bridges	3446.23 Stretch O-H associated, intermolecular hydrogen bridges	3446.23 Stretch O-H associated, intermolecular hydrogen bridges	3446.23 Stretch O-H associated, intermolecular hydrogen bridges	3446.23 Stretch O-H associated, intermolecular hydrogen bridges

Table 2: DRX lines of ceramic foam synthesized

	Carbonized foam pretreated with carboxymethyl cellulose			Carbonized foam pretreated with Agar 5 type D only			Foam carbonized without pretreatment			Foam untreated			Foam resin pretreated with Urea: Formaldehyde 1:1 w/v		
	$h^2 + k^2 + l^2$	d (Å)	[int]	$h^2 + k^2 + l^2$	d (Å)	[int]	$h^2 + k^2 + l^2$	d (Å)	[int]	$h^2 + k^2 + l^2$	d (Å)	[int]	$h^2 + k^2 + l^2$	d (Å)	[int]
2θ															
16,396	6	5,401	220	9	5,417	221	8	5,403	220	7	5,382	-	7	5,396	-
19,551	1	4,537	100	1	4,550	100	1	4,539	100	1	4,536	100	1	4,528	100
26,245	2	3,393	110	3	3,398	111	2	3,392	110	3	3,385	111	2	3,386	110
33,164	5	2,699	210	6	2,697	211	5	2,696	210	5	2,692	210	5	2,692	2,699
35,196	8	2,548	220	9	2,551	300	8	2,548	220	7	2,541	-	7	2,544	-
40,793	8	2,210	220	10	2,212	310	9	2,210	221	8	2,207	220	8	2,207	220
42,500	4	2,125	200	5	2,125	210	4	2,123	200	3	2,121	111	3	2,123	111
54,194	7	1,691	-	8	1,691	220	8	1,692	220	7	1,691	-	6	1,690	211
57,494	2	1,602	110	2	1,602	110	2	1,603	110	2	1,599	110	2	1,601	110
60,602	7	1,527	-	8	1,527	220	7	1,527	-	7	1,525	-	6	1,526	211
A ²		0,118			0,100			0,115			0,119			0,131	
Arista (Å)		2,242			2,432			2,267			2,236			2,129	

RESULTS AND DISCUSSION

Figs. 1(a) and (b) show a variation of porosity which is determined using the Archimedes method, and density which is determined according to ASTM C271-94 of the ceramic foam produced as a function of the slurry density. From Fig. 1(a), it is clear that the porosity of the ceramic foam decreases as the slurry density increases, as reported in the literature¹. As the porosity decreases, the density of the ceramic foam increases as shown in Fig. 1(b) and then decreases to a value of 1.543, then increases due possibly to increase the number of pores per unit volume. The quality of ceramic foam is strongly influenced by the density of the slurry, as this reflects the degree of porosity. Reducing the porosity will consequently increase the density of ceramic foam from 1.2798 to 1.54332 g/cm³. However, it was found that a slurry density greater than 1.54332 g/cm³ is undesirable, as this promotes the formation of cavities inside the ceramic foam which could be attributed to poor slurry flow and coating.

Infrared spectroscopy is one method frequently used to identify characteristics groups (see Table 1 and Figure 2). In this case, this technique is used to characterise the materials as aluminosilicates foams, pretreated with different types of impregnation and then carbonized. In the spectra obtained, a broad and intense band located between 1200 cm⁻¹ and 800 cm⁻¹ can be seen, which generally represents the asymmetrical stress vibration of Si-O-Si and Al. The band located at around 1645 cm⁻¹ for each system corresponds to the deformation vibration of the H-OH bond, as the high content of the impregnation solution poly(vinylpyrrolidone) that penetrates the pores preventing the evaporation of water. The increased intensity of the band may be associated with a greater number of water molecules in the material, so this band is not observed in untreated foam. This is further evidenced by the OH groups associated with the water retained by the material, as indicated by the absorption bands near 3500 cm⁻¹ which exhibit minimum strength. The bands in the region between 600 cm⁻¹ and 900 cm⁻¹ are related to stretching vibrations of the Al-O bond,

specifically to Al ions with coordination number 4. Those located in the region between 400 cm⁻¹ and 600 cm⁻¹ may be associated with deformation vibrations of Si-O-Si and Si-O-Al. It is reported that the intensity of this band may be associated with a higher crystallinity of the material, which would indicate that an increase in the SiO₂/Al₂O₃ ratio causes an increase in the presence of crystalline systems in the material, which is expected to negatively affect the mechanical performance.

The persistence of bands in the region between 1200-800 cm⁻¹ and 470 cm⁻¹, corresponding to the vibrations of Si-O-Si, Al and Si-O, seem to indicate that these are be aluminosilicate foams, a three-dimensional structure of tetrahedral [SiO₄]⁴⁻ compact with a predisposition to high porosity. The absorption band of Si-O can occur at 900 cm⁻¹ to 1200 cm⁻¹. In this step, a decrease in the disturbance generated in the silica lattice would show the presence of the tetra-coordinated aluminium atoms listed there, as mentioned previously. The measurements show that the use of urea-formaldehyde resin and carboxymethyl cellulose makes this band diminish or disappear, probably because it starts to show the beginning of a different organisation, but not daring to predict whether this rearrangement is more or less sensitive to the use of resin.

Analyzing the diffraction X ray (DRX) results show that all the images of the aluminosilicate foam powder samples of present great similarity, and others reveal that the presence of the impregnation used in the study contributes to the generation of semi-crystalline or crystalline products (see Table 2 and Figure 3). From the experimental data, calculations are performed of the cell parameters, assuming a cubic structure. The diagrams obtained show no shift in the position of the signal corresponding to the basal spacing (1 0 0), but present higher values in terms of *d* except in the case of the resin, probably because the latter did not develop a significant and in the intercalated impregnating other systems, however it should be noted that sometimes the silicate lattice spacing varies depending on their degree of evolution hydration origin, etc. These changes in the value of *d* show the effective integration of the different

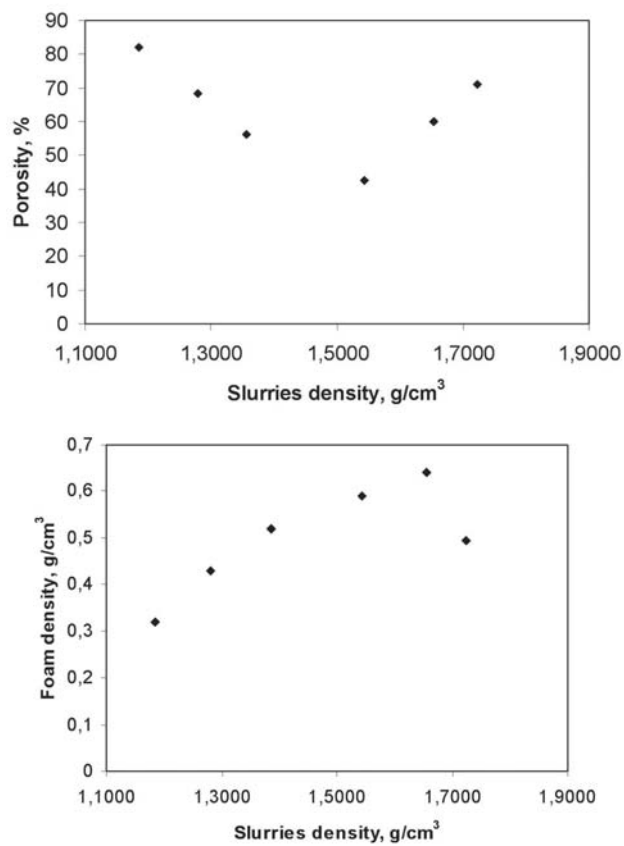


Fig. 1: (a) Porosity and (b) bulk density of ceramic foam as a function of increasing slurry density

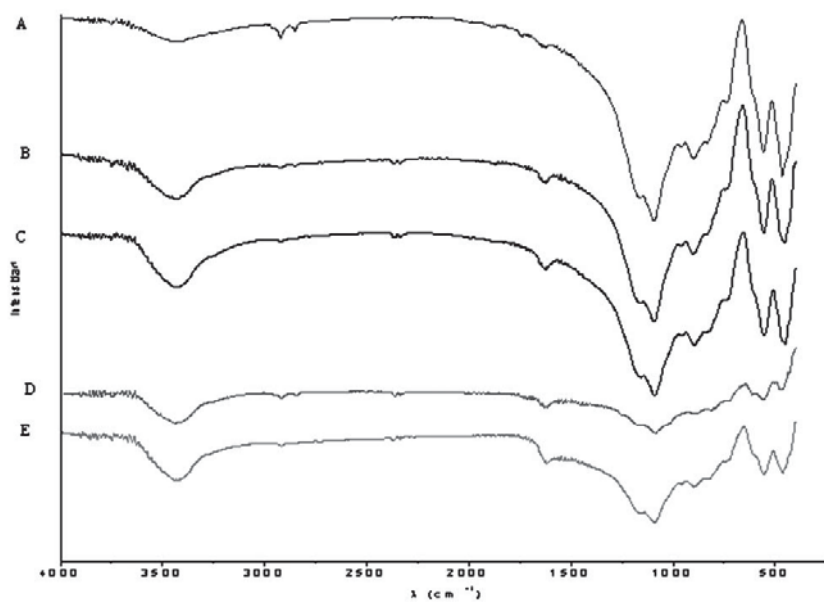


Fig. 2: Infrared spectra of different synthesised ceramic foams

species in the interlayer space of the aluminosilicate material as a result of the impregnation action.

This result is confirmed by the reduction in basal spacing, after impregnation, resulting in a more stable species and a larger cell volume.

Figure 4 show a photograph of the ceramic foam produced in this research. Figure 4a show the foam synthesized according to the procedure proposed initially, and Figure 4b shows the sample treated at a high temperature to analyse its stability with respect to this variable. It can be seen that its lattice is virtually the same, which is observable

without thermal treatment, so the foam can be used as an isolated thermal layer, for example.

The big advantage is that very open structures without openings could be realized with sufficient strength (up to 3MPa in 3p-bending). Moreover, the sponge-replica technique allows for varying the cell size by changing the sponge template. Figure 5 shows a series of scanning electron microphotographic plates. Figure 5a corresponds to the ceramic foam from the normal procedure. This is characterised by large, well-defined pores. Figure 5b corresponds to the CMC-coated ceramic foam, the phenomenon observed

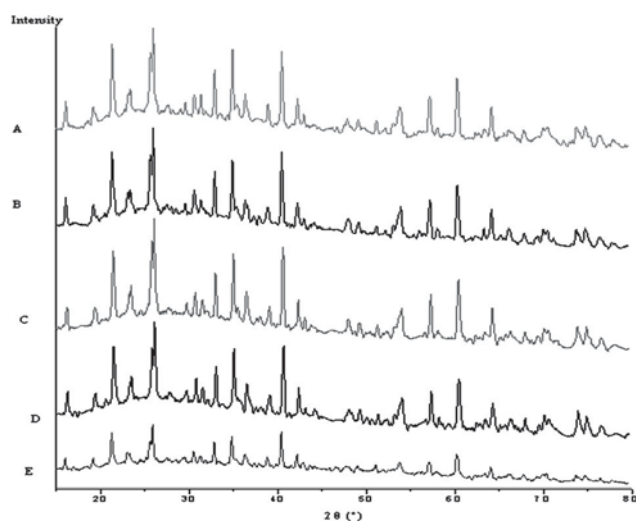


Fig. 3: DRX of ceramic foam synthesised

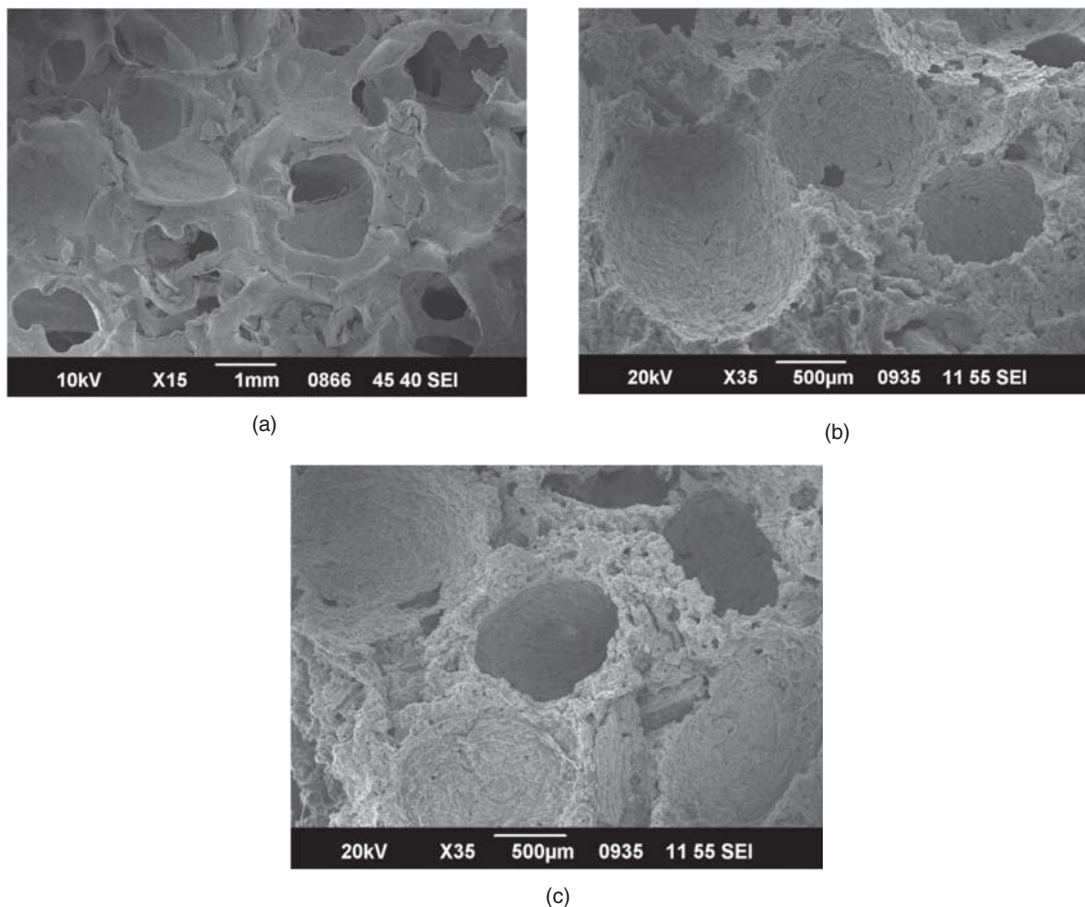


(a)



(b)

Fig. 4: Images of ceramic foams: a) Ceramic synthesised by normal procedure, b) Ceramic foam under high thermal treatment



**Fig.5: Scanning electron microscope of ceramic foams. a) Ceramic foam by normal procedure
b) Ceramic foam with coated CMC. c) Ceramic foam with coated urea-formaldehyde resin**

here is very interesting as the porosity is completely closed. This is important because in the resistance and temperature isolation tests this ceramic realized the best results. Finally, the ceramic foam treated with urea-formaldehyde (see Figure 5c) also shows blocked pores, although with minor resistance to temperature. On the other hand, the nitrogen adsorption isotherms did not develop on the surface area (not shown) whose highest value was achieved on the initial ceramic foam with a value of $7 \text{ m}^2/\text{g}$, whilst the CMC-coated ceramic foam presented an area of up to $2 \text{ m}^2/\text{g}$, which we believe contributed to the high performance of the synthesized foams regarding their insulation against temperature.

When testing the ability of insulation for temperature results showed that ceramic foam coated with CMC and phenol-formaldehyde resin, showed a major capacity, registering temperatures up to $1200 \text{ }^\circ\text{C}$ so that the temperature in the external environment was greater than $40 \text{ }^\circ\text{C}$. These tests are not described in this work and that will be the subject of another publication which is fully explained as the experiments conducted and results achieved

CONCLUSIONS

Ceramic foams were successfully fabricated using the polymeric foam replication method. It was observed that the properties of

ceramic foam are greatly influenced by the density of the ceramic slurry. An increase in the density of the ceramic slurry enhances the strength of the foam as well as its density, thus making the foam denser. Coating with CMC and urea-formaldehyde resin showed an improvement in the properties of ceramic foam, turning it into a material with excellent insulation properties. This result is explained by the fact that these materials cause a closure of the pores, shown by the measurements of nitrogen adsorption isotherms. Temperatures of up to 1200°C were

registered without that the structure of foams significantly affect

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