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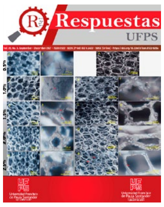

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Fabrication of low-cost SiC foams from sugar and recycled polymeric templates

Fabricación de espumas de SiC de bajo costo a partir de azúcar y plantillas poliméricas recicladas

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RESUMEN

Macroporous ceramic foams are used in different fields due to their unique properties, which include: low density, low thermal conductivity, high permeability, high temperature stability and high resistance to chemical attack. Highly porous silicon carbide (SiC) foams are materials of great interest for absorption, catalytic support, and thermal insulation applications, among others, due to their chemical resistance, large surface area, low flow resistance, low pressure drop, as well as high resistance to temperature and corrosion. In this work, highly porous, SiC foams were fabricated via template replica, using recycled polymeric foams as sacrificial templates. A sucrose-based resin containing silica powder was used as a foam precursor. Polymeric templates were impregnated, followed by thermal treatment at 1500 °C under inert atmosphere. The effect of C/SiO2 mass ratio (1.0-1.75) in the precursor and the use of alumina (0.5 - 2.5 %wt/v) as a sintering additive were evaluated in terms of the morphology of the fabricated foams, as well as SiC yield.

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ABSTRACT

Palabras Claves:
Green roof,
Vertical garden,
Sustainable drainage

Las espumas cerámicas macroporosas son utilizadas en diferentes campos debido a sus propiedades únicas, que incluyen: baja densidad, baja conductividad térmica, alta permeabilidad, estabilidad a altas temperaturas y alta resistencia al ataque químico. Las espumas de carburo de silicio (SiC) altamente porosas son materiales de gran interés en diferentes aplicaciones industriales como absorción, soportes catalíticos, aislamiento térmico, entre otros, debido a su inercia química, gran área superficial, baja resistencia al flujo, baja caída de presión, así como alta resistencia a la temperatura y a la corrosión. En este trabajo, se fabricaron espumas de SiC altamente porosas mediante una técnica de réplica en plantilla, utilizando espumas poliméricas recicladas como plantillas de sacrificio. Como precursor, se usó una resina a base de sacarosa con contenido de sílice en polvo. Las plantillas poliméricas se impregnaron, seguido de tratamiento térmico a 1500 °C bajo atmósfera inerte. El efecto de la relación de masa C/SiO2 (1.0-1.75) en el precursor y el uso de alúmina (0.5 - 2.5 % p/v) como aditivo de sinterización se evaluaron en términos de la morfología de las espumas resultantes, así como del rendimiento de SiC.

Introduction

Macroporous ceramic foams are materials of great interest in a wide range of industrial applications, due to their unique properties, which include: low density, low thermal conductivity, high permeability, high temperature stability, low dielectric constant and high resistance to chemical attack [1]. For instance, ceramic foams are a key component in the fabrication of filters for molten metal, diesel/hot gas engine exhaust filters, catalyst supports, thermal insulators for furnaces and aerospace applications, as well as gas combustion burners and lightweight construction materials [2]. By tuning pore size and shape, the properties of the ceramic foam can also be adjusted in order to meet the functional demands of a specific application [3].

In terms of fabrication techniques, different approaches for the manufacture of interconnected macroporous foams have been reported. Such methods include: (i) partial sintering [4-5], (ii) sacrificial template [6-7], (iii) direct foaming [8-9], (iv) binding [10], and (v) replica technique [11]. All of these approaches are suitable for the production of foams with specific pore size range, pore size distribution and porosity [12]. In particular, the replica method is a simple technique that consists of copying the pore structure and morphology of a template, which is usually a polymeric material that is impregnated with the foam precursor and subsequently subjected to heat treatment [13]. Thus, the porosity, pore size and morphology of the resulting ceramic foam can be easily controlled by defining the properties of the polymeric template.

Highly porous silicon carbide (SiC) foams have emerged as attractive materials for absorption, catalytic support, and thermal insulation applications, among others, due to their chemical resistance, large surface area, low flow resistance, low pressure drop, as well as high resistance to temperature and corrosion [14-15]. Commonly, SiC foams are manufactured from SiC powders, polysiloxane, and phenolic resins, which are raw materials that can be expensive or highly toxic to the environment [16-18].

In the present work, highly porous SiC foams were fabricated via the template replica technique, using recycled polymeric sponges as the SiC foam template. A sucrose-based resin containing silica (SiO_2) powder was used as the precursor. The polymeric sponges were impregnated with the precursor, followed by heat treatment at 1500 °C under inert atmosphere. The resulting SiC foams were morphologically and chemically characterized by Fourier transform infrared spectroscopy (FT-IR), confocal microscopy and X-ray diffraction (XRD). The use of renewable and/or low-cost precursors such as regular table sugar and SiO_2, as well as recycled polymeric templates, offers an economical and more environmentally friendly synthesis route, while still providing tight control over the morphology and structure of the fabricated SiC foams, relative to traditional approaches.

Material and methods

Preparation of the precursor resin

A sucrose resin (carbon precursor), was prepared from a 0.4 g/mL aqueous sucrose solution acidified with HNO_3, which was prepared in a Teflon® beaker. The solution was treated at 90 °C for 48 h. After this, the viscosity of the resulting resin was adjusted to 9000 cP using deionized water, followed by addition of powdered silica (particle size ~7 nm, Sigma), using the following C/SiO_2 mass ratios: 1.0, 1.25, 1.5, and 1.75 (Figure 1). An additional set of samples was prepared including alumina (Al_2O_3) as a sintering additive at 0.5, 1.0, 1.5, 2.0, and 2.5 % wt/v, according to the procedure described above.

Fabrication of SiC macroporous foams

Once the precursor resin was prepared, commercially available polyurethane sponges (1.5 x 1.5 x 2.0 cm, 1068.64 ± 409.44 µm pore size) were impregnated with the resin, and therefore, used as the sacrificial template. The excess resin was removed from the sponges by extrusion, followed by curing at 250 °C for 1 h, using a ramp of 1 °C/min. Subsequently, samples were pyrolyzed at 800 °C using a ramp of 2 °C/min, and then sintered at 1450 °C at 5 °C/min, with 2 h dwell time, under inert atmosphere.

Characterization of SiC macroporous foams

The morphological properties of the resulting SiC foams were evaluated using a Hirox KH-7700 confocal optical microscope, at 35X and 210X magnification. The chemical composition of the scaffolds was characterized by FT-IR using a Cary 630 spectrometer, whereas X-ray diffraction (XRD) analysis was carried out on a Bruker D8 Advance diffractometer with DaVinci geometry. The measurement range was 2 - 70 ° 2θ, with CuKα1 radiation and a step scan with a sampling time of 0.6 seconds.

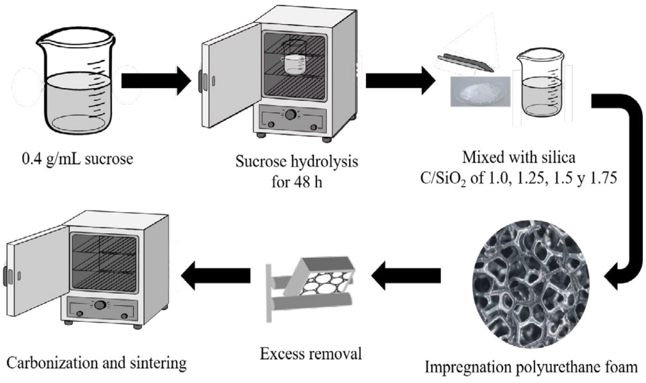


Figure 1. Fabrication of SiC macroporous foams. Source: authors.

Results and discussion

Effect of C/SiO_2 mass ratio

The formation mechanism of silicon carbide (SiC) from silica and carbon has been previously proposed to occur according to the following reactions, in which Equation (6) indicates the general reaction [19]:

$$SiO_2(s) + C(s) \rightarrow SiO(g) + CO(g) \qquad (1)$$

$$SiO_2(s) + CO(g) \rightarrow SiO(g) + CO_2(g) \qquad (2)$$

$$SiO(g) + C(s) \rightarrow SiC(s) + CO(g) \qquad (3)$$

$$SiO(g) + 2CO(g) \rightarrow SiC(s) + CO_2(g) \qquad (4)$$

$$CO_2(g) + C(s) \rightarrow 2CO(g) \qquad (5)$$

$$\boldsymbol{SiO_2(s) + 3C(s) \rightarrow SiC(s) + 2CO(g)} \qquad \mathbf{(6)}$$

As it can be observed in Equations 1-5, solid silicon dioxide reacts with solid carbon to produce silicon monoxide and carbon monoxide gases. Then, silicon monoxide gas reacts with solid carbon to form solid silicon carbide and carbon monoxide gas. Simultaneously, silicon monoxide can also react with carbon monoxide to yield silicon carbide and carbon dioxide [20].

Furthermore, the proportion of carbon and silica in the precursor resin is a key factor that directly affects the mechanism of SiC production. The stoichiometric C/SiO_2 molar ratio is 3, as shown in Equation (6). According to previous works, when the C/SiO_2 ratio is much smaller than the stoichiometric ratio, the formation of silicon carbide cores is limited due to a lack of carbon, which results in the growth of SiC fibers instead [21]. Therefore, in order to assess the effect of the C/SiO_2 mass ratio on the morphology of the resulting SiC foams, precursor resins with C/SiO_2 mass rations that varied from 1 to 1.75 (7 to 14 molar ratio) were prepared and further used for the synthesis of SiC foams.

FT-IR infrared spectroscopy analysis

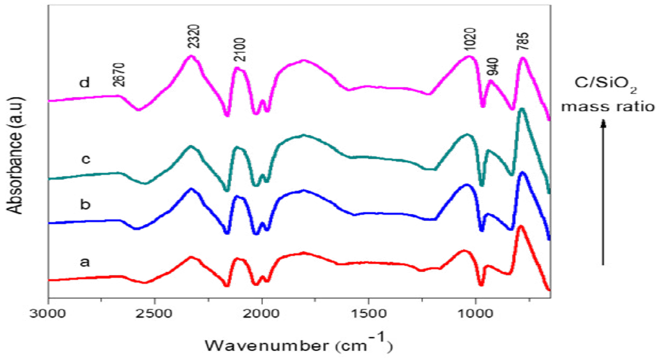


Figure 2. FT-IR spectra of SiC foams prepared using different C/SiO_2 mass ratios: (a) 1.0, (b) 1.25, (c) 1.5, and (d) 1.75. Source: authors.

Figure 2 shows the FT-IR spectra of SiC foams prepared from precursor resins containing different C/SiO_2 mass ratios. The bands observed at 2670 cm^{-1}, 2320 cm^{-1} and 2100 cm^{-1} are attributed to the stretching vibrations of C-H, C-C and Si-H bonds, respectively. These bonds are present in all samples, regardless of the C/SiO_2 ratio, since they can be related to carbon and silica residues that reacted with the hydroxyl groups of sucrose [22]. The 1020 cm^{-1} band is attributed to asymmetric stretching vibrations of the Si-O bond, which is directly related to the presence of silica in the samples. The bands observed at 940 cm^{-1} and 780 cm^{-1} are related to the vibrational mode of longitudinal optics (LO) and transverse optics (TO) of the Si-C bond, respectively, which indicate the formation of SiC [22]. Moreover, in order to gain more information regarding the abundance of functional groups, Fourier self-deconvolution was performed. Table 1 shows peak area estimations for the Si-C and Si-O bands, which indicated higher values for the foams prepared using a C/SiO_2 mass ratio of 1.5, suggesting higher SiC conversion for this formulation.

Table 1. FT-IR peak area for the Si-C and Si-O signals of each fabricated foam.

C/SiO_2 mass ratio	**Si-C area**	**Si-O area**
1	21.25	6.30
1.25	20.78	5.52
1.5	23.59	9.50
1.75	16.46	9.08

Source: authors.

Confocal microscopy analysis

Morphological characterization of the fabricated SiC foams was conducted via confocal microscopy. As it can be observed, the synthesized foams retained the morphology of the polyurethane template (Figure 3a), and thus, macroporous SiC foams with a 1068.64 ± 409.44 µm pore size were obtained. In addition, the foams prepared using C/SiO_2 mass ratios of 1.0 and 1.25 (Figures 3b-c and 3f-g) exhibited a highly heterogeneous surface, which included surface cracking. This could be due to the increased SiO_2 content in the precursor, which in turn limited the contact between C and SiO_2 for the generation of active sites for SiC nucleation, as well as restricted the availability of C as a reducing agent required for initial SiO formation.

On the other hand, the 1.75 C/SiO_2 ratio (Figures 3e and 3i) rendered ceramic foams that appeared to have a carbon-rich phase (red arrows) and a SiC phase (blue arrows) that were unevenly distributed, which could have been caused by the low SiO_2 content in the precursor resin, which in turn led to a low SiC conversion. Moreover, using a C/SiO_2 mass ratio of 1.5 resulted in foams with improved morphological homogeneity, in addition to SiC nucleation on the surface, as indicated by the blue arrows in Figure 3h, which could be related to an increased SiC yield, result that is consistent with the FT-IR deconvolution data (Table 1). Based on this information, the foams prepared from a precursor containing a C/SiO_2 mass ratio of 1.5 were selected for further investigation.

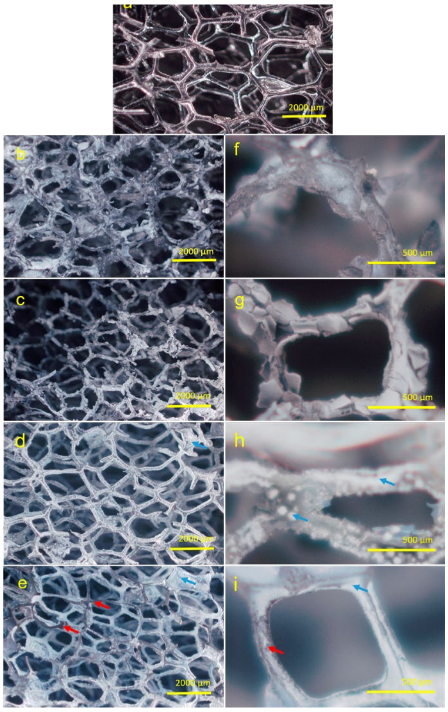


Figure 3. Representative confocal image of a polyurethane foam template (a), as well as images of SiC foams prepared using C/SiO_2 mass ratios of: 1.0 (b, f), 1.25 (c, g), 1.5 (d, h), and 1.75 (e, i). Magnification: 35X and 210X. Source: authors.

X-ray diffraction analysis

In order to gain more insight into the composition and structural characteristics of the foams fabricated from a precursor resin with a 1.5 C/SiO_2 mass ratio, X-ray diffraction was performed. As shown in Figure 4, a peak at $2\theta = 22$ ° revealed the presence of cristobalite (SiO_2), while the two peaks observed at $2\theta = 36°$ and 61° corresponded to the crystalline planes (β) (111) and (220) of SiC, respectively [23]. The presence of residual SiO_2 indicated that the synthesis reaction was incomplete under the sintering conditions that were used, which is consistent with previous reports [24]. Furthermore, a quantitative XRD analysis evidenced that the composition of the abovementioned foam was 94.6% SiC and 5.4% SiO_2.

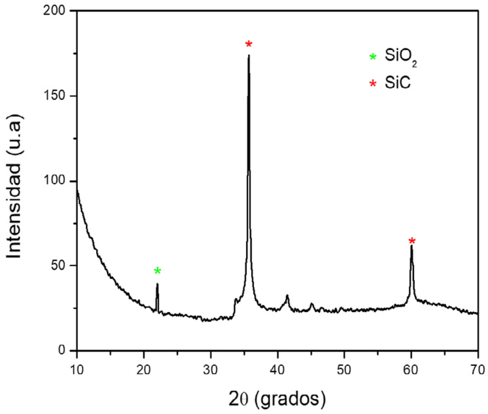


Figure 4. XRD spectrum for SiC foams fabricated using a C/SiO_2 mass ratio of 1.5. Source: authors

Incorporation of alumina as sintering additive

It has been previously suggested that the reaction between oxide additives and silicon carbide generates a partial pressure that is sufficient to limit the extent of gaseous SiO release during synthesis, which in turn favors SiC conversion [25]. Furthermore, the inclusion of alumina (Al_2O_3) increases the relative density of sintered SiC by allowing the diffusion of Al_2O_3 species into the sample, decreasing material contraction [21, 26]. In this context, the effect of the incorporation of Al_2O_3 (0.5-2.5 % wt/v) in the impregnation resin (C/SiO_2 mass ratio = 1.5) was evaluated in terms of the composition and morphology of the sintered SiC foams.

FT-IR characterization

The FT-IR spectra shown in Figure 5 reveal that, as the Al_2O_3 content in the precursor resin increases, the synthesized SiC foam presents an increase in the signal for the 780 cm^{-1} band, whereas the 930 cm^{-1} absorption band decreases. The first one is attributed to fundamental Si-C stretch vibration, while the latter is related to symmetric stretching vibrations of the Si-O bond [22]. Further peak area estimations suggested that higher SiC conversions are achieved as the additive content in the resin is increased from 0.5 to 2.5 % wt/v (Table 2). These results are consistent with previous reports that have indicated that the major role of Al as an additive is to reduce densification temperatures by forming liquid and vapor phases that extend and moisten the SiC grains [27].

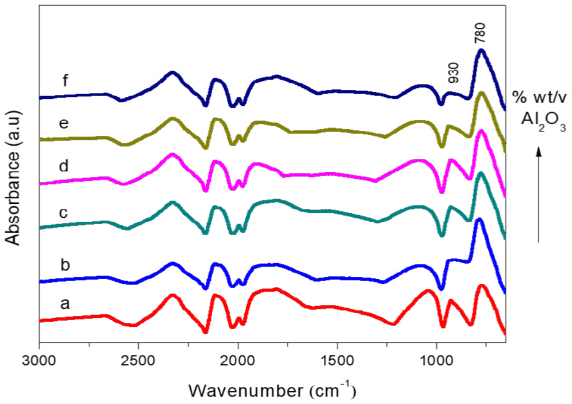


Figure 5. FT-IR spectra of SiC foams prepared using a C/SiO_2 mass ratio of 1.5 and the following Al_2O_3 content: (a) 0.0, (b) 0.5, (c) 1.0, (d) 1.5, (e) 2.0, and (f) 2.5 % wt/v. Source: authors.

Table 2 shows peak area estimations for the Si-C and Si-O bands, which indicated higher values for the foams prepared using a Al_2O_3 %wt/v of 0.5, suggesting higher SiC conversion for this formulation.

Table 2. FT-IR peak area for the Si-C and Si-O bands of foams synthesized in the presence of Al_2O_3.

Al_2O_3 %wt/v	Si-C area	Si-O area
0	23.59	9.50
0.5	41.63	15.42
1.0	38.76	14.23
1.5	36.23	15.79
2.0	31.05	9.78
2.5	33.65	8.67

Source: authors.

Confocal microscopy analysis

Figure 6 shows representative confocal images of the different foams synthesized from a precursor resin with a 1.5 C/SiO_2 mass ratio and varying Al_2O_3 content. In general, increased formation of SiC nuclei and fibers was observed on the surface of the foams, as indicated by the red arrows, although significant surface cracking was also evidenced (Figures 6f-j). Energy-dispersive X-ray spectroscopy (EDS) analysis on the 2.5 %wt/v Al_2O_3 sample (Figure 7), shows that the surface of this foam was primarily covered by SiC filaments, as well as Si and SiO filaments. The presence of the two latter ones suggested Si entrapment during sintering, which could have been caused by the oxide retention exerted by Al_2O_3 that also might have induced surface cracking.

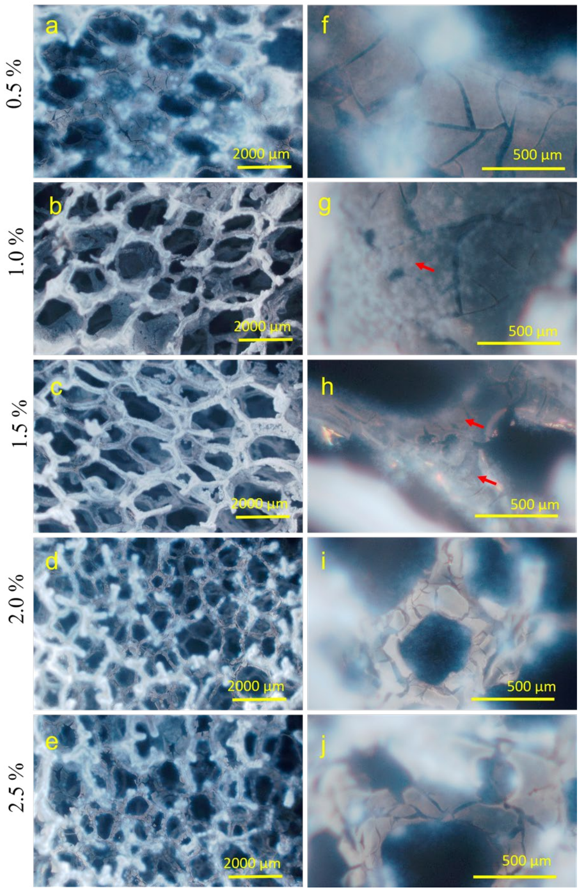
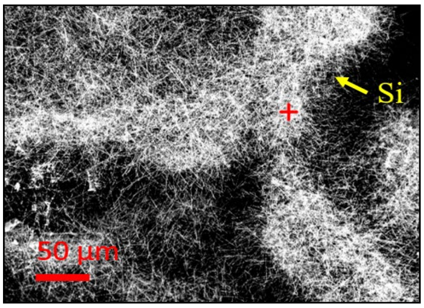


Figure 6. Confocal images of SiC foams prepared using a C/SiO_2 mass ratio of 1.5 and the following Al_2O_3 content: (a, f) 0.5, (b, g) 1.0, (c, h) 1.5, (d, i) 2.0 and (e, j) 2.5 % wt/v. Magnification: 35X and 210X. Source: authors.



Element	Wt%	At%
SiK	58.64	68.12
OK	01.04	02.12
CK	08.49	23.05
AlK	01.37	01.66
AuK	30.46	05.05

Figure 7. SEM-EDS of SiC foams prepared using a C/SiO_2 mass ratio of 1.5 and 2.5 % wt/v Al_2O_3. Source: authors.

Conclusions

In this work, high purity macroporous SiC foams (94.6% SiC) were synthesized employing a simple replica technique and low-cost materials, such as table sugar and silica. The methodology developed here offers a straightforward and economical alternative for the manufacture of SiC foams with controlled porosity and morphology, which could be used for a wide range of industrial applications. Although the incorporation of alumina as sintering additive appeared to improve the SiC yield, foam surface homogeneity was negatively impacted by its presence in the precursor resin. Moreover, the use of a pre-ceramic polymeric solution will be further investigated as a potential foam precursor, since it could improve the template impregnation process (compared to the use of a suspension) and the partial melting of the polymer during pyrolysis, which could render SiC foams with enhanced material properties.

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