Highly-porous hierarchical SiC structures obtained by filament printing and partial sintering

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Abstract

Three-dimensional (3D) porous silicon carbide (SiC) structures with total porosity in the range of 64-85% are achieved from nanosized SiC powders by filament printing and partial sintering in a spark plasma sintering (SPS) furnace. The effects of the SPS temperature (1500 and 1700 °C) and the addition of oxide sintering aids (7 wt. % $\text{Y}_2\text{O}_3+\text{Al}_2\text{O}_3$) on the porosity of the scaffolds are quantitatively compared. More specifically, hierarchical porosity consisting in the presence of meso-pores (< 50 nm) in the struts and macro-pores (in the range of 500-700 μm) defined by the patterned structure is demonstrated for the 1500 °C SPS treatment. The strength of the structures is analyzed as a function of the density as well as the cooling profiles once subjected to rapid heating under a direct flame. By this simple method, an adaptable family of robust light 3D SiC structures with hierarchical porosity is accomplished.

Introduction

Stable, strong, and temperature-resistant porous ceramics are attractive materials that show a wide scope of potential uses, such as for heat dissipation, filters, sensors, microfluidics, solar energy absorption or catalysis [1]. In particular, SiC-type ceramics are prominent for those uses and, actually, a variety of methods for creating SiC or SiOC porous ceramics have been reported [2]. These methods include partial sintering, reaction-infiltration of different types of carbon preforms with molten Si, the sacrificial

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template and replica methods, and the pyrolysis of polymer precursors. The porosity level normally varies in the range of 30 - 90% and pore sizes can fluctuate from micro- to meso- and macro-pores depending on the selected processing route [2-3]. Partial sintering stands out as one of the simplest processes to produce macro-porous (100 nm - 10 mm) ceramics, where the total porosity as well as the pore size are controlled by both the initial grain size and the degree of sintering [3, 4]. Actually, it has been reported that the raw powder size should be about 2-5 times larger than the desired pore size when using the partial sintering route [4]. For example, membrane supports of SiC with 40% porosity and pores in the range 80 – 100 nm were achieved by partially sintering SiC powders of ~100 nm of size, at temperatures in the scale of 1500-1800 °C, using a conventional graphite furnace and a small amount of Al₂O₃ as sintering aid [5].

The option of using three-dimensional (3D) printing to create macro-porosity offers the advantage of controlling the shape and size of the large pore or open cells defined by the architecture. In particular, the direct ink writing (DIW) of SiC scaffolds, containing between 7 and 20 wt.% of oxide sintering aids (a Y₂O₃+Al₂O₃ mixture), and subsequent densification by spark plasma sintering (SPS) at temperatures of 1700 - 1800 °C [6-7], was effective for building spanned structures. These structures had ~60 vol. % of macro-pores defined by the woodpile structure, but the skeletons were practically dense,—with close porosity of ~1% when employing micron size SiC raw powders and ~10% for nano-sized powders.

On the other hand, as Flek et al. pointed out [8], introducing a certain structural hierarchy in engineering ceramics by designing multi-scale lattice materials, as nature often does, produces low stiffness and bending-dominated architectures. Structuring at different scales can be beneficial for different functionalities as well; for instance, in the case of silica-based biomaterials, the tailoring of the scaffolds' hierarchy -with different

pore size levels and precise architectures- was crucial for the bone tissue regeneration [9]. In the case of zeolites, the hierarchical structure of porosity at three levels (macro-meso-micro) has been proved to favor their catalytic activity [10]. More recently, enhanced mechanical specific strength was confirmed for alumina ceramics having ordered porosity across multiple length scales, which was achieved by combining DIW and emulsion/foam templating [11]. Similarly, high specific compressive strength was demonstrated in hierarchically structured Al_2O_3 ceramics but with fully-open porosity. In this case, structures were developed by employing capillary suspensions and DIW [12]. Using also a DIW method, researchers succeeded in making porosity-tunable 3D hierarchical architectures of TiO_2 with the aim of building 3D micro-leaves for artificial photosynthesis purposes, exhibiting microporous architectures comparable to those of natural leaves [13].

Focusing on lightweight SiC ceramics with hierarchical porosity, it is worth mentioning a work about SiC foams covered with entangled silicon oxynitride nanowires grown on the surface by a catalytic process [14]. Using a different approach, SiC foams with two scales of macro-porosity (in the ranges of 1-10 μm and 15-50 μm , respectively) were achieved by freeze casting of SiC-fibers, which showed higher strengths than analogous but unordered porous aerogels [15]. However, so far there have been no attempts to build hierarchically structured porous SiC materials by DIW, except for previous work by some of the current authors [16]. In that work, a certain hierarchy of porosity was granted by growing aligned multiwall carbon nanotubes -using chemical vapor deposition methods- on the filaments of the 3D printed SiC scaffolds, which produced both decreased macropores size in the structures and smaller size porosity in the outer nanotubes mat.

In the present work, we investigate the use of DIW and partial sintering for creating SiC scaffolds with a hierarchical pore structure, in particular, with small pores distributed in the struts and large macro-pores defined by the printed structure. The use of the partial sintering method with the SPS furnace offers additional advantage such as rapid heating and short sintering schedules, thus reducing high temperature stability issues.

Accordingly, light cellular SiC materials (up to 85% porosity) with ordered porosity – including multiscale porosity, such as meso-pores (~30 nm) in the struts and macro-pores (in the hundreds of a μm scale) defined by the logpile structure- have been achieved via filament printing using nano-sized SiC powders by tuning the amount of oxide sintering aids and the sintering temperature. These SiC structures are quite strong despite their high porosity and demonstrate considerable temperature and corrosion resistances, which make them very attractive for a wide range of applications, including catalytic supports, filters, heat dissipation or radiant gas burners [17-19].

Experimental part

The starting SiC powders were nano-sized β -SiC (NanoAmor, average size $d_{50} = 50$ nm, polytype 3C). The oxygen content of these β -SiC powders is ~5 wt.%. Two batches of powder were utilized in the present work: i) the as-purchased raw β -SiC powder, whose resulting inks were subsequently labeled as N0 (plain SiC), and ii) a SiC-based composition containing 2 wt.% of Al_2O_3 ($d_{50} = 0.37$ μm , CR-15; BaikaloX, France) and 5 wt.% of Y_2O_3 powders ($d_{50} = 2.09$ μm , AT; H.C.Starck, GmbH) as sintering additives, next labeled as N7 (7 wt. % of sintering aids). This powder composition was prepared by mixing/milling all powders in a Teflon lined attritor container (during 2 h) using Al_2O_3 balls and alcohol media; afterwards, the solvent was removed in a rotator-evaporator. Inks for DIW were prepared by dispersing the powders in aqueous solutions, containing both high molecular weight and low molecular weight

polyethylenimine, PEI, (H-PEI, $M_w = 25000 \text{ g}\cdot\text{mol}^{-1}$, 99 wt.% concentration, L-PEI, $M_w = 2000 \text{ g}\cdot\text{mol}^{-1}$, 50 wt. % concentration; Aldrich Chemical Co. USA). Powders were gradually added and homogenized in a planetary centrifugal mixer (AR-250; Thinky Company, USA) for 1 min. Methylcellulose (Methocel F4M, $M_w = 3500 \text{ g}\cdot\text{mol}^{-1}$, 5 wt.% concentration; Dow Chemical Company, USA) was used to prevent phase separation during ink extrusion.

The viscosity of the slurries was determined with a rheometer (CVO 100 D, Bohlin Instruments, UK) equipped with cone-and-plate geometry (4° cone angle) that was covered with a fitting tool to reduce evaporation. The apparent viscosity (η_{app}) of the inks was measured as a function of increasing shear rate in the range $0.01 - 150 \text{ s}^{-1}$. Oscillatory tests were also done at 1 Hz to determine the two terms of the complex shear modulus, i.e. the storage (G') and loss moduli (G'') of each ink. Rectangular lattices with a logpile structure were prototyped with a designing software (RoboCAD 4.0, 3-D Inks LLC, Stillwater, OK). Syringes of 3 cm^3 (EFD Inc., USA) were filled with the corresponding ink that was extruded through the nozzle with diameter of $330 \mu\text{m}$ (Precision Tips; EFD Inc.) using a custom three-axis robocasting system (A-3200, 3-D Inks LLC). Printing was done at room temperature on flat alumina substrates. The ink feeding speed was automatically controlled at a constant volumetric flow rate of $0.25D^2v$, where D is the inner diameter of the nozzle and v is the table speed ($10 \text{ mm}\cdot\text{s}^{-1}$ for the present structures). Square lattices of $\sim 13 \times 13 \times 11 \text{ mm}^3$ with 1 mm span (green state) between filaments were assembled by depositing a linear array of parallel filaments, layer-by-layer in such a way that they are orthogonal in adjacent layers.

Air-dried samples were put in a box furnace at 600°C for 2 h in air to burn out the organic additives and, afterwards, treated in the SPS (Dr. Sinter, SPS-510CE; Fuji Electronic Industrial Co., Ltd, Japan). The SPS tests were carried out at two different

temperatures, 1500 and 1700°C, for 5 min in Ar atmosphere at 6 Pa of pressure, using a purposely designed graphite die tool to avoid the collapse of the structures when a minimum contact load was applied to the die. Four types of materials were correspondingly obtained, namely N0-1500, N0-1700, N7-1500 and N7-1700, in reference to the ink compositions (N0, N7) and their corresponding sintering temperatures (1500 and 1700 °C).

Bulk density (ρ_{bulk}) of the structures was determined by weighing and measuring the scaffolds. Dimension and weight changes of the ceramic lattices after the different sintering runs were also measured. The apparent density of the as-sintered structures was measured by the water immersion method, calculated as $\rho_{\text{app}} = [m / (m - m_{\text{H}_2\text{O}})] \cdot \rho_{\text{H}_2\text{O}}$, where m , $m_{\text{H}_2\text{O}}$ and $\rho_{\text{H}_2\text{O}}$ are the weight of the dried specimen, the weight of the submerged specimen and the density of water, respectively. The true density that corresponds to the strut density was equally obtained by $\rho_{\text{strut}} = [m / (m_{\text{sat}} - m_{\text{H}_2\text{O}})] \cdot \rho_{\text{H}_2\text{O}}$, where m_{sat} is the weight of the water saturated specimen. Theoretical densities were estimated, according to the composition and theoretical densities of the original powders ($\rho_{\text{SiC}} = 3.21 \text{ g} \cdot \text{cm}^{-3}$, $\rho_{\text{Y}_2\text{O}_3} = 5.01 \text{ g} \cdot \text{cm}^{-3}$, $\rho_{\text{Al}_2\text{O}_3} = 3.97 \text{ g} \cdot \text{cm}^{-3}$).

The crystalline phases were analyzed by X-ray diffraction procedures on ground samples (XRD; Siemens D5000, Munich, Germany). The specimens were observed at low magnification in a tabletop scanning electron microscope (SEM, TM-1000; Hitachi, Tokyo, Japan) and with a field emission scanning electron microscope (FESEM; Hitachi S-4700, Tokyo, Japan) for details of the microstructure requiring higher magnification.

Nitrogen adsorption-desorption isotherm measurements were performed on a Tristar 3000 volumetric adsorption analyzer (Micromeritics Corp, USA) in a wide pressure partial range at 77K. Specimens of N0-1500, N0-1700 and N7-1500 were used in these

measurements; it was not possible to achieve reliable data for N7-1700 because of the very low adsorption. The Barrett–Joyner–Halenda (BJH) method was used to determine the pore size distribution in the meso-pore region. The specific surface area was estimated by the BET method.

The 3D specimens -one for each composition/SPS treatment- were heated using a micro-torch gas burner with a butane/air mixture during ~ 60 s, at a fixed distance of 2 cm and freely left to cool down. Two different experimental setups were evaluated, in one the 3D structure was placed on a bulky metal piece and in the second, the resting piece was an insulating fiber mat (see images of the setups on the Supplementary Information, Fig. S1). The temperature on the exposed surface (square cell side) of the structures was recorded with a thermal imaging infrared camera (FLIR A325sc, USA), and the cooling temperature profiles were extracted. Parallel tests were followed for a commercial dense bulk SiC (Hexoloy S.A., Saint-Gobain, France) cut to alike dimensions of the outer SiC lattices and used for comparative purposes.

Structures were tested under compression using a universal testing machine (ZwickiLine Z5.0TS, Zwick-Roell, Germany) and a displacement rate of $0.5 \text{ mm} \cdot \text{min}^{-1}$ until crushing. The specimens were previously ground at the top/bottom surfaces (square cell-side) to ensure a homogeneous distribution of the load on the whole scaffold. Three structures were tested for each material. The strength was calculated from the peak load divided by the contact surface, and the apparent elastic modulus was estimated from the lineal section of the load/displacement plots.

Results and discussion

Water-based inks were prepared in the same way as reported in previous works [6,7], but adjusting the amount of surfactants for the present powders and compositions (N0 and N7), as detailed in Table 1. The solids content is similar for both inks, ~61 wt.%. Rheological tests show alike η_{app} for the both inks (Fig. 1a), which display a typical shear thinning response, performing as gelled colloidal suspensions with a pseudoplastic behavior [6]. The storage modulus G' that dominates at lower shear stresses is $\cong 10^4$ Pa for N0 (Fig. 1b) and about three times higher for the N7 ink, which also retains its value at higher stresses and, consequently, shows a higher yield stress ($\sigma_y = 350$ Pa) than that of the N0 ink ($\sigma_y = 250$ Pa).

Table 1.- Composition of the inks used for printing the 3D structures. The content of water only refers to the added water.

	N0		N7	
	Weight (%)	Volume (%)	Weight (%)	Volume (%)
ceramic powders	61.2	33.3	61.4	33.0
H-PEI	3.7	6.3	3.8	6.5
L-PEI*	3.8	6.3	3.8	6.3
MC*	6.1	10.1	6.2	10.4
H ₂ O	25.2	44.0	24.8	43.8

The relative lineal shrinkage (Fig. 2) of N0 structures sintered at 1500 and 1700 °C is quite small ($\leq 5\%$), as expected in the absence of liquid phase formation, whereas N7 structure reaches up to ~28% of linear shrinkage for the 1700 °C treatment. These differences are illustrated by both images inserted in Fig. 2, also demonstrating that the structures maintain the original geometry after sintering. The filament diameter

typically fluctuates from $\sim 290\ \mu\text{m}$ -for both N0 structures- to values around 270 and $230\ \mu\text{m}$ -for the N7-1500 and N7-1700 scaffolds, respectively- matching their sinterability. Obviously, the macro-porous size defined by the structure channels is correspondingly affected, typically varying from $\sim 700\ \mu\text{m}$ for the specimens with relative shrinkages under 10% to $\sim 500\ \mu\text{m}$ for the N7-1700 scaffold (see Fig. 3).

Figure 1. (a) Apparent viscosity of the inks as a function of shear rate and (b) storage (G') and loss (G'') moduli for both inks (N0 and N7).

Mass losses of the calcined SiC structures are relatively large (12-20%) in consonance with the inks compositions (Table 1). For sintered structures, mass losses correlate with the treatment temperature and the presence of sintering aids in the composition (Fig. 2), being determined by both the open porosity and the increased instability of the oxide phases when the temperature rises, i.e. the SiO_2 in the raw SiC powders, besides the Al_2O_3 and Y_2O_3 sintering aids [20-21].

Figure 2. Data of relative shrinkage and mass loss after SPS treatments for the different SiC scaffolds (previously calcined at 600 °C) with attached images for the N0-1500 and N7-1700 structures.

All density values are compared in Fig. 4 for each specimen type. The ρ_{bulk} of the scaffolds varies from 0.5-0.7 g·cm⁻³ for the N0-1500, N0-1700 and N7-1500 specimens to ~1.2 g·cm⁻³ for the N7-1700 specimen. This two-fold increase in density denotes that the liquid phase sintering mechanism plays a significant role for N7 composition above 1500 °C [21]. On the other hand, ρ_{app} are similar for all the specimens and also close to the theoretical for each structure (Fig. 4), indicating that porosity is predominantly open and accessible. The total porosity of the structures ranges from ~64 % for the N7-1700 to ~84 % for the N0-1700 (Fig. 4).

Figure 3. Typical channel sizes, i.e. macro-pores, for (a) N7-1500 and (b) N7-1700 scaffolds.

The specimen N7-1700 with the highest ρ_{bulk} shows the densest filaments as well, ρ_{strut} around $2.6 \text{ g}\cdot\text{cm}^{-3}$, whereas the rest of the specimens exhibit strut densities in the range $1.3\text{-}1.5 \text{ g}\cdot\text{cm}^{-3}$ and total porosities of $\sim 80 \%$ (Fig. 4). If we compare these densities with the respective theoretical values, i.e. $3.21 \text{ g}\cdot\text{cm}^{-3}$ (N0) and $3.28 \text{ g}\cdot\text{cm}^{-3}$ (N7) we observe that for the N0 (both temperatures) and N7-1500 structures the densities of the skeletons are about 40-46 % of their theoretical densities, whereas for SiC N7-1700 structure reaches $\sim 80\%$ of the theoretical density.

Figure 4. Values for the bulk, strut and apparent densities of the different scaffolds, together with the total porosity of the whole structures.

The variation of the SiC grain size is also remarkable, as it can be observed in the fracture surface images of the different skeletons (Fig. 5). The microstructures of N0 and N7 scaffolds (both treated at 1500 °C) are very fine, with grain sizes in the range 50-100 nm (Fig. 5a,c), alike the size of the original powders. Conversely, the materials treated at 1700 °C (Fig. 5b,d) reveal the occurrence of notable grain growth, with sizes in the 0.5-3.0 μm range, but attributable to different mechanisms for N0 and N7. In fact, the growth of faceted SiC crystal (Fig. 5b) reveals the predominance of a gas-phase sintering mechanism (evaporation-condensation) for the N0-1700 specimen; whereas for the N7-1700 scaffold, a microstructure of equiaxed homogenous grains (Fig. 5d), typical of liquid phase sintered SiC materials though a solution-precipitation-grain growth mechanism is observed [23]. Accordingly, the sizes of pores in the struts should be also affected as is perceived in the SEM micrographs (Fig. 5). Actually, the gas-phase SiC grain growth reveals a quite open microstructure in the struts of the N0-1700

with partially connected crystals and large size pores as compared to the N0-1500 and N7-1500 scaffolds.

Figure 5. Typical microstructures on the fracture surface of a filament in the scaffolds of a) N0-1500, b) N0-1700, c) N7-1500 and d) N7-1700.

According to these observations, the N₂ adsorption-desorption isotherms (Fig. 6a) of the scaffolds show hysteresis for N0-1500 and N7-1500, which is an indication of the presence of meso-pores; whereas, the N0-1700 scaffold does not show any mesoporosity in the struts. The plot of the pore size distribution (Fig. 6b), according to the BJH model, indicates the occurrence of a peak of meso-pores at 30 nm (N0-1500) and 40 nm (N7-1500). N0-1700 is a very interesting structure since, despite showing larger pore sizes (> 70 nm) in the struts, it still exhibits porosity at different scales (from

a few to hundreds of μm , Fig. 7). Moreover, it presents the highest porosity among the structures (Fig. 4)

Specific surface area and total volume of pores with sizes between 1.8 and 300 nm as well as the average pore diameter of meso-pores are reflected in Table 2. It is interesting to note that S_{BET} for N0-1500 is close to the value of the original powders ($35\text{--}40\text{ m}^2\cdot\text{g}^{-1}$), whereas for N7-1500 decreases to half that value and even more abruptly for the N0-1700. In consonance, the total volume of pores under 300 nm is higher ($0.078\text{ cm}^3\cdot\text{g}^{-1}$) for N0-1500 specimens than for the others presented in this work. The average meso-pore size for the N0-1500 struts is about 1/3 the original size of the SiC powders, being therefore coincident with the rule that pore size is within a half and a fifth of the powders size [4].

Figure 6. (a) N_2 adsorption/desorption isotherms of both compositions showing hysteresis for the 1500 $^{\circ}\text{C}$ treated scaffolds and (b) BJH pore size distribution calculated from the desorption branch.

Figure 7. Images of N0-1700 scaffold showing a representative view of large channels (a), the surface of a rod with macro-pores (b) and the faceted SiC grains in the surface of the rod at higher magnification (c).

Table 2. Specific surface area, total volume of pores between 1.7 and 300 nm, and average diameter for meso-pores (BJH desorption) for the indicated structures.

	N0-1500	N0-1700	N7-1500
S_{BET} ($\text{m}^2 \cdot \text{g}^{-1}$)	21.5	0.8	12.2
volume of pores ($\text{cm}^3 \text{ g}^{-1}$)	0.078	0.0027	0.038
d (nm)	17	50	27

These materials present slight differences regarding the phase analysis, All the structures consist of a mixture of the cubic phase, β -SiC (3C), and two hexagonal polytypes, α -SiC, while both N7 structures show, in addition, the presence of yttrium aluminum monoclinic, YAM, ($\text{Al}_2\text{Y}_4\text{O}_9$), in agreement with the occurrence of liquid phase sintering process that predicts the precipitation of different Y-aluminate phases depending on the SPS sintering conditions [24].

On the other hand, it has recently been shown that porous nano-sized SiC materials (around 60% porosity and 35 nm of grain size) possess low thermal conductivity values ($\sim 2 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$), effect that authors attributed to the existence of a high density of stacking faults and, accordingly, their potential application as thermal insulator was claimed[25]. However, for these kinds of open cell structures radiative and convective heat transfer to their surroundings may be prevailing over conduction [26]. To get an simple appraisal of their heat transfer behavior, present 3D structures were subjected to a torch flame that produced a rapid heating on the exposed surface, and the corresponding free cooling of the surface was recorded as a function of time. The cooling profiles for each structure are plotted in Fig. 8 where the analogous cooling profile for dense Hexoloy material is included (these data correspond to tests where specimens rested on a metal piece; see Fig. S1). It should be mentioned that no signs of degradation were evidenced for any of the tested materials and that the maximum temperature achieved on the exposed surface (T_0) depended on the particular material. Certainly, values of $T_0 \sim 1000 \text{ }^\circ\text{C}$ were reached for the 3D structures with porosities around 80% (i.e. for N0-1500, N0-1700, N7-1500, see Fig. 4) after exposure times of 60 s, whereas a relatively lower temperature ($800 \text{ }^\circ\text{C}$) was achieved for the N7-1700 structure in agreement to its lower porosity (Fig. 4). Moreover, an even lower peak temperature ($\sim 500 \text{ }^\circ\text{C}$) was measured for the dense SiC material, which under the given experimental heating conditions clearly reached a limit temperature because of the higher heat dissipation by conduction to the surroundings (namely the metal the bench), as compared to the 3D structures. Accordingly, the highly-porous structures demonstrated much lower thermal inertia.

It should be mentioned that for similar tests but for specimens resting on the insulating fiber mat, a raise in the peak temperatures of 250 °C was observed for the Hexoloy SiC material, but certainly lower for the porous 3D materials (~ 100 °C), as it can be seen in the Supplementary Information (Table S1 and Fig. S2). This result, compared to the above reported test, indicates that heat dissipation by conduction notably decreases for the dense SiC when using an insulating support that occurs. In fact, the differences in the limit temperatures achieved for the two kinds of materials –with structured porosity and dense- reduces from about 500 °C to 300 °C when conduction is mostly suppressed (Table S1).

Despite the non-linearity of the complete heat transfer equation due to the radiative term, it is commonly found that third-order exponential functions –having different time constants and amplitudes- fit quite well the cooling of an object [27]. In effect , the cooling profiles for present 3D the structures (Fig. 8) showed good fitting to expressions of the type:

$$T(t) = y_0 + A_1 e^{-t/a} + A_2 e^{-t/b} \quad \text{eq. [1]}$$

with two exponential terms. Fitting parameters were relatively similar for all the 3D SiC structures (Table 3). The first exponential dominates in the high temperature range where the radiative dissipation mainly governs. However, for temperatures between 500 and 550 °C, the first exponential fades and the second exponential solely dominates, as it can be seen in Fig. 9 for the N0-1500 structure, which is the typical functional form for the Newton's cooling law associated to convective cooling. Conversely, for the dense SiC material, the cooling curve was well fitted just using the convection term (Table 3). Larger values of the pre-exponential term, A_1 , are found for N0-1500 and N7-1500 scaffolds, which infers a higher contribution of the radiative term for the

materials with meso-porosity; whereas, the densest material (N7-1700) showed significantly lower contribution of the radiative term.

Figure 8. a) Plot of cooling profiles for the SiC structures and the dense material after exposure to the flame torch (specimens resting on brass). Examples of thermographic images after 5 s of cooling of b) dense SiC Hexoloy and c) N7-1500.

Furthermore, the weight of the convection term in eq. [1] is quite similar for all the scaffolds but significantly lower than for the dense SiC (see parameters A2 and b in Table 3). It should be pointed out that, for the latter material, the cooling profile from a temperature (~ 800 $^{\circ}\text{C}$), i.e. when an insulating support was used, is perfectly fitted with just a convection term, (see Figure S2 of the Supplementary Information). Therefore, these highly-porous SiC structures, especially those containing meso-porosity, demonstrate extraordinary thermal dissipation and low thermal inertia.

Table 3. Fitting parameter for eq. [1] for each material type

	N0-1500	N0-1700	N7-1500	N7-1700	HEXOLOY
y_0	63	121	82	64	69
A_1	367	246	270	115	-
a	1.6	1.5	1.7	1.3	-
A_2	691	691	597	641	1040
b	16.4	17.3	22.5	19.9	21.6

Figure 9. Cooling profile of N0-1500 structure showing experimental points and the second order exponential fitting curve. Both exponential terms are separately plotted to contrast the different regimes of dominance.

For highly porous structures as the present (60-85 %) is imperative to attain certain robustness. Hence, typical loading curves for the different structures are compared in

Fig. 10, where the higher stiffness and loading capacity of N7-1700 is perceived, whereas the rest of the structures show higher deformation up to fracture. Peaks in the stress/strain plots of N7 structures are indicative of single failure events, although structures still maintain their bearing capability until total collapse.

Figure 10. Representative stress-strain curves under compression for the 3D SiC structures

Compressive strength and elastic modulus data are correspondingly represented as a function of ρ_{bulk} for all the tested specimens (Fig. 11). Both properties increase with density as expected. Lines in the plots of Fig. 11 represent polynomial regression fitting of degree 1.5 for strength and quadratic for the elastic modulus, which are frequent for cellular materials [28].

Strengths are above 5 MPa for all the structures, with values up to around 20-30 MPa for the structure with of $\rho_{\text{bulk}} = 1.1 \text{ g}\cdot\text{cm}^{-3}$. Average strengths in the range 1- 16 MPa for porosities of 75-86% [28-31] and in the range 20-30 MPa for porosities of 55-60% [31-32] have been reported for cellular SiC. Compressive strength values for a different

highly porous cellular SiC materials, fabricated by diverse routes (freeze casting, replica of polymeric foams with a slurry or graphite filled polymeric precursors), are including in plot of Fig. 11a). A straightforward comparison of present hierarchical structures (N0-1500 and N7-1700) and cellular SiC materials of comparable density (Fig. 11a) indicates that having porosity at different scales (meso- and macro-pores) has a positive effect on the compressive strength.

Figure 11. a) Compression strengths and b) elastic modulus for the 3D structures.

Dotted lines correspond to polynomial regression fitting of degree 1.5 for strength and quadratic for the modulus. Data points (★) for different highly porous cellular SiC materials are also plotted in a) with indication of the corresponding work.

Summarizing, we have demonstrated that the partial sintering of 3D filament printed SiC structures is a basic effective route to achieve light SiC materials (60-85% porosity) with a hierarchical pore structure, of macro-pores of hundreds of μm defined by 3D construct and much smaller size pores, including meso-pores in the struts for the s lower sintering temperatures (1500 °C). The total volume of pores can practically be controlled by selecting the sintering aids and the temperature. Having porosity at

different scales (meso- and macro- level) definitively benefits the strength and thermal dissipation performance of present highly porous 3D structures. This family of materials is suitable for quite a number of applications and, particularly, as filters/absorbers, gas burners or in fields as catalysis and thermal protection/dissipation.

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Supplementary Information

Highly- porous hierarchical SiC structures obtained by filament printing and partial sintering

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Results on the heating/cooling tests for the 3D SiC structures and a dense SiC (Hexoloy, Saint Gobain) are shown below.

All specimens are of similar dimensions and outer geometry. The figures S1, S2 and Table S1 provide information on the two experimental setups, the peak temperatures reached after heating with the micro-torch for a 3D structure and the dense SiC, and a comparison of the cooling profiles of the dense SiC for both conditions (metallic or insulating bench)

Figure S1. Images of the experimental setup for the heating experiments using the micro-torch. On the top the 3D SiC specimen (N0-1500) rests on a brass piece, whereas on the bottom it seats on a ceramic fiber mat. Rest of the conditions remained equal.

Table S1. Comparison of peak temperatures achieved in the 3D SiC structure (N0-1500) and the dense SiC after heating with a micro-torch for 60s for both experimental setups shown in Fig. S1.

Specimen	Peak temperature (°C)
N0-1500	1090
N0-1500*	1190
Hexoloy	520
Hexoloy*	770

*Specimens tested over insulating fiber mat

Figure S2. Cooling profiles for dense SiC (Hexoloy) for the two different experimental setups. Around 250°C higher peak temperature is observed for the specimen resting on the insulating fiber, but the functional forms are equal as curves can be superimposed .