

BIO-INSPIRED CERAMIC/CARBON COMPOSITES

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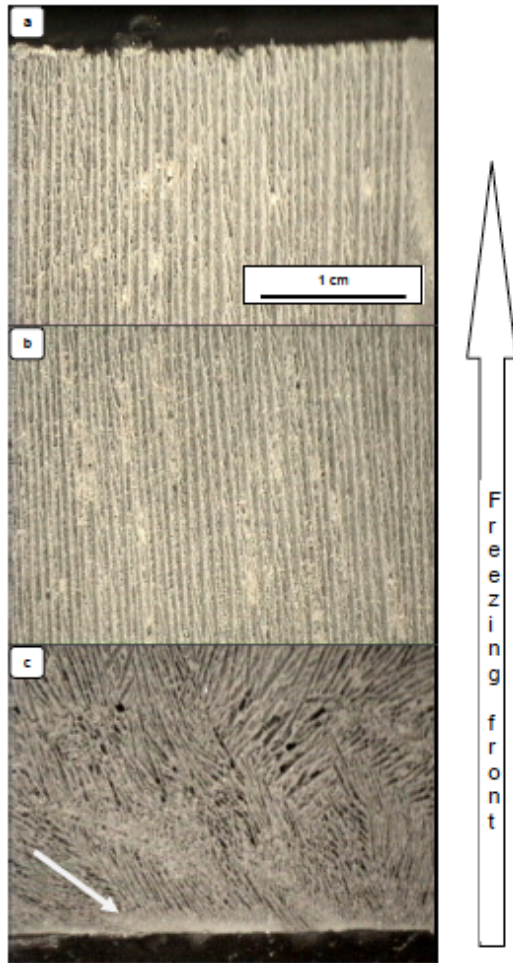


Figure 1. Optical micrograph showing the cross section of a freeze casted SiC scaffold. (a) Bottom of the sample, in contact with the cold finger, (b) middle region and (c) top. The micrograph show the typical cellular structure that forms in the bottom (the arrow marks the area in contact with the cold finger) as the ice advances lamellae align with the temperature gradient creating a uniform layered scaffold.

Sintering of SiC scaffolds

One of the major difficulties encountered in the sintering of the porous SiC scaffolds fabricated by freeze casting was to achieve full densification of the lamellae while controlling grain growth. Scaffold sintering has to be pressureless to preserve the porous structures and as it was described in previous report low sintering temperatures resulted in fine grains but poor densification while high-sintering temperatures promoted densification but also grain growth with formation of large SiC platelets. This happened using oxide and non-oxide sintering additives and it will be advantageous to develop a process that will allow the formation of scaffolds with dense lamellae while controlling grain growth. This is important, as dense lamellae are required for the fabrication of strong composites through the infiltration of the scaffolds with a second phase. To address this problem, we have investigated an alternative approach based on the control of the sintering atmosphere using powder beds.

Silicon carbide suspensions with a solid content of 20 vol% (43 wt%), were prepared by dispersing α -SiC powders (grade UF25) in water for 24 hours using a ball mill with SiC balls. Tetramethylammoniumhydroxide (TMAH) was used as a dispersant (1.4 wt% to the ceramic powder). TMAH promotes the dissociation of the silanol groups present on the surface of SiC powder, increasing the zeta potential of SiC and promoting colloidal stability. Polyvinyl alcohol (14 wt% with respect to the ceramic powder) and sucrose (4 wt% with respect to the water) were added as binders. Sucrose is also used to control the structure of the growing ice crystals and promote the formation of lamellae with a characteristic microscopic roughness. Alumina and yttria were added as additives to trigger liquid state sintering. The total amount was 4 wt% of the solution with a weight ratio $\text{Al}_2\text{O}_3/\text{Y}_2\text{O}_3$ of 6/4. After milling the suspensions were de-aired by stirring in vacuum for one hour and placed on a Teflon

mould on the cold finger of the freeze caster. The temperature of the cold finger was then decreased at a constant rate of 5°C/min until the suspension was fully frozen. Subsequently, the water was eliminated by freeze-drying leaving a porous SiC scaffold ready for sintering.

Sintering of the SiC scaffolds was done in Ar atmosphere using a graphite furnace. The sample was placed on the top of a powder bed containing a mixture of SiC and Al₂O₃. The alumina content of the bed was 4 wt%. The samples were heated at 15°C/min up to 600°C and maintained at this temperature for one hour to eliminate the binders. Subsequently they were heated up to 1800°C at 10°C/min and sintered at this temperature for two hours to promote densification. The structure of the sintered samples was characterized by scanning electron microscopy and their density measured using the Archimedes method.

As expected, after freeze casting the samples exhibit a layered structure formed when the lamellar ice growing in the suspensions expels the ceramic particles as it grows directionally in the freeze caster (Figure 1). Sintering in the powder bed results in the formation of dense, uniform ceramic lamellae ~10 micron thick (Figure 2). The final density of the materials is ~1.4 g/cm³ with an open porosity of 53 vol% and closed porosity of 4 vol%. Preliminary measurements indicated compressive strengths that can reach values in excess of 150 MPa (in the direction parallel to the ceramic lamellae).

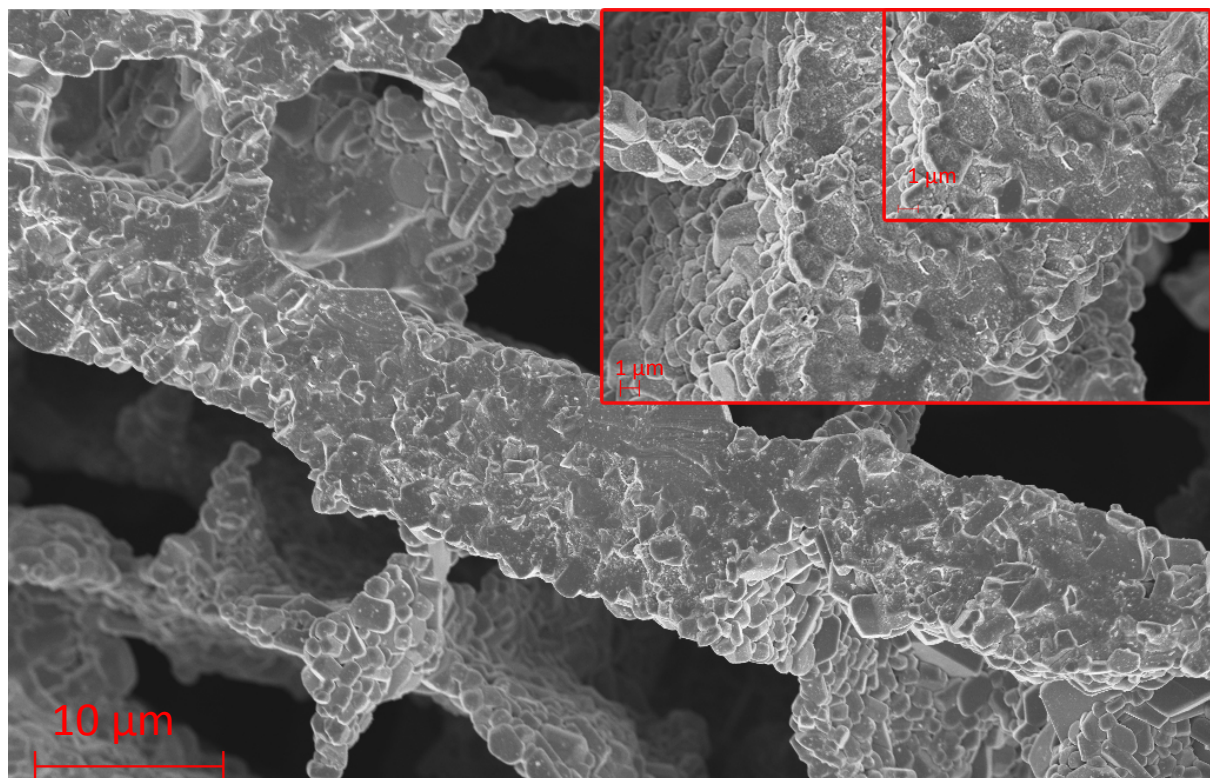


Figure 2. Sintered SiC scaffold showing the formation of dense lamellae with controlled grain growth.

High-resolution TEM analysis of carbon nanostructures formed on freeze casted scaffolds

In the previous report we described an approach to grow carbon nanostructures inside freeze casted scaffolds (see attached paper). This approach is based on the infiltration of a metallic precursor in the scaffold followed by in situ chemical vapour deposition (CVD) inside the porosity. We have now performed high-resolution transmission electron microscopy (HRTEM) analysis of the structures.

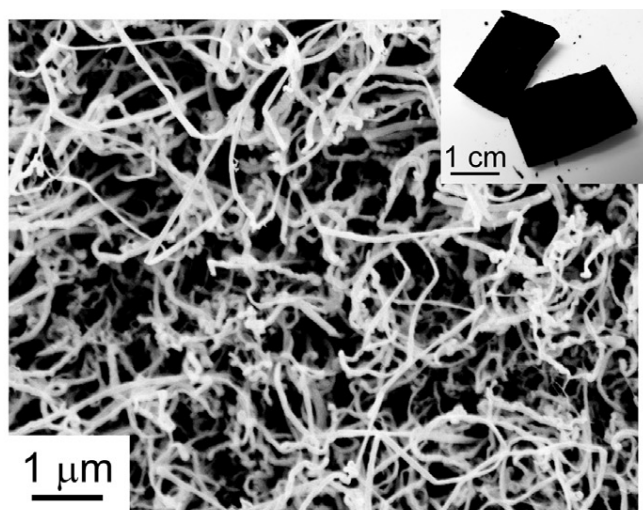


Figure 3. SEM micrographs of the interior walls of freeze casted alumina structures after CNT/nanofibre growth with 0.2 l/min methane. The inset shows homogenous coverage with carbon nanofibers/nanotubes in the interior of the Al_2O_3 scaffold (revealed after breaking the scaffold in 2 pieces).

Carbon nanostructures were grown inside a freeze casted alumina scaffold by first infiltrating a catalyst precursor followed by a reduction/formation of metallic catalyst particles and chemical vapour deposition. A 1.1 M solution of iron (III) nitrate in isopropanol was infiltrated in the scaffolds using a standard vacuum infiltration set-up (Buehler Cast NVac). Afterwards, the solvent was removed at 60°C under vacuum. For the CVD process the infiltrated sample was placed inside a quartz tube furnace and the system was purged with an Ar/H_2 gas mixture (90/10) for 30 minutes at a flow rate of 0.5 l/min as calibrated for air. The sample was heated at $\sim 1^\circ\text{C}/\text{min}$ to the growth temperature (between 700°C to 900°C). The presence of hydrogen leads to the reduction of the catalyst to form iron nanoparticles. Upon reaching the growth temperature methane was added to the gas mixture. Growth time was 20 minutes, after that time the methane flow was closed and the power to the furnace was cut-off. We observed the formation of fibre/nanotube structures in the internal pores of the scaffold (Figure 3) creating a hybrid ceramic/carbon material. HRTEM was carried out on a FEI Titan 80-300S/TEM operated at 300 kV, equipped with a monochromator and a Cs aberration image corrector. The HRTEM specimens were prepared by dispersing small flakes of the hybrid material in acetone and drop casting them on carbon coated TEM copper grids.

The TEM analysis revealed the formation of an organized distribution of carbon nanofibres and nanotubes inside the scaffold (Figure 4). Nanofibres grow from and bundle around the catalyst particles deposited on the ceramic walls while multi-walled nanotubes grow from the catalyst-covered walls into the pores. No evidence for amorphous carbon covering the catalyst particles is observed. The tubes have a small catalyst particle on top. This picture agrees with existing models of nanotube growth in which multi-wall CNTs grow from small

catalytic particles that can rest on a larger one that acts as a support while the smaller one is “lifted” by the growth of the nanotube. The distribution of nanotubes and nanofibres probably reflect the distribution of sizes of the catalyst particles formed after infiltration.

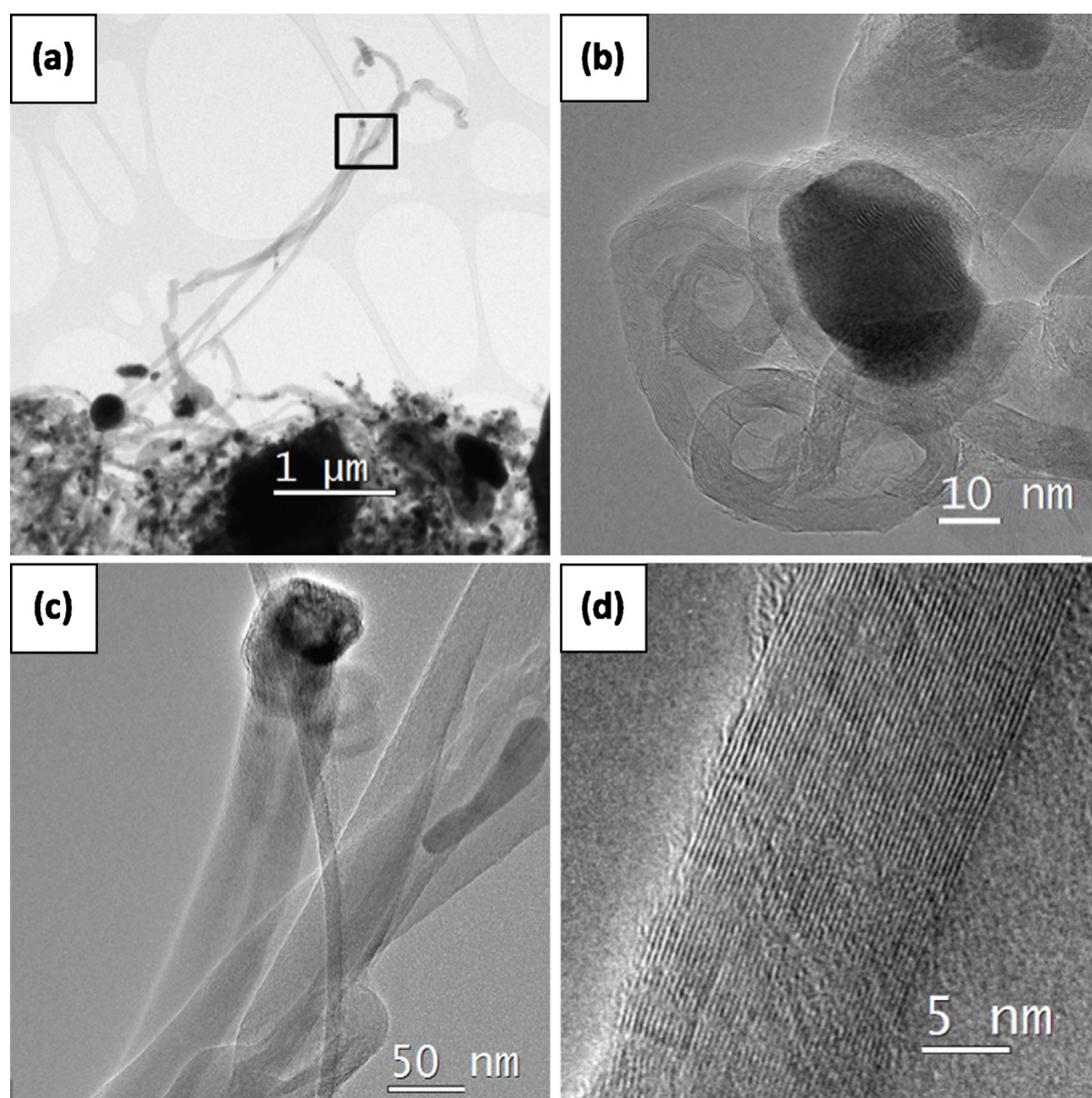


Figure 4. Transmission electron micrographs of the samples after growth showing the nanofibres and multi-walled CNTs. (a) Low magnification TEM of the hybrid material, showing the presence of different carbon nanostructures. Fe catalyst particles appear dark in the image. Nanofibres grow and bundle around the catalyst particle with several long multi-walled CNTs growing from the catalyst particle towards the pore. (b) Typical nanofibres growing from a Fe catalyst particle. (c) Enlarged image of the area indicated in (a) with the box, showing a multi-walled CNT growing from a Fe particle with a small catalyst particle on top. A high-resolution image of the left wall of the CNT in (c) is shown in (d).

Conclusions and Future Work

The results have shown that it is possible to develop a sintering approach to form SiC carbide scaffolds with dense lamellae that can be used in the fabrication of bio-inspired ceramic materials. Future work will include the mechanical and structural analysis down to the nano-level (using HRTEM) of the SiC structures in order to reveal the densification mechanism and optimize the sintering process.

High resolution TEM has revealed the organization of carbon nanofibers and nanotubes grown by an in situ CVD process, this work has revealed the importance of controlling the size of the catalyst particles (smaller particles promote nanotube formation) and will guide a further development of the chemical deposition approach to form the hybrid ceramic/carbon materials.