

IMPERIAL COLLEGE LONDON, DEPARTMENT OF MATERIALS

Bio-inspired ceramic based composites

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Declaration

I hereby declare that this thesis is my original work. Other contributions, which are not my own, have been truly and properly acknowledged.

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Abstract

The progress of a wide range of strategic fields from aerospace, construction, transportation or medicine depends on the ability to develop new materials combining different structural and functional properties, from lightweight to high fracture resistance. One way of achieving this is by borrowing design principles found in Natural materials such as bone or nacre and integrating them into man-made materials. A common characteristic of these Natural composites is the combination of hard and soft phases in hierarchical structures with characteristic dimensions spanning multiple length scales. The process of adapting natural structural features to new technologies is called “bio-inspiration”. This PhD project, attempts to mimic some of the structural motifs found in natural materials to produce innovative lightweight ceramic structures and ceramic-based composites with high fracture resistance.

Freeze casting (also known as ice-templating) was used to produce strong and lightweight SiC scaffolds using SiC particles with two different morphologies: spherical nanoparticles (400 nm in diameter) and micro-fibres (~18 μm long and ~1.5 μm in diameter). In both cases the optimal rheological behaviour for the freeze casting slurries along with optimal sintering conditions for the consolidation of the freeze cast scaffolds have been identified. Freeze casting of nanoparticle suspensions resulted in porous layered scaffolds with wavelengths (lamella wall plus pore space) ranging from ~60 to ~15 microns and porosity between ~50% and ~75%. The packing of fibres during freeze casting allowed the formation of highly porous networks with porosities as high as 98%. The mechanical (compressive and flexural strength) and functional properties (electrical conductivity, thermal conductivity) of the scaffolds have been measured and related to their structure. These scaffolds have been employed as preforms to produce SiC based composites through infiltration of the residual porosity with two different polymers: PMMA and Epoxy resin. The distinctive layered architecture of the composites enables a combination of high flexural strength and fracture resistance. The main toughening mechanisms (crack deflection, crack bridging, plastic deformation etc.) have been identified.

To form metal-ceramic composites, layered freeze cast alumina preforms have been infiltrated with an aluminium alloy (Al-4Mg). The wettability of this alloy on alumina allows the infiltration of porous scaffolds without the application of external pressure. Therefore an extremely porous preform can be fully infiltrated without damaging the ceramic network. The microstructures of alumina preforms obtained from nanoparticles (400nm in diameter) or platelets (5-10 μ m in diameter and 300-500nm in thickness) have been compared. The use of platelets enables the fabrication of layered ceramic scaffolds with wall thickness of $\sim$ 5-6 μ m. Mechanical tests revealed that the layered freeze casted composites exhibit a combination of high fracture resistance and flexural strength, with values that are superior to other metal-ceramic composites. Materials fabricated using alumina platelets can reach the strengths up to $\sim$ 890MPa. All the materials exhibit stable crack propagation with a characteristic R-curve. An extensive study of crack interaction with the microstructural features has been performed to identify the key toughening mechanisms such as crack deflection, crack bridging, micro-cracking and plastic deformation.

The results of this thesis suggest that the structure of natural materials can be used as a blueprint in the development of new advanced composites. This requires processing techniques able to implement, in practical dimensions, the design concepts found in natural materials. However, a deep understanding of the relationships between structure and mechanical response encompassing the influence of structural parameters acting at multiple length scales is still needed to guide this effort.

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1 Chapter: Natural and biomimetic materials

1.1 Introduction

Since the beginning of the 20th century, many researchers have focused on analysing how natural materials achieve their exceptional functional and mechanical properties (fracture resistance, self-healing, adaptability to changing conditions etc.), despite the limited availability of basic constituents. This basic study has led to the beginning of a new branch of engineering, usually referred to biomimetics. Biomimetics is a multidisciplinary topic that involves biology, chemistry, physics and materials science [1]. The main objectives of this area of study are: understand the biological mechanisms behind the creation of complex architectures typical of natural materials; define which structural features control their performance; and finally study how it could be possible to translate these structural designs to synthetic materials [1,2]. Natural materials often present similar design concepts mainly due to the limited availability of organic and inorganic components [3]. Most of them are in fact largely composites of polymers (proteins and polysaccharides) and nano-metric ceramic components [4] with different grades of crystallization (calcium carbonate, calcium phosphate, silica). This is mostly due to the limited sources of chemical elements in Biology (e.g., C, N, O, H, Ca, P, S, Si)[5]. However, many of these structures show a unique combination of properties being at the same time light, strong, flexible and tough. These features are achieved by combining different structural solutions: hierarchy that spans several length scales, from nano to macro levels; combination of soft and hard materials within layered, columnar or fibrous arrangements each with different mechanical response and properties; engineered interfaces; graded porosity etc. The possibility to implement these structural solutions could lead to the production of new ceramic composites with superior properties usable in many different applications. In particular, it would allow developing materials with improved fracture toughness addressing the main problem that has hampered the technological application of structural ceramics. New class of low weight, stiff, strong and tough man-made artificial bio-inspired composites could be obtained taking a close look to the solutions employed by Nature. However, the materials production techniques that are available nowadays are still far from closely replicating the required

degree of architectural control. Natural structures are indeed assembled in an aqueous environment at ambient temperature and pressure with bottom-up processes (self-assembled) rather than top-down processes that are typical of synthetic routes. Nevertheless, the potential of using a nano-microstructural design approach to project materials with advanced mechanical properties has been proved in the last decades in many studies. For example, alumina polymer composites produced by freeze casting, mimicking the nacre-like brick and mortar composite, exhibits value of fracture toughness one order of magnitude higher than pure alumina, thanks to the many toughening mechanisms that occur in the biomimetic microstructure [6,7]. Using a similar approach, same types of mechanical enhancement has been achieved in other systems, such as silicon carbide/PMMA [8] or alumina platelets/PMMA/Copper/Glass composites [9,10].

1.2 Natural materials: Nacre, bone and other natural structures (teeth, shrimp dactyl club)

1.2.1 Bone and nacre

Among the many natural materials, bone and nacre are perfect examples of damage tolerant structures, where many different levels of hierarchies are combined to generate strong and tough architectures. Bone is an extraordinarily complex structure that combines several strengthening and toughening mechanisms with unique functionalities: adaptability to local stress, self-healing ability, regeneration. Bone structure is organized in seven levels of hierarchy [11] (Fig.1) that influence its properties, e.g., deformation and toughness.

Bone structure

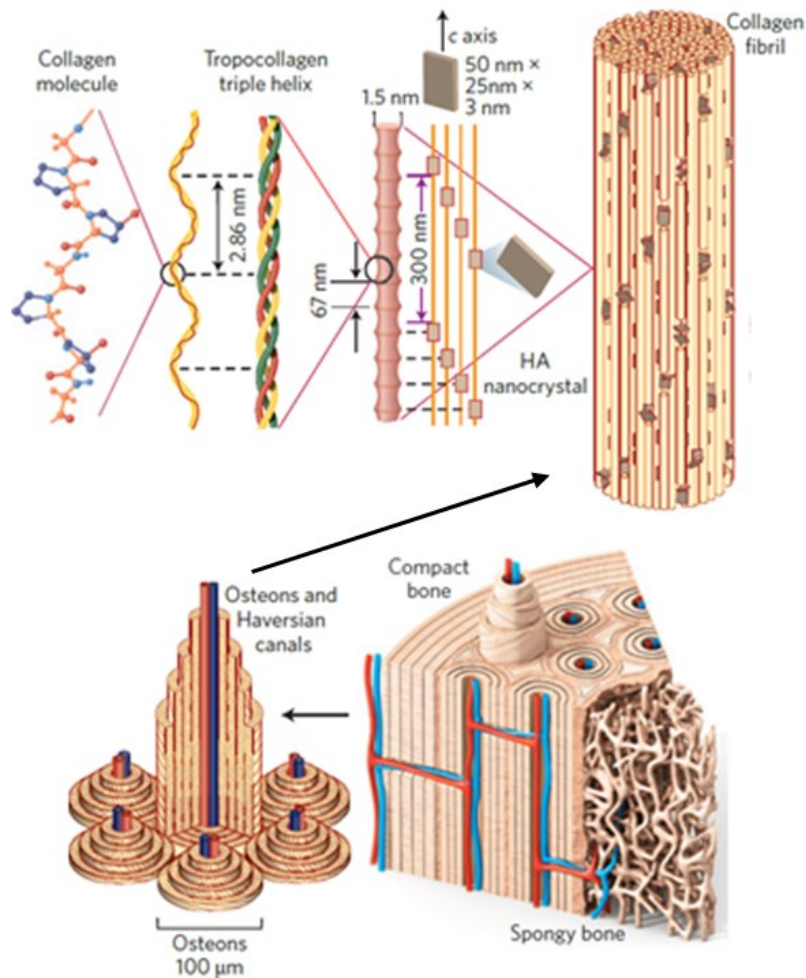


Fig. 1 Hierarchical structure of bone. Bone presents seven different levels of hierarchy from the nanoscale with the collagen fibrils to the microscale with the osteon. This specific organization provides the bone with solid mechanical response. Adapted from [3].

Macroscopically bone tissue can be divided in trabecular bone (spongy), that usually fills the interior part of the structure, and cortical (compact) bone that forms an outer protective hard layer [12]. Harvesian channel and osteons are found at micrometre scale($\sim 100\mu\text{m}$); at sub-micrometre levels the osteons have a lamellar structure where each lamella is formed with a periodic and staggered array of fibres ($\sim 10\mu\text{m}$); at nano-metre levels fibres are composed of mineralized collagen fibrils that are made of type-I collagen molecules and hydroxyapatite nanocrystals [3]. The basic building elements are therefore an organic matrix (collagen) and a mineral phase (hydroxyapatite). However, bone composition (mineral

contents) and structure change from bone to bone and are highly affected by different factors such as physiological function, age, sex and mechanical loading.

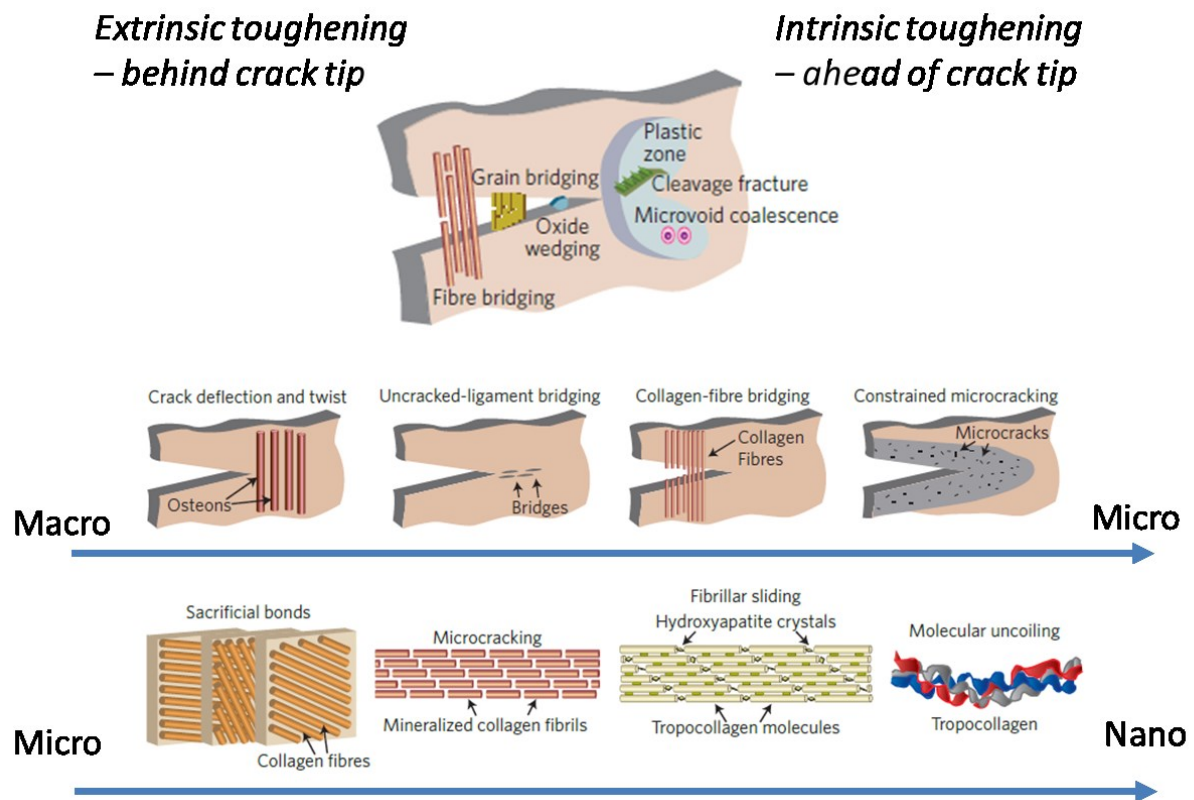


Fig. 2 Intrinsic and extrinsic mechanisms involved in the fracture resistance of bone. Many mechanisms are involved in the toughening of the bone from the macroscopically action of the osteons to the stretching of the collagen at lower scale. Adapted from [3].

The fracture resistance of cortical bone is a direct consequence of its complex and well organized hierarchical structure. Many different mechanisms of deformation and toughening can be identified at different length scales when load is applied (Fig.2). These can be divided in two main contributions: intrinsic mechanisms at the front of the crack tip that promote plastic deformation and tend to blunt the crack, and extrinsic mechanisms that are active behind the crack tip and operate to “shield” it from applied stresses [3]. Intrinsic and extrinsic toughening mechanisms are, however, coupled. Once the intrinsic mechanisms that usually take action at lower scale are saturated, bone starts to dissipate energy with the larger scale extrinsic mechanisms (10 to 100 μm). These latter ones give larger contribution to the fracture resistance of bone that shows increasing fracture toughness with crack propagation (R-curve)[13]. The main mechanism that dissipates

energy intrinsically is the process of fibrillar sliding. When load is applied tension stresses are applied on the mineral platelets and transferred between them during the shearing of the collagen fibrils. Crack deflection along the osteons is instead the most relevant extrinsic mechanism during crack propagation. Crack bridging by collagen fibres, uncracked ligaments and diffuse microcracking in front of the crack tip are the other important phenomena [14]. Bone shows anisotropy in terms of mechanical properties with fracture resistance that change from longitudinal to transversal direction. Fracture toughness values of K_{Ic} ranging from 2 to 8 MPa·m^{1/2} have been measured depending on the testing direction, with the higher values showed along the transverse direction [15–17]. Furthermore the mechanical properties of bone tend to change with the age and the risk to face a fracture increases significantly. One of the main causes is related to the decrease in bone mass that can induce a reduction of 40% of fracture toughness values in older bone [13].

Much simpler compared to the bone structure but still mechanically well performing is nacre (or mother of pearl). Nacre is composed of 95vol% of an inorganic brittle phase (calcium carbonate) and 5vol% of organic matrix [2]. Monolithic CaCO₃ has a work of fracture ≈3000 times lower in terms of energy than nacre [4]. Despite these weak structural compounds, nacre is strong, stiff, tough and impact resistant - mechanical properties that usually are considered mutually exclusive [18,19]. This outstanding mechanical response is related to the hierarchical microstructure of nacreous shells that generate several toughening mechanisms at different length scales (Fig.3). The inorganic phase is primarily composed of micrometer size polygonal mineral tablets of CaCO₃ carefully cemented in a lamellar structure. These aragonite (a crystallographic form of calcium carbonate) platelets with a thickness of 0.2-0.9µm [20] are alternated with very thin polymeric layers mainly composed of chitin and proteins (≈20nm), producing a structure known as “brick-mortar structure” [3]. Both materials, the calcium carbonate layers and the organic matrix, when considered separately, exhibit low mechanical properties, but the nacre’s strength and toughness are orders of magnitude higher [21]. This “brick-mortar” structure induces several toughening mechanisms such as: crack deflection at platelet/matrix interface, platelet pull-out, platelet sliding, viscoelastic dissipation of energy in the polymer layers that acts as an adhesive, platelets interlocking during sliding due to the nano-asperities on the platelets surface and energy dissipation by the breaking of pre-existing mineral bridges between different

platelets [1,3,5,22]. Some of these mechanisms act at the nanoscale whereas others at microscale and the simultaneous operation of both explain the outstanding mechanical properties of nacre.

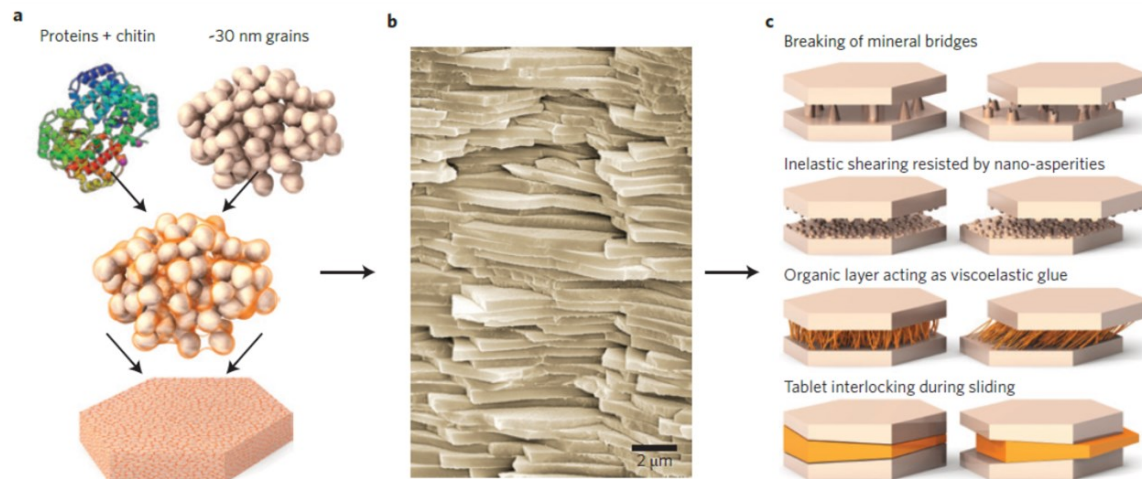


Fig. 3 Nacre structure and toughening mechanisms. a) Schematic representation of nacre structure composed of organic hexagonal-shape platelets covered by bio-polymer; b) real nacre microstructure; c) fracture mechanisms acting within the microstructures that confer to nacre high fracture toughness. Adapted from [3].

Many of these are extrinsic mechanisms that result in a rising R-curve. Several studies have been researching the main causes responsible for generating these different toughening mechanisms and different models have been proposed [4,23,24]. It is broadly accepted that bricks sliding is a crucial mechanisms in the high resistance to fracture of nacre [3]. Gao et al. [4] proposed a simplistic model where the mineral platelets were arranged in a polymeric matrix. In this model the mineral platelets sustain the tensile stress while the polymeric matrix transfers the load between the crystals via shear (Fig.4). In these load conditions, to ensure the integrity of the structure and optimize the mechanical performance, the platelets must be able to withstand large tensile test without fracture, whereas the polymer layers and the polymer/platelets interface must withstand shear stress without fracture.

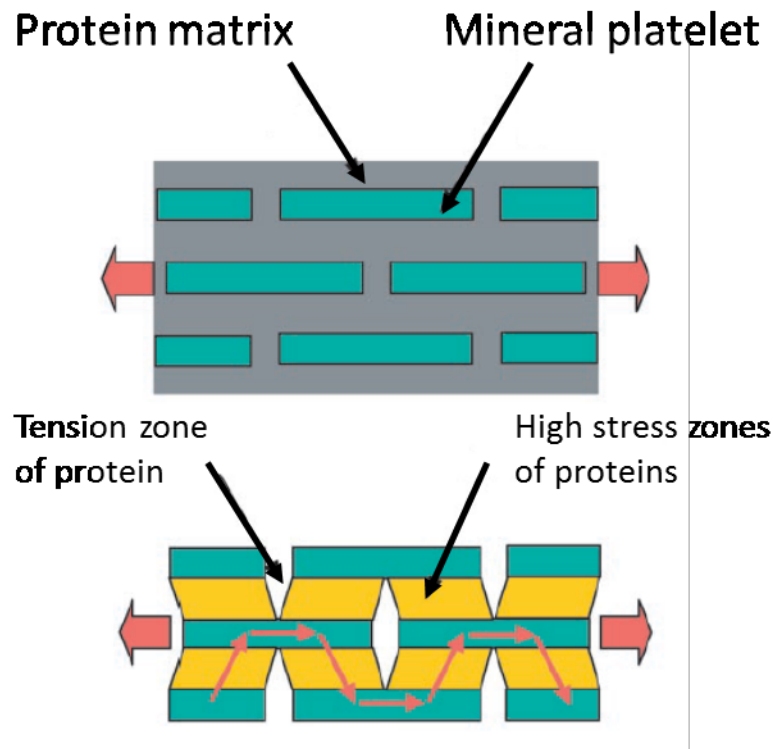


Fig. 4 Schematic representation of a bio-composite where the mineral crystals are surrounded by a protein matrix. The load is mostly carried from the mineral phases, the organic matrix help transferring load through the high shear zone between the mineral platelets. Adapted from [4].

The fracture toughness of the entire composite relies therefore on the tensile strength of mineral platelets. High mechanical strength is achieved with a nanometric grains structure and almost perfect defect-free platelets. Analyses conducted with AFM have in fact shown that each platelet is composed of nano-grains with an average size of 30-40nm [25] and that moreover they show ductile behaviour induced probably by an organic phase between each nano-grain [26,27]. These mechanisms acting at the nanoscale are necessary but not sufficient to explain the behaviour of nacre at macroscale. Other scientists attribute the high fracture toughness of nacre to the development of periodic dilatation bands as proposed by Evans et al. [23] and dovetail-like locking features at the end of each platelet that during crack propagation get interlocked, as proposed first by Espinoza et al. [24] (Fig.5). This waviness of the bricks generates progressive locking, hardening and spreading of non-linear deformation around cracks and defects. The same results have been proved by Espinosa et al. [28] testing nacre to fracture using an atomic force microscope coupled with digital image correlation. Moreover, the tablet surfaces have protuberances of 30~100nm in diameter and ~10nm in amplitude. When one asperity of one side remains blocked in a

valley formed by other two asperities on the other side, a lock is formed and energy is dissipated [29].

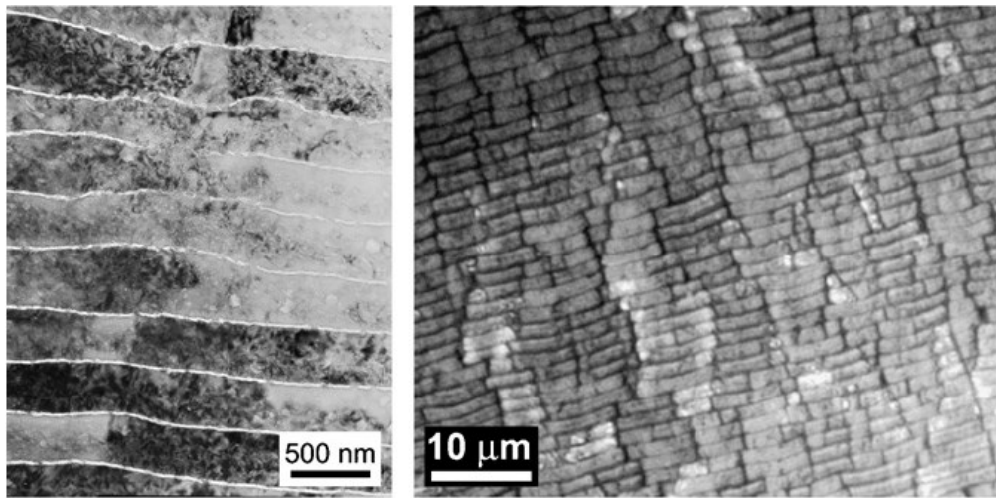


Fig. 5 Dovetail-like features characteristic of nacre bricks. TEM and optical pictures showing the waviness characteristic of the mineral platelets forming the nacre architecture and their dove-like tails, that generate efficient interlocking constrain. Adapted from [30].

Inelasticity, i.e. the ability to undergo to a significant inelastic deformation in tension, a key property to eliminate stress concentration at strain concentration sites, such as pores, flaws, imperfections etc., it is one of the significant mechanical properties showed form both bone and nacre, providing them with a low defect sensitivity [30]. More recently L.Li et al. [31] testing under nanoindentation a specific type of shell known as *Placuna placenta*, showed that the shell in the proximity of the penetration zone undergoes extensive nanoscale deformation by twinning followed by a series of additional inelastic energy dissipation mechanisms such as interfacial and intercrystalline nanocracking, viscoplastic stretching of interfacial organic material and nanograin formation and reorientation.

According to these studies it is possible to understand how multiple and complex are the fracture mechanisms that characterize the mechanical behaviour of nacre. These mechanisms are still under study in order to get a better understanding of the interaction between the different levels of structural organization to enable excellent macroscopic mechanical properties. Summarizing, nacre and bone structures show similar structural design and therefore comparable fracture mechanisms. They are characterized by composite structures with an alternation of inorganic/organic phases; the inorganic phase is

with form of mineral platelets with high aspect ratio and the organic phase is a bio-polymer [32]. They are both stronger in compression than in tension exhibiting an important amount of inelastic strain. Hysteresis can be observed in loading-unloading tests indicating permanent deformation [32]. This mechanical behaviour reducing the stress concentration at crack tips makes bone and nacre materials notch insensitive. This turns in the material's development of specific resistance curve (R-curve) behaviour observed when cracks slowly grow within their microstructures. For instance, nacre exhibits low crack initiation toughness ($\sim 2 \text{MPa}\cdot\text{m}^{1/2}$) that increases during subsequent crack growth ($\sim 8\text{-}10 \text{MPa}\cdot\text{m}^{1/2}$ at a crack size of 0.6mm) [33].

In the last decades extensive effort has been made in order to produce artificial materials with lower notch sensitivity - clear examples are fiber reinforced ceramic composites, transformation-toughened zirconia, ceramic laminates etc. Bone and nacre structures can be a key source of inspiration for engineering materials with advanced mechanical performance.

1.2.2 Other natural materials (From teeth to shrimp dactyl club)

There are many other examples of natural materials that thanks to millions of years of evolution have developed specific configurations to optimize their structural and functional properties. Teeth for instance are complex multi-layered structures that have played a critical role in the evolution of human beings and other species. They are attached in the jaw with a thin cementum interlayer and are mainly composed of three parts: the enamel and the dentin joined together with a complex interface called dentin-enamel junction (DEJ) and the underlying pulp [3]. The pulp does not have any mechanical function but it is filled with soft connective tissue containing blood vessels and nerves. The enamel is the outer part that carries out the function of mastication. It is the hardest tissue in human body with a mineral content of 96wt%. It provides to the tooth with wear and erosion resistance and it can withstand strong bite forces reaching 1kN [3] during millions of cycles. It is mainly composed of defective carbonate rich apatite prisms of 4-5 μm in diameter orientated perpendicular to the DEJ bounded together by proteins and peptides in a hierarchical structure. Enamel however is extremely brittle with initial fracture toughness values ranging from 0.44 to 0.91 $\text{MPa}\cdot\text{m}^{1/2}$ [34], though recent studies have shown that different

toughening mechanisms occur even in the enamel structure developing R-curve behaviour, with final values of fracture toughness that rise to $4\text{--}4.5\text{MPa}\cdot\text{m}^{1/2}$ after $300\text{--}500\mu\text{m}$ crack propagation [35]. Dentin contrarily has different structure and properties compared to enamel. The mineral content of the dentin is 70wt% and its structure is composed by a twisted matrix of mineralized collagen fibrils. At lower scale it is formed by tubules of $\sim 1\mu\text{m}$ diameter that run from the DEJ to the soft, interior pulp [36]. These cylindrical tubules are surrounded by thin mineral apex that, under load, produces microscopic cracks that induce effective extrinsic mechanism of toughening in the structure. These cracks moreover are many times deviated along the tubule lines. All these mechanisms along with the bridging of the intact area between the microcracks provide the dentin with tough load-bearing behaviour. Extremely interesting is the interface between these two different tissues, the dentin-enamel junction. This layer has a unique crack-arrest behaviour that creates an efficient barrier for cracks generated in the above enamel to propagate into the dentin. The DEJ is a transition area that can be considered as a mixture of enamel and dentin structure, where the side closer to the enamel has higher mineral content and the side closer to dentin higher collagen content. The DEJ has a three-level structure, $25\text{--}100\mu\text{m}$ scallops with their convexities directed toward the dentin and concavities toward the enamel; $2\text{--}5\mu\text{m}$ microscallop and even smaller scale structure [37]. The hardness of the enamel coupled with the toughness of the dentin and the crack arrest feature of the DEJ make teeth an extremely strong and crack resistant structure.

Nature offers many other efficient strategies to produce complex and highly structured architectures. Other examples apart from those already described above are the structure of bird feathers [38] where different levels of organization and alignment can be found in this porous structure with the intent of reducing the density meanwhile maintaining a structural and load support; the porous structure of toucan and hornbill beaks [39]; the hierarchical lamellar structure with different mineral content of the *Arapaimas* scales that provide them with an armor protection from piranha attacks [31]; the hierarchical helix structure of the *stomatopod dactyl club* that is considered to have higher specific strength and toughness than those of any synthetic composite materials [3]. In specific of this last example, the *stomatopods* use this external protuberance as a hammer to break the shells of its prey. These structures are capable of accelerations of 10.400g and of applied force

>700N [40]. Despite these large loads, the dactyl clubs are extremely damage tolerant. This ability is achieved through a multiphase variable composite structure with oriented crystalline hydroxyapatite and amorphous calcium phosphate and carbonate interlayered within a chitosan matrix.

1.3 Bio-inspired materials: nacre-like structure

Mimicking the macro, micro and nano design solutions that Nature uses in biological materials can lead to the production of high performance synthetic materials. As most of the biological materials show higher mechanical properties than those of their basic constituents, the use of advanced synthetic materials such as alumina, zirconia, silicon carbide etc. in bio-inspired hierarchical architectures could be a way to generate new classes of composite materials with unique mechanical responses. Even though the processing routes available nowadays are still far from faithfully replicating the complex biological mechanisms found in nature, in the last decades many examples of bio-inspired strong, stiff and tough ceramic based composites have been developed using different bio-mimicking techniques in order to produce porous scaffolds or bulk composites.

1.3.1 Nacre-like structures

Until now nacre is the only natural structure which has been possible to emulate over different length scales combining different processing techniques and is considered the “gold standard” of bio-mimicking. One of the first examples of nacre-like structure is found in the work of Clegg et al. [41], where SiC sheets coated with weak graphite interfaces were sintered together under pressure. The final composite showed an apparent fracture toughness of $15\text{MPa}\cdot\text{m}^{1/2}$. Laminated ceramic composites of $\text{Si}_3\text{N}_4/\text{BN}$, produced using extrusion and roll compaction followed by hot press sintering, showed similar behaviour with apparent fracture toughness of $24\text{-}28\text{MPa}\cdot\text{m}^{1/2}$ [42,43]. However, these structures show structural components much larger than those found in natural structures. Freeze casting, layer-by-layer deposition, solution casting, self-assembly, thin-film or tape deposition are the most modern techniques used to produce nacre-inspired structures. However, some of them only allow the production of small samples requiring long fabrication times that are not feasible for practical structural applications. One of the most

promising approaches in producing nacre-like structures is the infiltration of a ceramic scaffold produced by freeze casting with a polymeric or metallic phase [22]. Freeze casting has been used to produce $\text{Al}_2\text{O}_3/\text{PMMA}$ and $\text{Al}_2\text{O}_3/\text{Al-Si}$ composites with remarkable strength and toughness [6,7]. In both cases a rising R-curve behaviour has been observed with final values of K_{Jc} (the fracture toughness obtained with a J-integral approach) of $\sim 15 \text{ MPa}\cdot\text{m}^{1/2}$ and $\sim 40 \text{ MPa}\cdot\text{m}^{1/2}$ for the polymer-based and metal-based composites with lamellar structure respectively. Starting from the same freeze cast lamellar composite $\text{Al}_2\text{O}_3/\text{PMMA}$, hot pressing the lamellae in the direction perpendicular to the freezing direction produces a “brick and mortar” structure akin to the nacre one with a final value of K_{Jc} of $\sim 30 \text{ MPa}\cdot\text{m}^{1/2}$. More recently with a similar approach freeze casting followed by a pressure assisted sintering in SPS (spark plasma sintering) has been used to produce a 100% ceramic material of Al_2O_3 platelets and a glassy phase composed of CaO and SiO_2 [9]. This composite exhibited a combination of high toughness ($6.1 \text{ MPa}\cdot\text{m}^{1/2}$) and high strength (470MPa) and was able to maintain these properties at elevated temperature. Al_2O_3 platelets have also been used by Studart and his group with the intent to produce nacre-like ceramic-polymer composites [44,45]. They showed that by coating the platelets with super-paramagnetic nanoparticles they produce synthetic composites with tunable properties (wear resistance, shape memory effects, local reinforcement) aligning the platelets in different orientations using a low magnetic field.

Launey et al. [6,7] have developed freeze cast Al_2O_3 infiltrated with a polymeric or a metallic phase using in-situ analysis to identify the activation of several toughening mechanisms operating at different length scales. The main toughening mechanisms observed were: uncracked-ligament bridging behind the crack tip, delamination, microcracking, crack deflection, void growth, plastic deformation of the second soft phase and spread of micro-damage within the whole structure. Moreover in the “brick and mortar” structure produced by the hot pressing of $\text{Al}_2\text{O}_3/\text{PMMA}$ composites, they have observed mechanisms acting at smaller scales such as brick sliding and interlocking due to the nano-roughness characteristic of freeze cast lamellae, as well as the lubricating action of the polymeric phase [7]. In the “brick and mortar” composites the polymeric layers do not exert a load-bearing function but act only as a stress-relieving lubricant. Therefore this specific ceramic/polymer arrangement provides the ideal combination of strength and toughness showing real advantages of the

biomimetic approach. Following the same design idea of closely recreating the nacre “brick and mortar” structure, Bouville et al. [9] employed small and strong alumina platelets, aligned through freeze casting and fully densified with thin glassy interfaces by spark plasma sintering. With this approach they were able to produce ceramic/ceramic composites with a unique combination of strength, toughness and stiffness. They identified crack deflection, multiple cracking, crack bridging, crack branching and frictional sliding as the main toughening mechanisms occurring within their composites. A similar platelet arrangement has been achieved by Le Ferrand et al. [46] using the MASC (magnetically assisted slip casting) process. In this study they produced ceramic/ceramic, ceramic/polymer and ceramic/metal composites demonstrating the versatility of the technique.

Launey et al. [7] have pointed out the need to have strong interfaces between the two phases within their “brick and mortar” structures as a key factor to achieve better mechanical performance. Bouville et al. [9] in their ceramic/ceramic composites have identified the topological arrangement and stiffness ratio between the two brittle phases as crucial parameters to reduce stress concentration around the crack tip. Similar toughening mechanisms were identified in the work of Le Ferrand et al. [46]. The strength and fracture toughness of these ceramic/ceramic composites were higher even though they were made of the same constituents. This result underlines the significance of brick alignment within the microstructure as alignment is probably superior with the MASC process. In a different study other researchers from the Studart group used the alumina platelets in a colloidal bottom-up process to produce hybrid films that combined high tensile strength and ductile behaviour [47]. Alumina platelets have been also combined with hot-press assisted slip casting to use them as aligned basic building blocks for hierarchical structures in epoxy-based composites [48,49]. All these studies have shown that to better mimic the mechanical features of nacre it is necessary to have a strong interface between the ceramic and the soft/ductile reinforcing phase (but still weaker than the ceramic itself to favor crack propagation along it) and good alignment of the bricks in the loading direction. While distinct from the previous studies, but with the same intent of replicating design motifs found in natural materials, Mirkhalaf et al. [50] produced laser engraved glasses with improved fracture resistance. The principle behind this study was to generate micro-cracks within a glass matrix which could deflect and guide the main propagating crack and

furthermore promote interlocking and pullout toughening mechanisms. However, this type of approach can only be practically applied to glasses. Among all the methodologies explored, freeze casting and pressure-assisted slip casting are the most promising techniques to replicate nacre features at different length scales (nano-asperities, bridges, ceramic alignment etc.) in ceramic-based materials.

Bio-inspiration has proven the possibility of producing nacre-like materials with unique mechanical properties, however the appropriate assessment methods to measure their mechanical properties are still a matter of discussion. Launey et al. [6,7] used an in-situ SEM observation of the crack length and a J-integral approach to estimate the toughening mechanisms for the $\text{Al}_2\text{O}_3/\text{PMMA}$ composites, whereas they employed an indirect compliance method for the crack length evaluation in the $\text{Al}_2\text{O}_3/\text{Al-Si}$ composites utilizing a theoretical equation obtained from finite element analysis. The compliance approach has also been employed in the works of Bouville and Le Ferrand [9,46] where the crack length has been evaluated with an iterative analysis based on the compliance values obtained during testing. In all these studies the tests were done on SENB specimens under 3PB conditions which could lead to an overestimation of the final values. Moreover the crack tip certainly experienced a load different from the recorded load as crack deflection is one of the more active mechanisms occurring within this type of composite. In contrast to this, other studies such as the ones of Clegg [41] and Mirkhalaf et al. [50] quantified toughening by evaluating the work of fracture as the area below the stress-strain curves.

1.3.2 Freeze casting

Ice templating or freeze casting is nowadays a popular technique to shape macroporous materials [51]. It allows the production of highly anisotropic porous ceramics through the controlled solidification of a solvent (generally water) in a dispersed slurry. The ice crystals tend to grow in a preferential direction if a directional gradient temperature is applied within the slurry. During their growth, they eject the ceramic particles from the ice front effectively templating the porosity. Once the suspension is completely frozen the ice crystals are sublimated by a freeze drying process and the resulting green body is an exact replica of

the ice structure. This structure is often sintered to consolidate the particles within the lamellae and provide strength to the porous scaffold.

Freeze casting, along with the production of anisotropic porous scaffolds, is often associated with the idea of biomimic nacre-like architectures and it has been extensively studied with this purpose in the last decades. Although it came back in vogue recently, the first observation of cellular structures formed by freeze-gelation dates back to 1908 when Lottermoser [52] published a work on the freezing of hydrosols. Freeze gelation is a similar process to freeze casting, but it relies on the use of silica solution in which the component powders are dispersed. After this first use, at the beginning of the 20th century freeze casting has been employed to produce dense parts. In the 1954 Maxwell et al. [53] used the freeze route to fabricate turbosupercharge blades from refractory powders. They cast high-solid-content titanium carbide slurries in complex molds and froze them to better retain the shape. In this case freezing route was employed to produce dense complex-shaped components. The use of freeze casting to produce porous materials began from the '80s. Mahler [54] produced in 1980 silica fibres by phase separation during freezing aqueous polysilicic acid. In 1985 Tong [55] studied the mechanisms of lamellar ice crystals growth in frozen agar gels and specifically the influence of freezing rate on the crystal structure and final porosity. However only in 2001, with the work of Fukasawa et al. [56], the idea of using freeze casting to fabricate novel porous ceramic structures from a water-based ceramic slurry was formulated and since then, being freeze casting a physical process and therefore applicable to a wide range of materials, 100s of papers have been published in this field. More recently with the work of Deville et al. [57] freeze casting has been used to produce nacre-inspired ceramic based composites with superior mechanical properties.

The increasing demand of synthetic materials with high mechanical properties that can withstand hostile working conditions led, in the last decades, to the development of new ideas of design and forming processes. Freeze casting is a result of these needs.

Having established the excellent mechanical properties of nacre derived from its particular hierarchical structure, the freeze casting technique has been developed to mimic its lamellar structure and to produce therefore porous ceramic materials with higher mechanical properties. Freeze casting of water-based ceramic slurries (ice-templating) uses the

directional solidification of the solvent to produce the skeleton for a nacre-like lamellar structure. The physical process that is at the base of freeze casting can be divided in four fundamental steps as reported in Fig.6. The first important step (a) is the production of a homogeneous ceramic suspension. The ceramic suspension in step (b) is subsequently frozen in a controlled manner. The controlled freezing of the solution produces the growth of lamellar ice crystals inside the solution - see below - that interact with the ceramic particles forcing them to form the layered structure. The final porosity in the scaffold is a replica of the original ice structure [58]. The third step (c) is the sublimation of the ice produced during the freezing, and the last step (d) is the sintering of the green body that leads to the final product. Other steps are needed to create a scaffold that may replicate nacre's microstructure, but the main steps are well summarized in Fig.6:

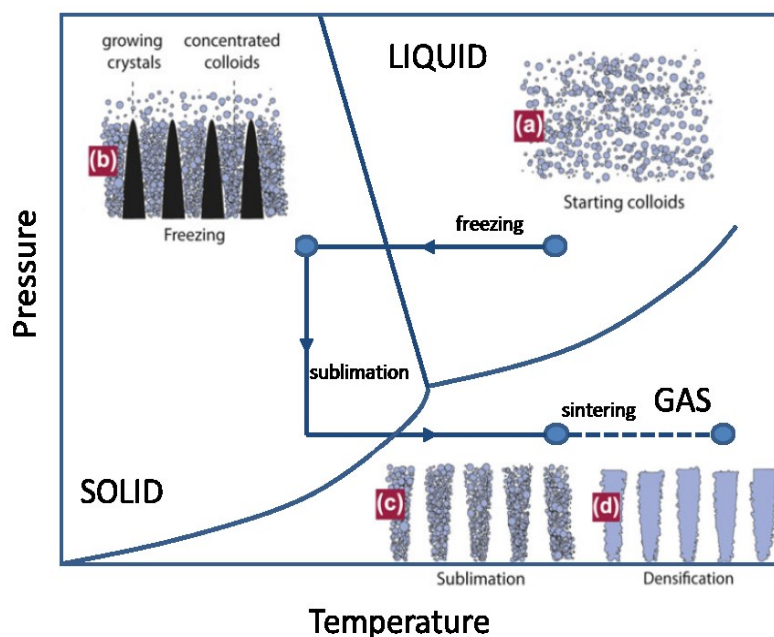


Fig. 6 Fundamental steps necessary to obtain a freeze casted ceramic scaffold. a) Stable ceramic slurry; b) Freezing of the suspension; c) sublimation of the ice crystals, a green body is obtained; d) densification of the green through a firing process. Adapted from[59].

The ceramic powders have to be homogeneously dispersed in the solvent, usually water but it can be different, (camphene-based, tert-butyl alcohol) [59]. Dispersants and plasticizers are frequently used. The stability of the solution is an important parameter to be controlled to avoid sedimentation during the freezing. However, sedimentation could be intentionally

generated to create samples with graded porosity. Particle sedimentation depends on the particle's density and size and the solvent's density and viscosity [60]. It is possible to evaluate the sedimentation speed taking into account the balance of forces acting on an ideal spherical particle of radius r and mass m immersed in a fluid of density ρ_L . Two forces will act on the particle, the gravitational acceleration and an opposing force given by Archimedes' principle. The consequential force on the sphere is:

$$F = (m - \rho_L V)g = (\rho_P - \rho_L)g \frac{4}{3}\pi r^3 \quad (1.1)$$

where V and r are the sphere volume and radius respectively, ρ_P the particle density and g the gravitational constant. According to the Stokes's law [61], a friction force acting in the opposite direction of the sphere motion, it has to be considered when the density of the sphere is higher or lower than the liquid density. This resisting force depends on the radius and velocity v_P of the particles, and on the dynamic viscosity η of the liquid:

$$F_f = 6\pi r \eta v_P \quad (1.2)$$

Combining equations 1.1 and 1.2 it is possible to calculate the particle's terminal velocity:

$$v_P = \frac{2(\rho_P - \rho_L)g}{9} \frac{r^2}{\eta} \quad (1.3)$$

Stroke's law takes in consideration only laminar flow. The transition from laminar to turbulent occurs at a critical velocity given by the following relationship:

$$v_{trans} = \frac{Re\eta}{2\rho_L r} \quad (1.4)$$

Considering a Reynolds number $Re=0.2$ (laminar flow) and combining equations 1.3 and 1.4, it is possible to calculate the maximum radius as:

$$r_{max} = \left(\frac{0.45\eta^2}{(\rho_P - \rho_L)\rho_L g} \right)^{1/3} \quad (1.5)$$

Being the particles used in freeze casting usually really small in diameter (from 100nm to 2 μ m) they are always subject to a laminar flow with sedimentation velocities ranging from 26nm s^{-1} to 11 μ m s^{-1} [62]. The colloidal particles - as explained below - move when the solvent is frozen, therefore the interaction between particles become a crucial factor for the

forming process and the final microstructure. At the same time, if a polar solvent is used (e.g. water), the immersed particles are likely to charge superficially depending upon their nature and surrounding medium. Different models have been developed to better describe the electrical double layer (EDL) generated by the interaction of the particle surface and the polar solvent. The simultaneous effects generated by the use of dispersants and the electrical double layer result in an electrosteric stabilization [61]. Dispersants are usually employed to reduce particle aggregation and flocculation. Both phenomena have to be avoided to not produce heterogeneities within the final product. The dispersants used in freeze casting are those normally used in ceramic processing. They are ionic polymers that, once added in the solution, are absorbed on the surface of the particles. These polymeric chains extend from the particles surface into the water promoting a steric stabilization of the solution [63]. As reported in different studies [64,65] the dispersant concentration can drastically affect the rheological behaviour of a ceramic suspension, and therefore has to be well determined. Binders are also usually added in the slurry to give to the green body enough strength to be handled after freeze-drying before the sintering process. They are also added to prevent defects and crack formation during drying.

As already mentioned, freeze casting is a material shaping technique based on the directional freezing of a colloidal suspension obtained by the use of a temperature gradient. During the freezing of the liquid media, if the right conditions are satisfied, the particles in the slurry are ejected from the ice crystals that are growing and they are compacted in the gap formed by two adjacent crystals in a dense lamella [58]. The final pores of the sintered material are a replica of the original ice crystals (Fig.7).

A simple model can be used to describe the necessary conditions of rejection of ceramic particles from the solidification front, using the variation of surface energy $\Delta\sigma$ associated with the process [61]:

$$\Delta\sigma = \sigma_{sp} - (\sigma_{lp} + \sigma_{sl}) > 0 \quad (1.6)$$

where σ_{sp} , σ_{lp} and σ_{sl} are respectively the interfacial free energies of solid-particle, liquid-particle and solid-liquid.

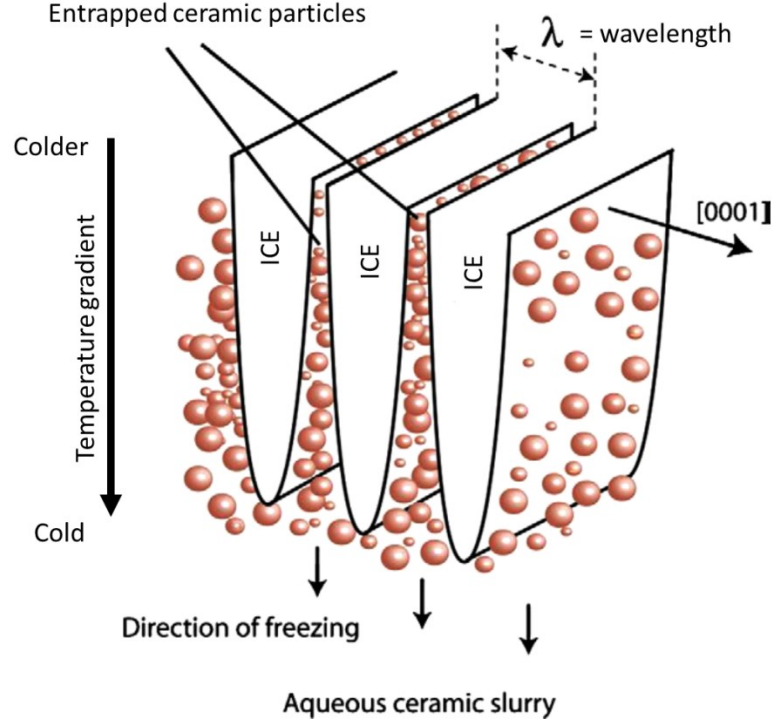


Fig. 7 Particle rejection from the freezing front. During the growth of the ice crystals in the direction of the freezing process, the ceramic particles are ejected from the freezing front and compacted in adjacent lamellae. Adapted from [58].

When this criterion is satisfied the ceramic particles can be rejected [61]. However this is a necessary but not sufficient condition. If the ice front moves too fast particles could still be trapped. It is possible therefore to define a critical velocity, v_c , when $v > v_c$ the particles are entrapped. This critical velocity can be evaluated with the following equation [66]:

$$v_c = \frac{\rho_l}{9\eta\rho_s} \left[-\frac{A}{2\pi D d_o} - g D d_o (\rho_p - \rho_L) \right] \quad (1.7)$$

where D is the particle diameter, A is the Hamaker constant of the aqueous system, η is the viscosity of the liquid phase, d_o is the minimum distance between the particle and the freezing front, ρ_p is the particle density, ρ_s and ρ_l are the densities of the solid and liquid phases, and g is the gravitational constant.

During the freezing of a colloidal suspension, different behaviours of the media are encountered. At the beginning of the process, the freezing front is planar, afterward, due to a thermodynamic instability experienced by the solid-liquid interface generated by temperature fluctuations, solute concentration gradient or the presence of insoluble

particles, the solidification front evolves from planar to columnar and from columnar to lamellar [58](Fig.8).

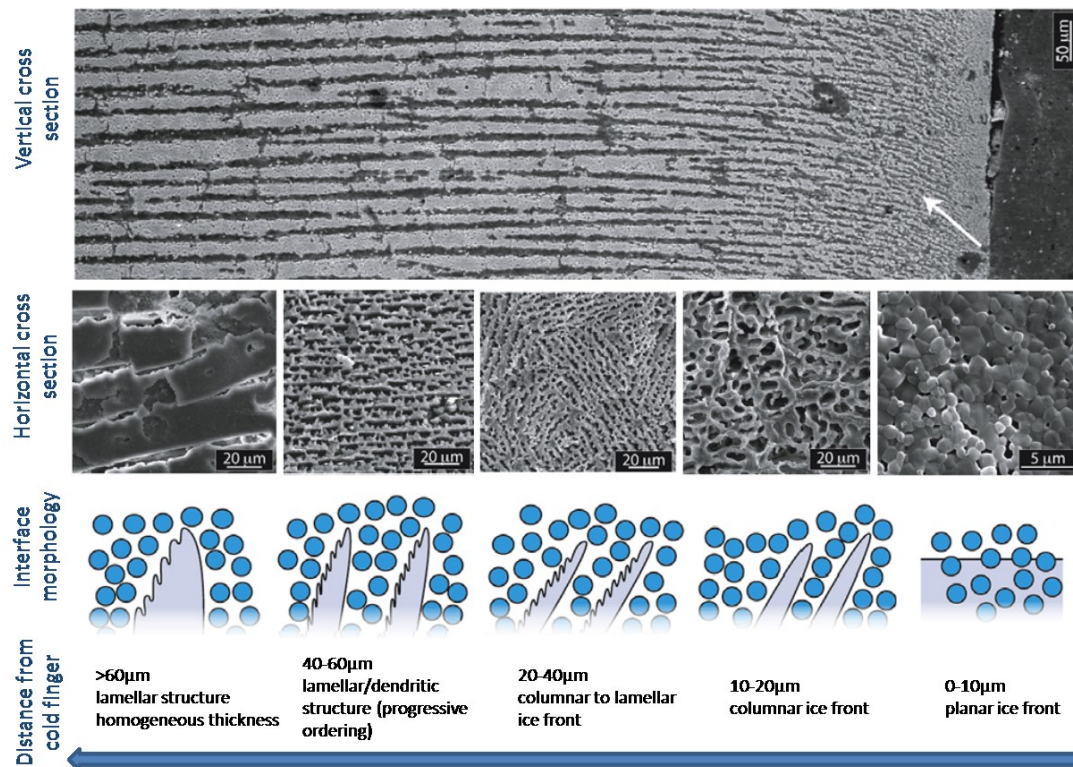


Fig. 8 Microstructure evolution during freeze casting. The ice front morphology changes as the distance from the cold finger increases. Different transition regions can be individuated within a freeze casted scaffold, from the dense bottom part to the cellular and finally to lamellar one. Adapted from [58].

A deep analysis of the initial stage of the solidification process of a colloidal suspension has been conducted by Deville et al. [67]. The first models used to explain the processes occurring during freeze casting came from postmortem observation on sintered scaffolds. Deville et al. freeze cast an alumina suspension in-situ by X-ray tomography analysis that could give them a dynamic observation of the solidification process at different stages [68]. Different morphological regions were observed in the freeze cast sample. In the first zone, nucleation of ice crystals with random crystallographic orientation occurs at extremely high speed of the freezing front ($>750 \mu\text{m/s}$). At this ice crystal formation speed most of the particles get entrapped in the ice front. As the freezing front slows down (crystal growth slows down dramatically in the first 4s reaching an almost steady state of $50 \mu\text{m/s}$) two different populations of ice crystals were observed. A first population of lamellar crystals with their main axis (a and b) oriented along z with the freezing direction (z -crystals), and a

second population with a more random distribution lying approximately in the xy plane (r-crystals). These ice crystals have the same crystallography but the planes along which the growth of the crystals are energetically favored (a and b -axis), are oriented in different direction to the temperature gradient. At this stage particles start to be rejected from the solid-liquid interface. All crystals with the a and b -axis perpendicular to the z -direction rapidly align to the temperature gradient direction, being the favorable direction of growth. As the crystals grow, the particle packing between crystals becomes more and more effective, reducing the number of particles entrapped. At a certain distance from the cold surface the r-crystals stop growing, leaving only the z-crystal to grow within the liquid phase. When the ice crystals reach the stage where the interface velocity moves at steady-state (around $39\mu\text{m/s}$)[68] particles are ejected from the moving solidification front and lamellar shape crystals are produced. Features characteristic of dendritic growth can be observed on the lateral side of the lamellae, such as tip splitting and side branch instability. Such side branch instability however do not have enough time to grow because by the time they form the solidification front moves further along the z -axis changing the concentration of the particles. They usually terminate after a few microns or they can reach the next adjacent crystal producing a bridge between lamellae. In the first freeze casting set up, as that one employed in this study, the lamellar crystals tend to organize in domains (Fig.9) with similar orientation that can be generated due to the original disordered nucleation conditions.

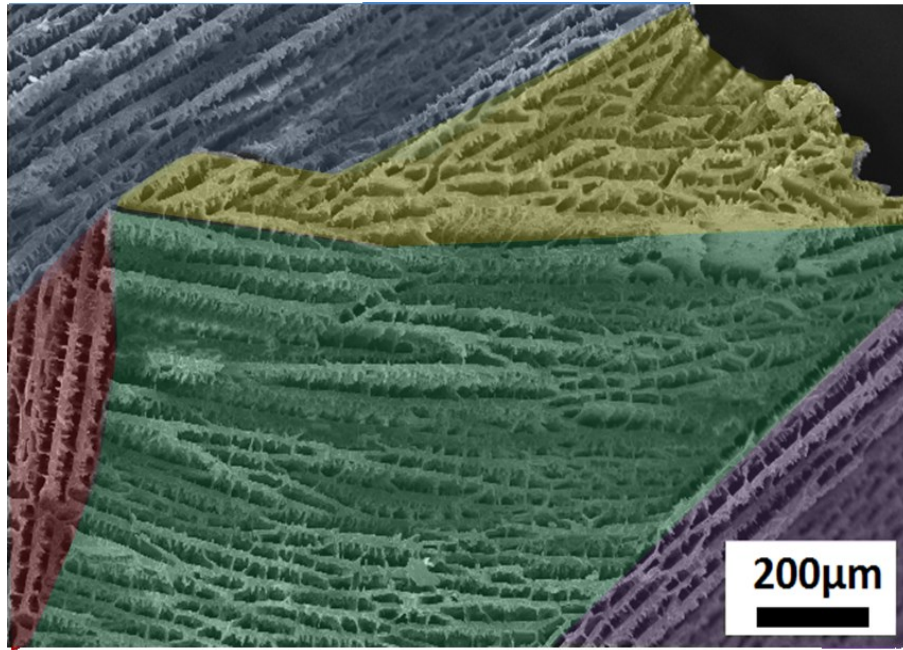


Fig. 9 Domains formation in freeze cast scaffolds. Different ice crystal population generates lamellae with different orientation creating domains within the final scaffold.

Recently new freeze casting set up and conditions have been developed to control the nucleation stage and therefore the whole lamellar alignment. These studies revealed that the imposition of a double gradient of temperature can drastically influence the ice crystal orientation and determine a better alignment throughout the whole sample. Bouville et al. [10] developed a new freeze casting set up called “freeze casting under flow”, but recently Bai et al. [69] showed that sampling using a PDMS wedge in normal freeze casting set up could generate a dual temperature gradient and therefore a better alignment. In this study the alignment of ice-templated walls has been achieved using a simple pattern ice nucleation surface as described in previous works [70].

Many other different parameters can affect the final microstructure and they may be used to control it: the cooling rate, particle size and concentration, the use or not of a templated surface on the cold finger during freezing. Fig. 10 summarizes the correlations that have been found between the slurry concentration and the final porosity and Fig. 11 between the ice front velocity and the wavelength (lamella plus pore) thickness. Increasing the solid loading of the freeze casted slurry the final porosity of the scaffold decreases; moreover when faster freezing conditions are imposed at the cold finger a reduction in the lamellae thickness can be appreciated.

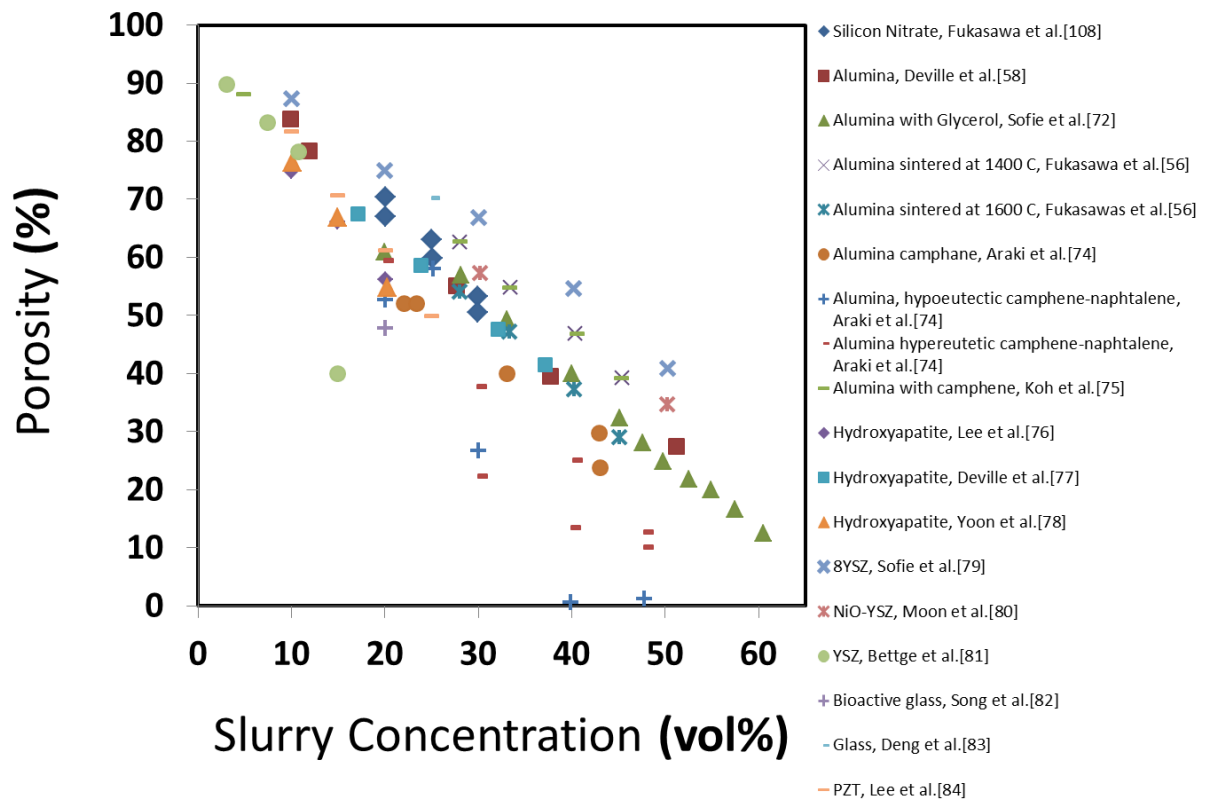


Fig. 10 Total porosity vs slurry solid loading. From the graph it is possible to appreciate that increasing the slurries concentration the final porosity of the freeze casted scaffolds tends to decrease. The values showed in the graph are taken from the following references [56,58,71–84]. Adapted from [85].

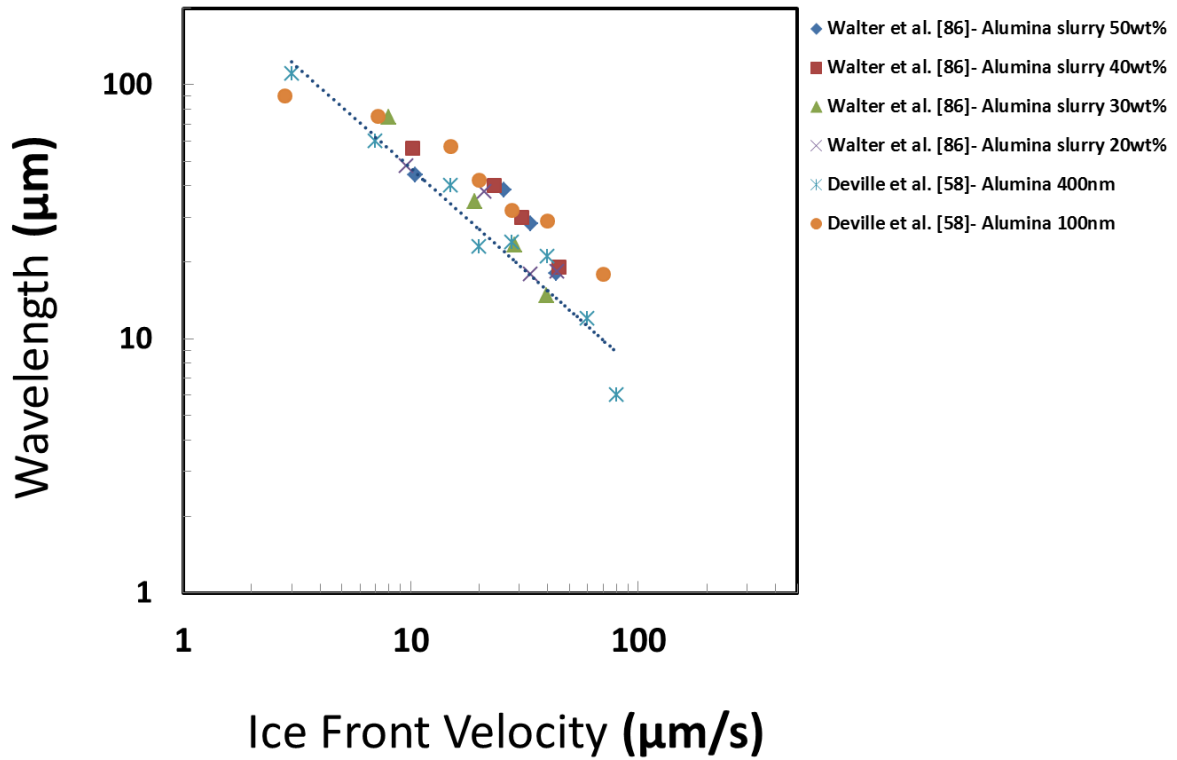


Fig. 11 Wavelength vs ice front velocity. The wavelength λ is considered as the sum of the thickness of a lamella and the following pore space. Increasing the freezing rate the wavelength decreases. The values are obtained from the following references [58,86]. The data can be plotted with a power law with exponent of -0.8.

Another strategy widely used to have a certain control in the final microstructure is the use of specific additives. Additives in fact, can be added to the slurry to change the morphology of the microstructure obtained during the freezing. By using different types and concentrations of additives, it is possible to change some features of the final structure such as thickness and roughness of the ceramic walls, and the presence of ceramic bridges between lamellae [70](Fig.12).

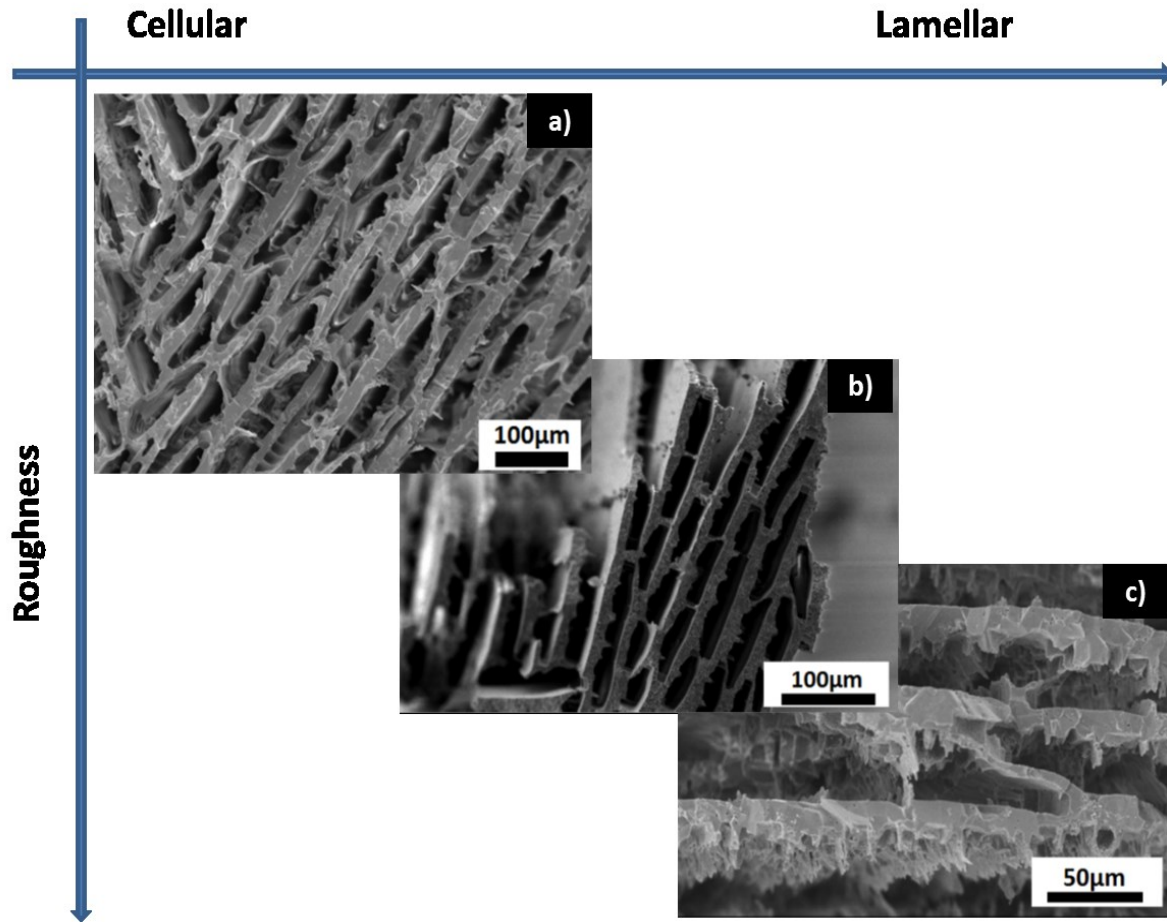


Fig. 12 Effects of additives on freeze casted microstructure. The microstructure, changing the additives, it can go from a cellular structure to a more lamellar structure with different degrees of roughness. a) 2 wt% of Ethanol; b) 4wt% Sucrose; c) 0wt% of additives.

A frozen lamellar composite of ceramic particles and ice is obtained after freeze casting. To eliminate the solvent, the scaffold is kept under low temperature and low pressure conditions. These sublimation conditions allow the ice to be converted from the solid state to the gas state. After the sublimation of the ice, a ceramic scaffold with a lamellar structure is obtained, where the porous spaces are a replica of the solid solvent. For different solvents different sublimation conditions are needed. The green body obtained retains its shape due to the action of the binder that holds the ceramic particles together.

In order to obtain a strong freeze cast ceramic scaffold a sintering step is required. The freeze-dried green body can be sintered with different pressureless assisted sintering techniques, due to its low mechanical properties. Whatever is the sintering process chosen, a binder burnout step has to be taken into account to eliminate the binder, the dispersant

and any additives used during the freezing and to avoid possible crack formation or inhomogeneous shrinkage. During the sintering process, thanks to different matter transport mechanisms, densification is achieved during which the microporosity between the ceramic micro-particles in the walls is eliminated, while the lamellar macroporosity is conserved.

Therefore freeze casting has been used to produce porous cellular ceramic scaffolds with aligned porosity employed as preforms for assembling nacre-like composite materials.

1.3.3 Porous ceramic scaffold by freeze casting

Porous ceramic materials with their combination of lightweight and advanced properties (high temperature resistance, gas and liquid permeability, chemical and corrosion resistance etc.) find application in many different fields such as filters, insulators [87], catalytic support [88], bio-scaffolds [89] or simply as preforms for ceramic/metal [6,90], ceramic/polymer [7,91,92], ceramic/ceramic composites [93,94]. Typical processing routes for the fabrication of porous ceramic bodies are the replica method, sacrificial template, gel casting and direct foaming; more modern techniques include rapid prototyping or additive manufacturing [95]. Freeze casting can be considered a sacrificial template technique. As a matter of fact freeze casting is often referred to as ice-templating. It can be used for any kind of materials, from ceramic to metal particles or polymer, as long as it is possible to disperse them in a solvent and the particles can be rejected from the growing crystals [59]. The resulting scaffold obtained after the sublimation of the frozen solvent can be used as a green body or sintered depending on the characteristics of the raw material and the desired structure or application. The starting suspension has to be stable to avoid any sedimentation phenomenon that could produce gradients of porosity in the final material. Many factors should be considered to avoid sedimentation during freeze casting: the nature of the compounds, the size of the particles, the density, the thermal conductivity and surface charge [59]. The most relevant one is particle size; beyond a critical particle size in fact, the particles are encapsulated by the moving interface. The final porosity of the freeze casted scaffold can be also tailored in terms of volume fraction and pores morphology. Changing the solid loading, it is possible to obtain scaffolds with porosities ranging from 30 up to 90vol%. A variety of pore morphologies can be achieved by carefully choosing the solvent

and solidification conditions [85]. The solidification for instance can be unidirectional or not. Different thermal gradients can be imposed forcing the solvent crystal to grow in specific directions [80,96]. Apart from thermal gradients, electromagnetic fields can be applied during the solidification influencing the crystal growth and their final direction [97,98]. Furthermore it is possible to change the wavelength (λ , is equal to the sum of one lamellae and one pore thickness) of the structure changing the freezing rate. As already reported, a higher freezing rate produces smaller crystals and therefore finer pore sizes [66,85]. It has been also shown that the use of additives, changing the phase diagram of the solvent, alter the growth behaviour of crystals, which define the final morphology of the pores [70]. Finally the nature of the solvent and its crystallographic properties define the morphology of the final structure, i.e., lamellar with water, dendritic with camphene or prismatic with tert-butyl alcohol [85]. Thus it is clear that many parameters can be changed and controlled to achieve tunable microstructure that can better respond to a specific application and working conditions. Therefore a large variety of porous materials have been produced using freeze casting from ceramics such alumina [72,99–101], yttria-stabilised zirconia [102,103], silicon carbide [104], hydroxyapatite [105,106], tricalcium phosphate [77], silicon nitrate [107,108] to metals such titanium [109].

1.4 Bio-inspired composite vs engineered design ceramics

It has become clear that for man-made materials, although there are exceptions, toughness and strength are usually mutually exclusive [19]. New design solutions developed by engineers and material scientists, aimed at increasing the fracture toughness of a material usually have detrimental effects on the strength and hardness and vice versa. For instance refining the grain size and therefore reducing the size of the pre-existing flaws has a beneficial effect on the strength of the ceramic. However smaller grains provide less resistance to crack-propagation. Lacking in plastic deformation, most pure ceramic materials such as SiC, Al₂O₃, Si₃N₄ etc., can show high values of strength, but are extremely sensitivity to flaws, often experiencing catastrophic failure. Bulk ceramics show very low toughness values ranging from 1 to 4MPa·m^{1/2} [110]. Toughening ceramics has been achieved inducing extrinsic toughening mechanisms within their microstructures. Mechanisms such as crack deflection, crack-tip shielding or in situ phase transformation are

the main ones used to build tough bulk ceramics. All these extrinsic mechanisms result in a R-curve behaviour as they need a propagating crack to become effective. On this regard, material scientists came out with different solutions. Examples are partially-stabilized zirconia, where the volumetric expansion associated with the in situ transformation from tetragonal to monoclinic acts as the main toughening mechanism showing final fracture toughness values ranging from 12 to 20MPa·m^{1/2} [111,112]; or SiC or Si₃N₄ elongated grains that generating also elastic bridging that have toughness ranging from 4 to 9MPa·m^{1/2} etc. [113].

A possible solution to produce materials that can present acceptable values of strength and high toughness at the same time is to use composites where two or more different materials are combined in one structure to improve the final properties. For this reason, fibres, whiskers or particles have been dispersed as reinforcement to increase strength/stiffness of materials. For toughening, crack bridging is still the most relevant mechanism, especially for ceramic-matrix composites; utilizing fibres such as carbon, glass or ceramic (SiC fibres-Nicalon) with engineered interfaces (weak interfaces between the fibres and the matrix) when the matrix fails the fibres can bridge the crack propagation postponing the failure of the structure. With this approach it has been possible to produce ceramic/ceramic composites with fracture toughness $\geq 30\text{MPa}\cdot\text{m}^{1/2}$ [112]. Other engineering structures with improved mechanical properties are layered ceramic/metal structures. The organization of different layers of materials can lead to an improvement in terms of fracture toughness, wear resistance and strength. With this structural strategy it has been possible to achieve composites with a final strength around 400MPa, initial K_{Ic} of $\sim 12/14\text{MPa}\cdot\text{m}^{1/2}$ and final K_{Ic} values over $\sim 40\text{MPa}\cdot\text{m}^{1/2}$ [90,114].

Differently from man-made materials, as already discussed in previous paragraphs, natural structures, due to architectural designs that span over several dimensions, can achieve exceptional combinations of mechanical properties (strength, toughness, lightweight). Nature develops not only mechanically robust structures but also structural materials with specific functionalities. Every single constituent has a specific function that can change to better adapt at external environmental conditions. It has been already shown that mimicking the natural organization of natural materials in synthetic structures could lead to the production of new materials and devices with superior traits and the development of

new production technologies. Many are the examples already mentioned in the above paragraphs and many others can be mentioned such as the works of Bonderer et al. [47], Mirkhalaf et al. [50], Podsiadlo et al. [115], Launey et al. [7] etc. where have been shown that the use of new shaping technologies with an ingenious choice of the basic constituents can lead to the production of composites with higher mechanical and functional properties. There some advantages and disadvantages that man has over Nature. Contrarily to Nature for example engineers do not have any limitations to materials choice relying on advanced materials. Nature however uses smart self-assembly technologies to produce its structures that we are still far to be completely understood. Using this approach nano and micro features are produced in natural materials that we cannot replicate in synthetic materials. It is therefore extremely important to understand and select which are the mechanisms that control the general performance of natural structures and develop adequate fabrication procedures to implement them in artificial materials. The technologies developed so far still struggle to find industrial or more practical applications for various reasons, from the limited dimensions of the obtained samples to the difficulty to scale-up the entire production processes. Moreover, because these materials often combine different functional and traditional properties, the traditional characterization methodologies do not always fully describe their behaviour. The development of new models and characterization techniques that could better describe the whole structure as well as the contribution of every single constituent is necessary to effectively understand the potential benefit of these materials. Bio-inspiration is still a quite new branch of materials science but the recent advances have shown its great potential. The possibility of duplicating natural capabilities could lead one day to the production of “smart” materials that could someday self-repair or adapt to external stimuli and load conditions.

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2 Aims and Objectives

The aim of this work is the development of new types of bio-inspired ceramic-based composites combining stiff and soft phases and the study of their mechanical response. The ceramic phases are Al_2O_3 and SiC with different particle morphologies (nanoparticles, fibres or platelets) and the “soft” compliant phases will be either a metal (Al-alloys) or polymer (PMMA or epoxy resin). These composites aim to replicate the hierarchical structures found in natural materials like nacre, to reach unprecedented combinations of mechanical properties (strength and toughness). The approach is to follow a multidisciplinary effort towards comprehending, processing and characterizing the materials with the following specific aspects:

1. Combine different novel processing techniques including freeze casting (based on the freezing of ceramic suspensions) and metal pressureless infiltration for the fabrication of ceramic/metal composites mimicking the hierarchical structures of nacre. There are very few reports in literature regarding the infiltration of freeze cast porous ceramic preforms with metals and all of them follow a pressure infiltration process. In this study a much more ductile aluminium alloy is employed in order to produce composites with improved toughness. Finally, the effect of the alumina particle morphology is studied. Freeze cast preforms prepared from alumina platelets are used for the first time to produce layered composites.
2. Develop efficient sintering routes for the fabrication of highly porous SiC freeze cast scaffolds that can be subsequently used in the fabrication of composites through infiltration with a second phase (PMMA or epoxy resin). Differently from previous studies, this PhD work focuses on the development of strong SiC freeze cast preforms by performing a systematic study to formulate guidelines for improving the sinterability of SiC porous scaffolds.
3. Investigate the role of the mechanical properties of the “soft phases” (metal or polymer) on the performance of freeze casted materials.
4. Combining systematic structural and mechanical characterization at different length-scales to study the toughening mechanisms acting on bio-inspired materials. This

includes structural characterization using state-of-the-art techniques such as X-ray tomography and systematic mechanical characterization of flexural strength, fracture toughness and fracture resistance behaviour (R-curve).

3 Experimental methods

3.1 Freeze casting

All the necessary steps to produce freeze casted scaffolds are summarized in Fig. 13:

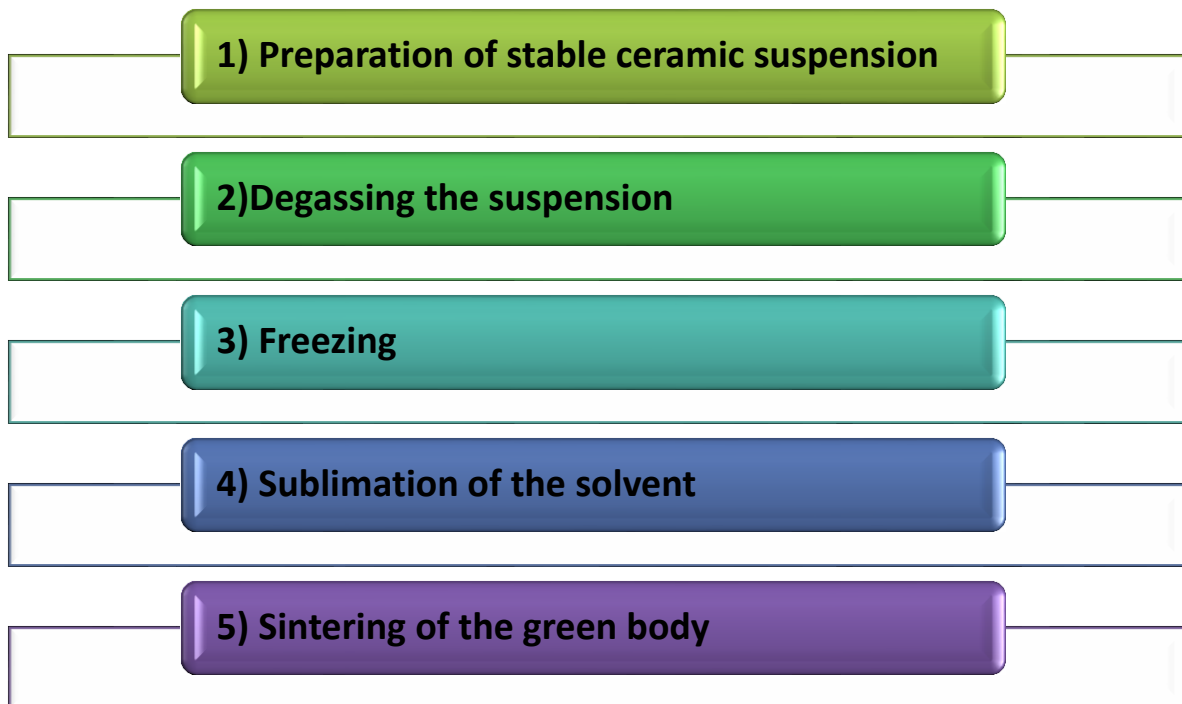


Fig. 13 Steps to obtain a freeze casted scaffold.

The ceramic suspensions were prepared carefully weighing all the fundamental components: ceramic particles, water, dispersant, binder and any eventual additive. The suspensions were then ball milled at room temperature and at 300rpm (Capco Test equipment, 12VS, UK) to break down any possible aggregates between the particles for at least 24hr. Milling media of the same materials as the employed ceramic particles were used to avoid any contamination. Milling balls of 10mm in diameter were used. Subsequently, after removal of the milling balls, the suspensions were de-gassed with a low

vacuum pump for at least 30min to remove any air bubbles produced during the milling. More specific details of

The freeze casting equipment used is shown in Fig.14. Slurries were poured into a Teflon mould placed at the top of a cold finger and frozen using liquid nitrogen. The freezing rate was controlled by a heater located on the copper rod and thermocouples placed in the freezing bath and close to the cold finger. The temperature control unit could be programmed to reduce the temperature from 20°C to -150°C with cooling rates ranging from 1 to 20°C/min.

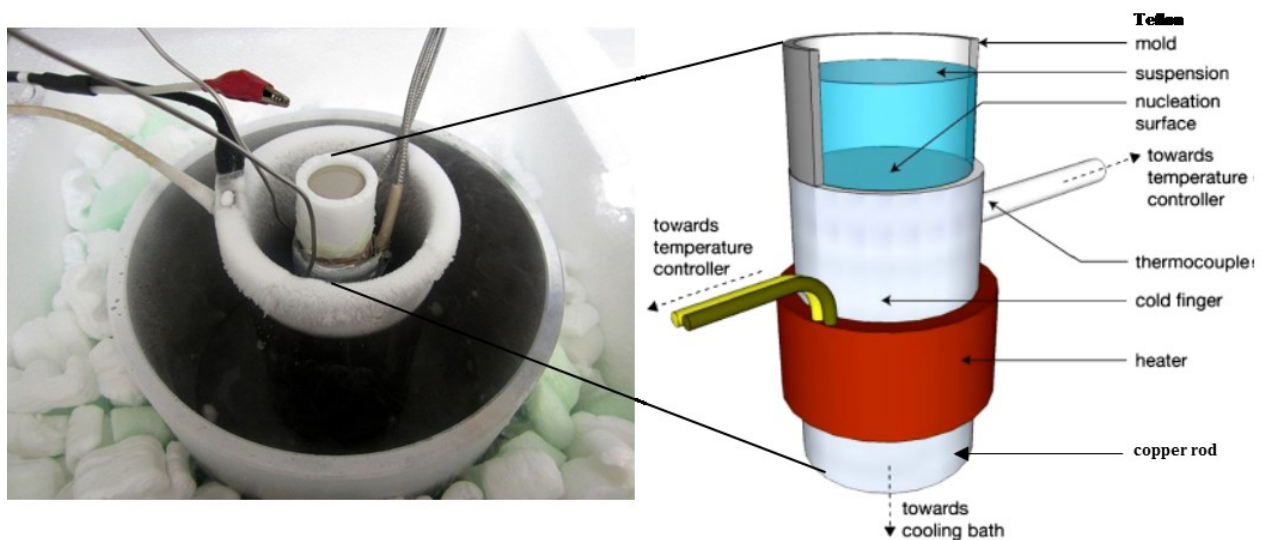


Fig. 14 Freeze casting equipment. The ceramic suspension is poured in a Teflon mould and placed on the cold finger. The temperature gradient imposed is controlled with a series of thermocouples. Adapted from [1].

Lamellae alignment during freeze casting could be controlled by patterning the cold finger surface in contact with the slurry to favour a preferential freezing direction [1]. In this study an insulating tape scratched horizontally was used to favour the preferential nucleation of ice crystals.

After freeze casting, the obtained samples were quickly transferred to a freeze dryer, see Fig.15 (Freezone 4.5 by Labconco, USA), where they were held at -50°C under a pressure of 0.03 mbar for 24h allowing the ice to sublime.



Fig. 15 Freeze dryer.

3.2 Particle size analysis

Particle size was measured using a particle size analyser (Mastersizer 2000, Malvern, Worcestershire, UK). This technique measures the particle size distribution through the diffraction of a laser beam from the particles dispersed in water. The particle size distribution is calculated by measuring the angular variation in intensity of the light scattered; small particles scatter light at larger angles than bigger ones (Fig.16). Using Mie's theory [2], the angular scattering intensity data are then analysed to calculate the size of the particles responsible for creating the scattering pattern. The particle size is reported as volume equivalent sphere diameter. This technique allows measuring particle size ranging from submicron to the millimetre size.

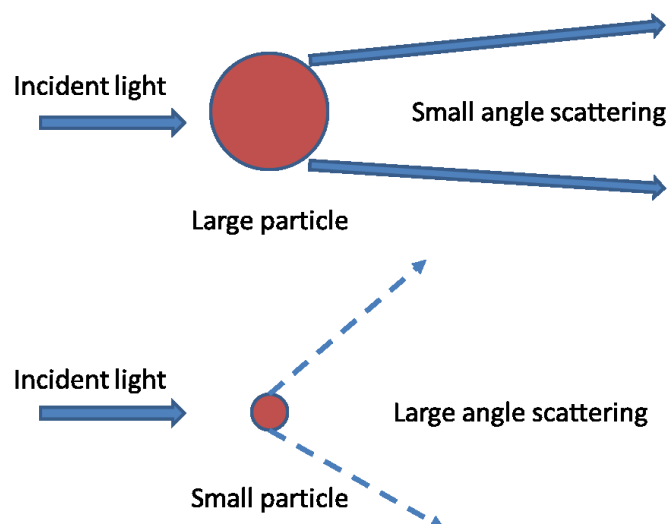


Fig. 16 Light scattering in colloidal media.

3.3 Rheometry

The rheology of the suspensions was characterized before being freeze cast. The flow behaviour and viscosity of the slurries were measured using a Discovery Hybrid Rheometer HR1 (TA Instruments). The analyses were done with two different geometries depending on the type of suspension studied. Cone-plate ($\varnothing = 60\text{mm}$, $\theta=2^\circ$, Truncation= $58\mu\text{m}$) or plate-plate ($\varnothing = 40\text{mm}$) in both cases using a solvent trap cover. Specifically the plate-plate system has been employed when short SiC fibres slurries were analysed, to avoid the entanglement of the fibres during the test. Rheometry refers to experimental techniques developed to define the rheological properties of a material, usually a liquid or a “soft solid”, and determines the relationships between deformation and stresses. Rheology is the science that studies the viscosity or the viscoelastic response of a fluid under different stress or external stimuli that could be oscillatory, steady, squeeze or pull. Usually the tests are conducted on liquid flowing in simple geometrical system that generating simple flow conditions are fully described in terms of fluid mechanics. External physical conditions imposed on the fluid influence the measured properties. For instance at higher shear stresses the molecules tend to orientate in the direction of the flow decreasing their level of aggregation or interaction and therefore the viscosity decrease. Therefore is always necessary to describe which type of solicitation is imposed to the fluid. In the case of a

simple steady state shear flow with a velocity $v_x = \dot{\gamma}y$ (Fig.17), the $\tau_{xy} = -\eta d\dot{\gamma}_{xy}/dt$, where τ_{xy} is the shear stress in the plane y-x and $\dot{\gamma} = d\dot{\gamma}_{xy}/dt$ is the velocity at which the shear stress is applied on the same plane (shear rate) [3]. It is possible in this way evaluate the viscosity η .

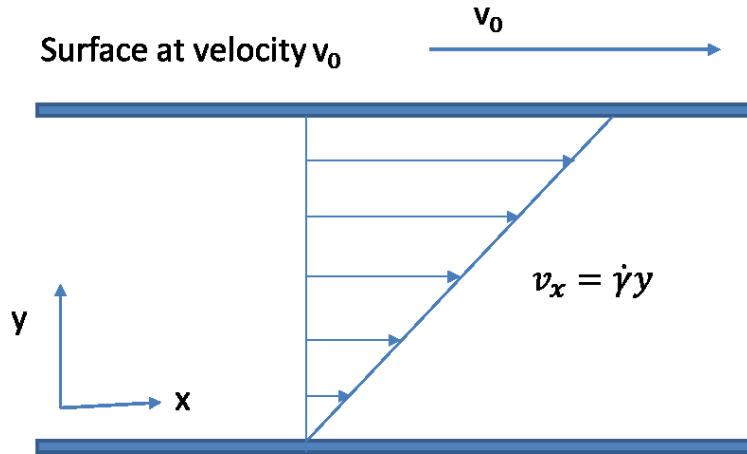


Fig. 17 Steady state shear flow.

From a molecular point of view, the nature of the flow imposed from a specific type of external solicitation is determined from the interatomic and intermolecular forces acting on the macromolecules. Therefore several different phenomenological equations have been developed to describe different types of fluid behaviour. For instance Newtonian fluids are that category of substance which rheological behaviour is independent from the applied stress and strain rate imposed; they can be fully characterized by a single coefficient of viscosity η that is simply related to the nature of the materials and to its temperature.

$$\tau = \eta \left(\frac{-dv_x}{dy} \right) \quad (3.1)$$

However only a small group of fluids show constant viscosity. For the majority of the substances the viscosity tends to change with the strain rate (Fig.18). These are called non-Newtonian fluids and they can be either shear-thickening or shear-thinning and η is defined as apparent viscosity [3].

$$\tau = K(\dot{\gamma})^n \quad (3.2)$$

where K is the consistency index and n is the shear thinning constant that indicates how far the tested substance is from a Newtonian behaviour.

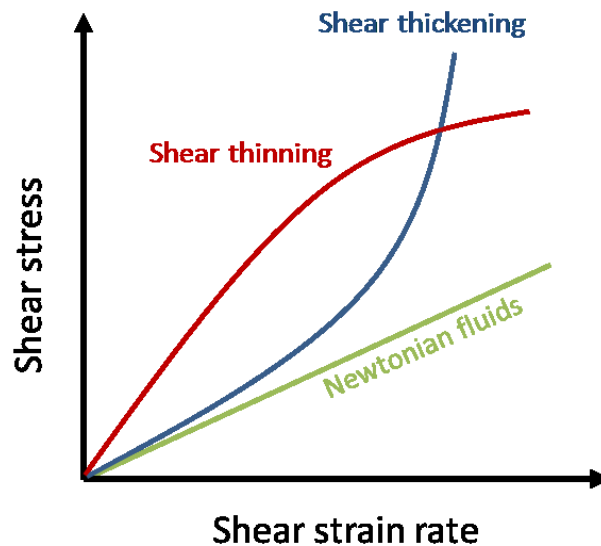


Fig. 18 Shear stress vs shear rate for shear thinning, shear thickening and Newtonian fluid behaviours.

These kinds of systems are in fact more complex to analyse and the only viscosity is inadequate to fully describe their behaviour. They are characterized using different rheological properties that relate the stress and strain rate tensors under different flow conditions. In this study a cone-plate or plate-plate rheometer were employed. The cone-plate consists of a flat plate and a low angle cone ($\theta=2^\circ$); the plate-plate consists of two parallel plates as described in Fig.19:

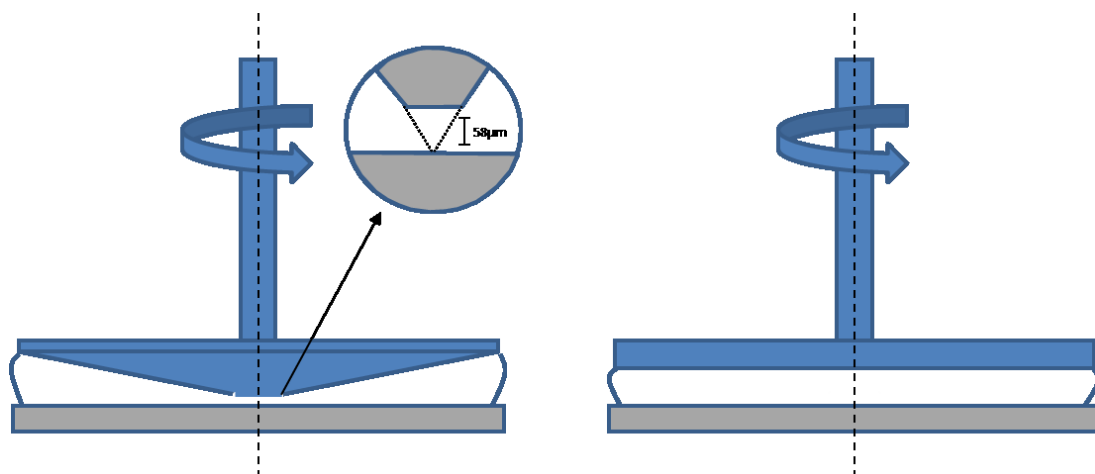


Fig. 19 Schemes of cone-plate and plate-plate rheometer. The cone-plate system is preferred for low viscosity ceramic slurries and a fixed gap of 58 μm is usually employed. In this study a plate-plate system with a gap ranging between 500 to 800 μm has been employed when suspensions containing shot SiC fibres were analysed. Adapted from [4].

The systems are formed from a rotating cone or plate with a radiant velocity w (radians/second) and a fixed plate. The suspension was loaded in the interspace between the cone/plate and the fixed plate. For the analyses the system was isothermal (temperature control at room temperature) and the fluid incompressible. Moreover inertia and centrifugal forces were calibrated for both geometries. A solvent trap was always employed to avoid the evaporation of the solvent during the test and all tests were run at room temperature. Viscosities of the suspensions were determined in strain control imposing a shear rate ranging from 0.1 to 1000 s^{-1} .

3.4 Dilatometry

Dilatometry was employed to better identify sintering temperatures for SiC powders. Dilatometry measures the expansion or the shrinkage of materials as a function of temperature. Sintering of compact ceramic powders is usually associated with shrinkage. This shrinkage is mostly associated with the elimination of interstitial pores between the powders or with changes in the pores morphologies and size. Different volumetric change can be observed in association to other phenomena such as thermal expansion. The dilatometer allows a continuous tracking of the sample shrinkage and therefore it is often used to analyse the sintering behaviour of powder compacts [5]. The dilatometer used (Netzsch, DIL 402 C - Fig.20) enables the heating of the pellets up to 2000 $^{\circ}\text{C}$ and in-situ

recording of the sample dimensions changes as the sintering occurs. It is possible to heat the samples with rates between 0.01°C/min to 50°C/min. The dilatometer measures maximum dimensional changes (Δl) between 500 to 5000 μm with a minimum resolution of 0.125/1.25nm. Cylindrical powder pellets (~5x20mm) with specific compositions, in terms of sintering aids and additives, were isostatically pressed (~300MPa) and loaded in the dilatometer furnace. The furnace and the pushing rod were both made of graphite and the experiments were performed up to 2000°C with a heating rate of 20°C under an argon flow to avoid any reaction of the powders with oxygen.

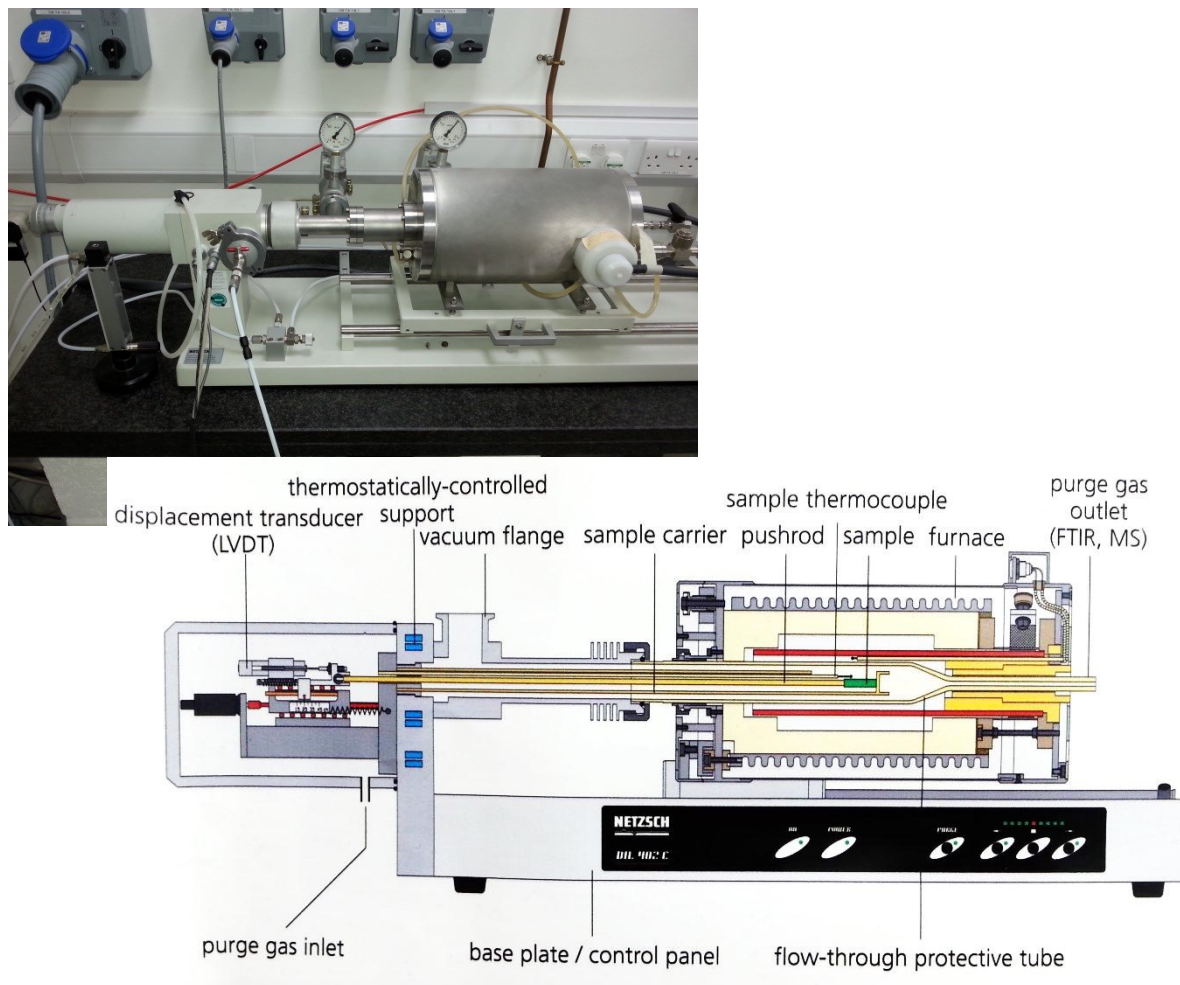


Fig. 20 Dilatometer Netzsch, DIL 402 C [25].

3.5 Sintering and densification

After freeze drying, the green bodies were sintered. Different sintering processes were used to prepare alumina and silicon carbide scaffolds.

The sintering of alumina green bodies was carried out in an electric furnace (Ultratherm by Pyrotherm Ltd, UK) in air with a firing schedule already used in other studies [1,6]. The SiC green bodies, due to their low sinterability, were sintered in different conditions using diverse sintering equipments such a conventional graphite furnace and spark plasma sintering (SPS)(employed also as graphite vacuum sintering furnace without using an applied pressure on the samples), in order to find the best densification route that could preserve the lamellar organization.

The graphite furnace (FCT Systeme GmbH, Rauenstein, Germany) was run in inert atmosphere under argon flow and the temperature was controlled with a tungsten rhenium thermocouple up to 1200°C, while at higher temperature around 1800-2000°C was measured with a pyrometer. The scaffolds were positioned inside a cylindrical graphite crucible of 15mm in height and 10mm in diameter.

Spark plasma sintering (FCT Systeme GmbH, HP D20, Rauenstein, Germany) (Fig.21), also known as field assisted sintering technique, uses DC current as source for heat generation. The current flowing in the graphite die allows very fast heating or cooling rate. The SPS process was run under vacuum and the temperature was controlled with a pyrometer. The samples also in this case were placed in a graphite crucible similar to that one used in the conventional graphite furnace. A minimum initial working pressure of 20MPa was applied on the graphite crucible employed, but not directly on the porous scaffolds. More details on the sintering conditions employed for the different materials are reported in Chapter 4,5 and 6.



Fig. 21 On the left the graphite furnace used at Imperial College London and on the right the SPS employed at Queen Mary College. A schematic representation of the graphite crucible employed in the SPS is reported.

3.6 Microstructure characterization

3.6.1 Scanning electron microscopy (SEM)

The scanning electron microscope generates high quality images by scanning the sample surface with a focused beam of electrons. The maximum resolution of an optical imaging system is limited by its diffraction limit (d) that from Abbé's theory [7] depends on the wavelength of the source and can be defined as:

$$d = \frac{\lambda}{2n\sin\alpha} \quad (3.3)$$

Where n is the reflective index of the medium where the source travels and α is the half-angle subtended by the optical objective lens. Electrons are the primary source used in SEM due to their short wavelength, the resolution is significantly improved compared with traditional optical microscopy techniques (it is possible to achieve resolution of $1\mu\text{m}$ or less). The electrons once collimated and focused with a series of lenses in a single beam (with a diameter of $\approx 1\mu\text{m}$), scan the surface of the specimen generating various signals which are detected to produce an image (Fig.22) [8]. Secondary electrons are one of the signals generated with the interaction between the primary electrons of the beam and the sample surface. Slight differences in surface topography produce noticeable variations in the strength of the secondary electrons produced that are used to reconstruct the image in a

scanning pattern synchronized with the electron beam scan of the sample surface [9]. This analysis allows a topographic evaluation of the sample surface and due to the depth of field of the SEM, irregular and complex surfaces can be inspected. The SEM has in fact a depth a field much larger than a normal optical microscope that rises from the geometry of the beam optics. The depth of field is the space between the best plane of focus where the image results still sharp and being larger in the SEM it allows the observation of rough surfaces. Other types of signals are generated during the interaction of the primary electrons beam and the samples. The interaction volume of the beam with the sample normally takes the shape of a teardrop as shown in Fig.22. The size of the interaction volume depends on different factors such as acceleration voltage, atomic number and specimen's density and it varies from 100nm to around 5 μ m into the surface [8]. Backscattered electrons (BSE), transmitted electrons, X-rays, cathodoluminescence radiation are also generated when the electron beam interacts with the sample surface. All these signals available in SEM made this technique one of the most versatile and powerful for materials characterization. Backscattered electrons are generated by elastic energetic interactions of the primary electrons with the nuclei of the samples' atoms. The intensity of the BSE signal depends on the average atomic number and density of the sample; images obtained with BSE electrons give useful compositional information. The inelastic interaction of the beam with the K-shell of the sample's atoms, besides producing secondary electrons, generates Auger electrons, X-rays and cathodoluminescence. The acquisition of the generated X-rays allows a localized chemical analysis, also known as energy dispersive spectroscopy (EDS). In case of not conductive materials the SEM samples were gold or chromium coated to avoid charging effects. Coatings of 10-20nm in thickness were deposited in a vacuum chamber via sputtering from a gold or chromium target for 2 minutes at 20mV (Quorum technologies, Emitech K575X). Microstructural analysis was performed using a Leo Gemini 1525 FEGSEM and a JSM 6010 LA in SE mode with a voltage ranging from 5 to 15kV.

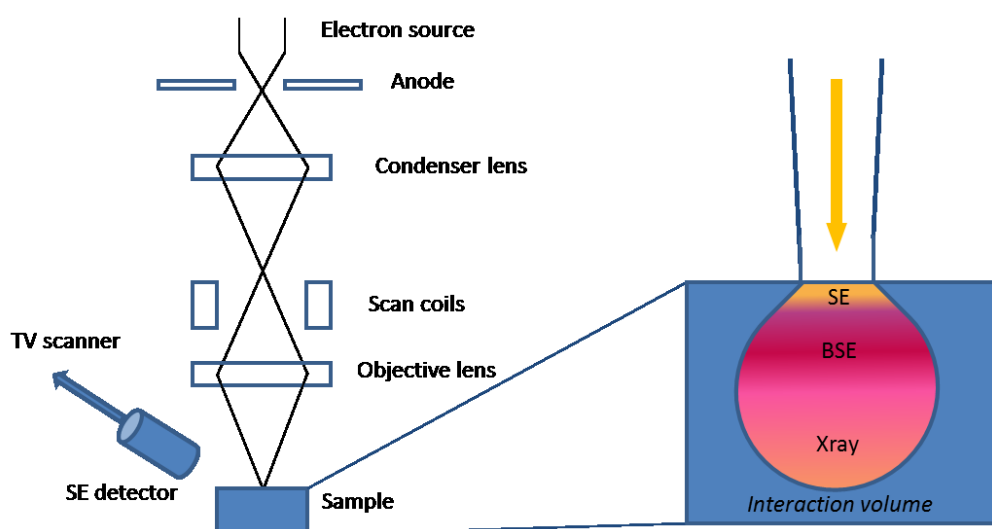


Fig. 22 Scanning electron microscopy. On the left side a schematic representation of the SEM functioning and on the right side the volume interaction of the electron beam with the sample surface. Adapted from [8].

3.6.2 X-ray diffraction analysis (XRD)

X-ray diffraction analysis was used to identify the different phases in sintered SiC scaffolds and the reaction compounds obtained during the pressureless infiltration of aluminium within alumina scaffolds. Phase composition analyses were performed by X-ray diffraction (XRD, PAN-analytical, Almelo, Netherlands). Scan data were collected with $\text{CuK}\alpha$ ($\lambda=1.54178$ Å) radiation at a step size of 0.1° and 150s for step.

An X-ray diffractometer consist of an X-ray generator, a series of filters and collimators, a sample holder and an X-ray detector (Fig.23).

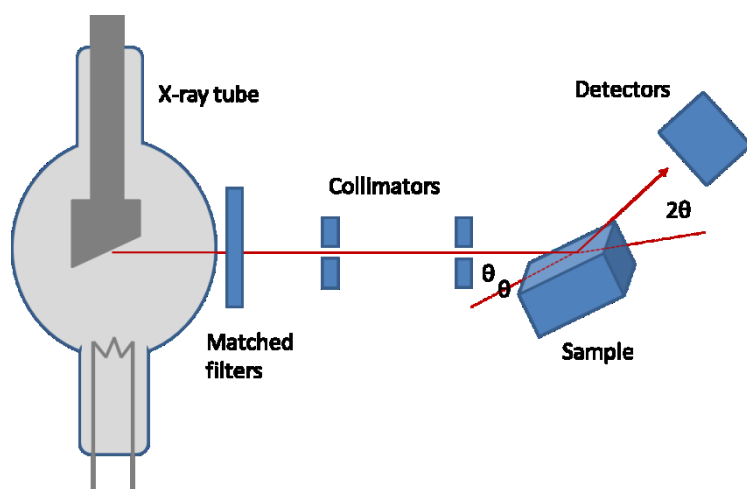


Fig. 23 X-ray diffractometer. Schematic representation of x-ray set up.

In the X-ray tube a beam of accelerated electrons impacts on a pure metal target like copper or molybdenum. When these electrons reach the right energy to expel inner (*K*) shell electrons of the target material, the decay of electrons from higher level shell generates X-rays with wavelength characteristics of the target material. The generated X-rays are then collimated towards the analysed sample that is rotated at an angle θ from the X-ray tube while the X-ray detector is placed at an angle of 2θ . Constructive interaction and diffraction of the X-ray from the sample takes place at angles that satisfy the Bragg's Law [10]:

$$\lambda = 2d\sin\theta \quad (3.4)$$

where λ is the wavelength of the incident X-ray, d is the spacing between the planes in the atomic lattice and θ is the diffraction angle, the angle between the incident X-ray and the scattering planes (Fig.24).

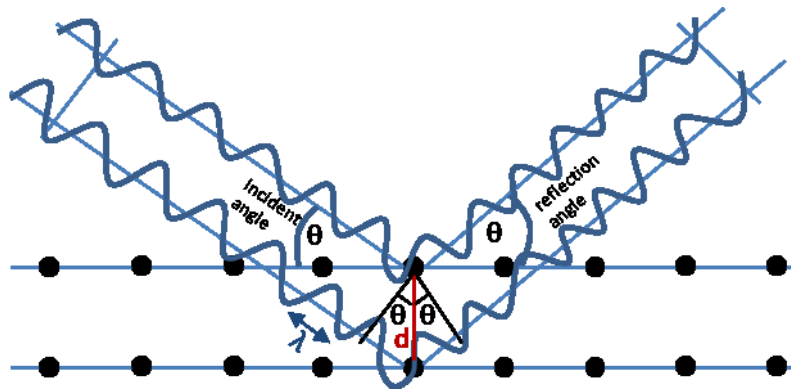


Fig. 24 Diffraction of X-ray in a crystal. Bragg's law. Adapted from [10].

The samples can be analysed in the diffractometer in form of powder or pellet. The powder will cover larger range of possible orientations. Thus for each possible diffraction angle there are crystals oriented correctly for Bragg diffraction. However, when pellets are employed, to increase the possible orientations that can produce a constructive interference with the X-ray source according to Bragg's law, the pellets are usually rotated. Moreover because the depth of penetration of the X-ray depends mainly from the density of

the sample, loose powder will give better information than pellets having a larger depth of penetration.

3.6.3 Transmission electron microscopy (TEM)

Transmission electron microscopy was used to analyse the structures and the chemistry of the grain boundaries for the silicon carbide liquid phase sintering. The samples and TEM results were obtained by Dr Na Ni. The analyses were performed using a FEI Titan 80/300. Transmission electron microscopy is a very powerful microscopy technique in which an electron beam is transmitted through an ultra-thin specimen (usually <200nm). Many different signals are generated through the interaction between the electron beam and the sample that allow a complete characterization of the sample at high resolution (Fig.25).

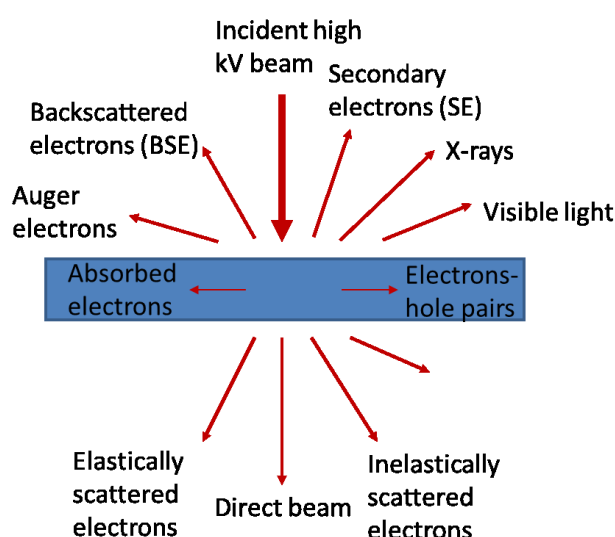


Fig. 25 Signals generated during TEM analysis.

TEM images are usually acquired in bright field (BF) and dark-field (DF) that are generated from the direct beam and the diffracted electrons respectively. The acquisition of transmitted electrons due to their smaller de Broglie wavelength, allows the generation of high resolution images. In this way even fine details can be analysed such as single column of atoms. Chemical analyses are also conducted using the characteristic X-rays.

3.6.4 X-ray microtomography

X-ray tomography is a non-destructive technique that allows imaging by sectioning of bulk samples, through the use of an X-ray source. It allows the analysis of interior features and obtains digital information on their 3D geometries and properties. The central elements in an X-ray tomography apparatus are an X-ray source, a detector to measure the X-ray intensity attenuation and a rotational stage where the object to be scanned has to be placed (Fig.26).

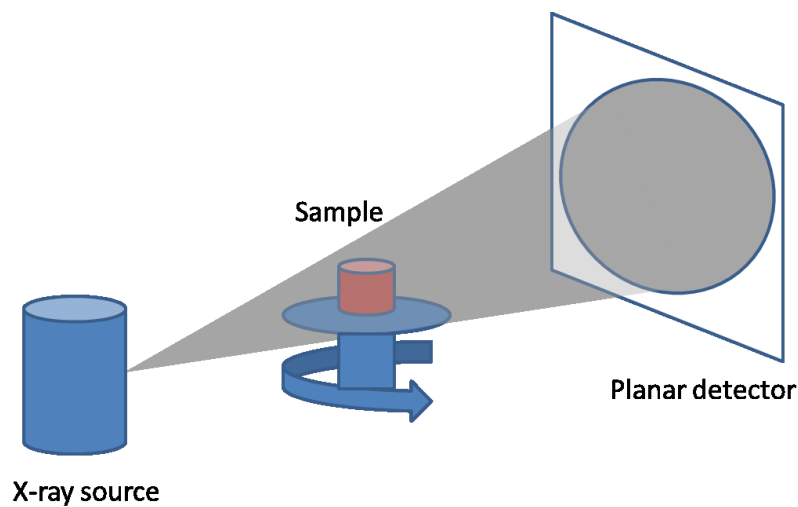


Fig. 26 Schematic representation of X-ray micro-tomography settings.

As the sample rotates, at each position a radiograph is acquired. After a rotation of 360° all the acquired radiographs are reconstructed into a 3D tomographic image with the use of specific software. Combining the 2D radiography with a 3D numerical reconstruction the X-ray microtomography can be used to analyse the internal microstructure of a wide range of materials. The resulting 3D volume is a reconstruction of a series of slices taken at different thickness within the scanned object. When the X-ray beam interacts with the sample, a portion of them are scattered or absorbed in relation with the density and composition of the material being imaged. X-ray attenuation corresponds to different grey levels in a tomographic image.

A standard laboratory tomography machine (GE, Phoenix vTomex, Germany), equipped with X-ray tube (*high power Nanofocus*) with a voltage from 40 to 160 kV was used (Fig.27). The

detector (*Varian*) was made of amorphous silicon; it had a pixel size of 127 μ m and dimensions of 1920 pixels in the horizontal direction by 1536 pixels in the vertical one. With this set-up resolutions of 2 μ m were achieved.



Fig. 27 X-ray microtomography Phoenix vTomex.

3.7 Density

The Archimedes' method was used to determine the density and porosity of the obtained scaffolds. The mass of the specimens were taken in three different states: dry mass, wet mass and mass in water. The dry mass was taken after drying at 100°C for 24h. To obtain the mass in water and the wet mass, the samples were infiltrated with boiling distilled water in a vacuum casting machine (Cast N'Vac, Buehler, Germany) and a specific kit for density measurement (Sartorius, YDK01, Goettingen, Germany) was use to evaluate the different weights. Once all the three measuments were taken, the following formulae were used to calculate the density, the relative density, the open porosity, the closed porosity and the total porosity:

$$density = \frac{dry\ mass}{wet\ mass - mass\ in\ water} * density\ of\ water \quad (3.5)$$

$$relative\ density = \frac{density}{density\ of\ 100\%\ solid} \quad (3.6)$$

$$\%open\ porosity = \frac{wet\ mass - dry\ mass}{wet\ mass - mass\ in\ water} \times 100 \quad (3.7)$$

$$\%total\ porosity = (1 - relative\ density) \times 100 \quad (3.8)$$

$$\%closed\ porosity = \%total\ porosity - \%open\ porosity \quad (3.9)$$

3.8 Mechanical characterization

3.8.1 Air-coupled ultrasound spectroscopy

Ultrasound spectroscopy is a non-destructive technique used in materials science to measure fundamental materials properties involving elasticity. Classic resonant ultrasound spectroscopy is based on the fact that solid objects vibrate when mechanically excited at specific frequencies which are related to the elasticity, the size and the shape of the analysed object. The advantage of this technique is that the entire elastic properties of the material are revealed with a single rapid measurement. Many other properties can be evaluated with this technique such as density, acoustic velocity, and acoustic attenuation [11]. In the classic ultrasound spectroscopy a coupling medium is often used such as water or gel to reduce the difference in acoustic impedance between the transducer, the medium and the sample [12]. However in many cases the use of a medium is not possible and therefore air-coupled spectroscopy is a valid alternative. The progresses made in signal processing and the development of new transducers makes this technique employable in different applications. During this analysis the ultrasonic waves are generated and propagate within the analysed materials. These acoustic waves transport energy in a wide frequency range. As the wave propagates within a medium these frequencies are altered and their analyses permit to extract information of the medium. The ultrasonic spectroscopy set-up employed used two air-coupled transducers, an emitter and receiver,

along with an excitation/reception system (Fig.28). From this analysis is possible to estimate the elastic modulus of the materials using the following equations [12]:

$$M = v^2 \rho \quad (3.10)$$

where M is the modulus of the wave, v is the velocity of the ultrasound and ρ is the density of the material. Knowing the modulus M and the Poisson's ratio of the system it is possible to calculate the Young's modulus E from this equation:

$$M = \frac{E(1 - \nu)}{(1 + \nu)(1 - 2\nu)} \quad (3.11)$$

The tests were performed by the group of Dr. Tomas Alvares Arena at the CSIC (Cosejo Superior de Investigaciones Cientificas) in Madrid, using a set up built in their laboratory.

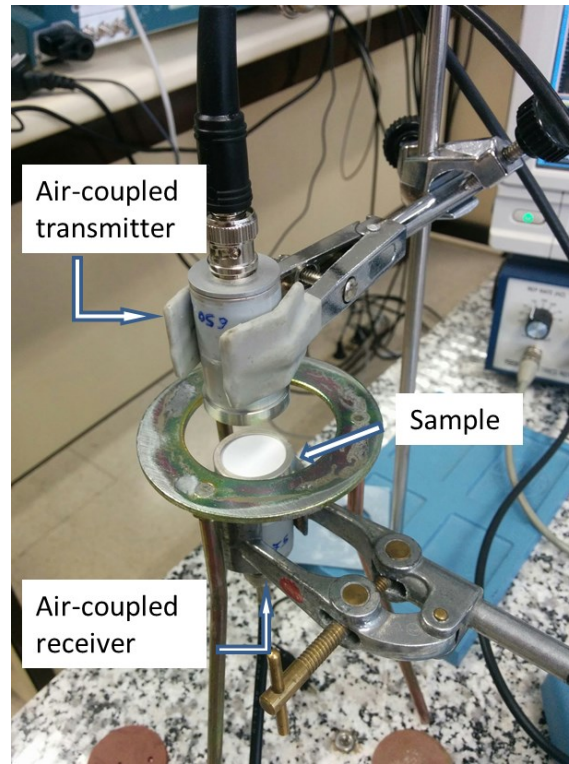


Fig. 28 Ultrasound spectroscopy apparatus.

3.8.2 Compression test

The compressive strength of a material is the force per unit area it can withstand under uniaxial compressive stresses:

$$\sigma_c = \frac{P}{A} \quad (3.12)$$

where P is the maximum load applied and A is the area over the load is applied.

The compression tests were performed on a universal testing machine Zwick/Roell Z010 with a loading cell of 10kN following the ASTM C133 [13]. A half metallic sphere was employed as recommended by the ASTM C133 [13] to better uniform the applied load. The test was performed at room temperature at a rate of 1.3mm/min and imposing a maximum deformation limit of 80%. All the tests were done at room temperature on cubic specimens with dimensions of 5x5x5mm³.

3.8.3 Flexural strength

Flexural strength was evaluated in four point bending mode. The method was chosen over three point bending due to its more homogeneous stress distribution. Flexural strength (σ_f) is the ability of a material to withstand an applied load on its longitudinal axis between the supporting points. When subject to a bending load the beam is under a combination of tensile, compression and shear stresses. The maximum stress achieved during the bending test is called flexural strength. The flexural strength was measured using a Zwick Roell machine Z010 with a 10kN loading cell according to the ASTM C1161 [14]. The ratio between length and thickness was kept around 10:1 while support and loading span of 16 and 8 mm respectively were used. Testing speed of 0.2mm/s in displacement control was applied accordingly to the ASTM C1161 [14]. Sample dimensions were approximately 20x2x3mm³ according with the ASTM standard employed. The maximum bending strength was calculated using the following equation:

$$\sigma_f = \frac{3PS_0}{4bd^2} \quad (3.13)$$

where P is the maximum load applied, S_0 is outer support span, b is the specimen sample width and d is the thickness.

3.8.4 Fracture toughness

Fracture toughness of a material represents its ability to resist to crack propagation. Single edge notched beams (SEN(B)) were employed to calculate the K_{Ic} of the prepared samples. Samples were tested in three or four point bending mode according to ASTM C1421 [15]. The samples were first pre-notched using a cutting machine (Isomet 1000, Buehler, UK) equipped with a 0.3mm diamond blade. Then the pre-notch was sharp with a razor blade continuously flushed with a 3 μ m diamond suspension (Fig.29). Bars were notched with approximate notch length a ratio ranging between $0.2 \leq a/W \leq 0.3$., where W is the sample thickness. The specimens were tested using a Zwick Roell Z010 testing machine loading the pre-notched surface under tension. The test was conducted at room temperature with a test speed of 0.1 mm/min. The average crack size was measured on the fracture surface of each sample post-mortem and considering the average values between a_{25} , a_{50} and a_{75} .

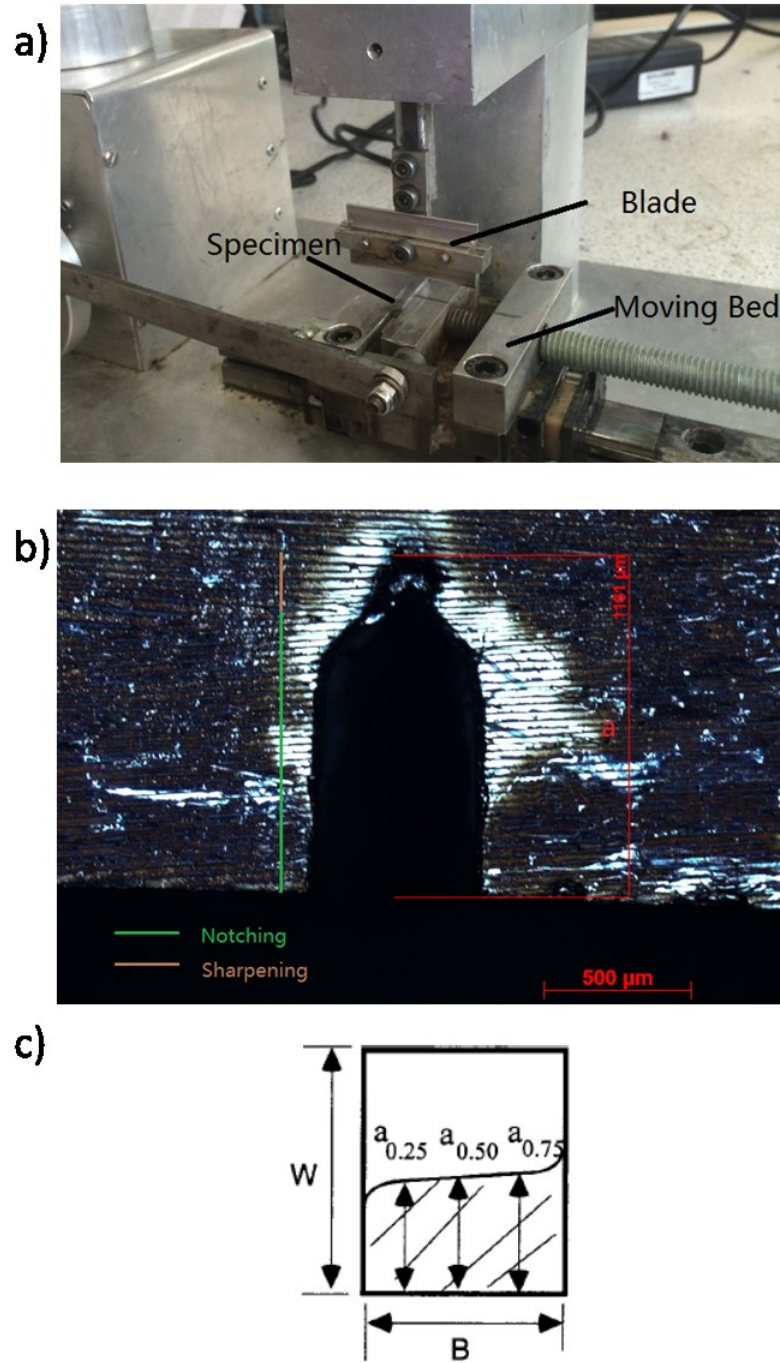


Fig. 29 Test specimen with pre-crack. a) Equipment used to sharp the notch obtained with the diamond blade; b) optical image of a pre-cracked sample; c) notch profile measurement according to the ASTM C1421 [15].

The fracture toughness K_{Ic} was calculated using the following equation for the three-point bending test [15]:

$$K_{Ic} = g \left[\frac{PS_0 10^{-6}}{BW^{3/2}} \right] \left[\frac{3[a/W]^{1/2}}{2[1 - a/W]^{3/2}} \right] \quad (3.14)$$

where:

$$g = g\left(\frac{a}{W}\right) = \frac{1.99 - [a/W] \left[2.15 - 3.93 \left[\frac{a}{W} \right] + 2.7[a/W]^2 \right]}{1 + 2[a/W]} \quad (3.15)$$

K_{Ic} is the fracture toughness ($\text{MPa}\cdot\text{m}^{1/2}$), a is the average notch length measured after testing (m), W is the sample thickness (m), B is the sample width (m), P is the maximum force at which the sample fails (N), S_o is the outer span length (m). When four point bending was employed the equations used were the following:

$$K_{Ic} = f \left[\frac{P[S_o - S_l]10^{-6}}{BW^{3/2}} \right] \left[\frac{3[a/W]^{1/2}}{2[1 - a/W]^{3/2}} \right] \quad (3.16)$$

where:

$$f = f(a/W) = 1.9887 - 1.326 \left[\frac{a}{W} \right] - \frac{\left\{ 3.49 - 0.68 \left[\frac{a}{W} \right] + 1.35 \left[\frac{a}{W} \right]^2 \right\} \left[\frac{a}{W} \right] \left\{ 1 - \left[\frac{a}{W} \right] \right\}}{\left\{ 1 + \left[\frac{a}{W} \right] \right\}^2} \quad (3.17)$$

where S_l is the inner span length. In both cases between 5 and 10 bars were tested in order to obtain a significant result and estimate the error.

3.8.5 Resistance curve (R-curve)

In brittle materials such as traditional ceramics, the fracture toughness is independent of the crack extension Δa . In this case these materials are characterized by a so-called flat crack resistance curve (R-curve) with $K_I = K_{Ic} = \text{const}$. In other cases the fracture toughness varies with the crack propagation generating a rising R-curve. In this specific condition the

energy needed to propagate the crack within the microstructure increases and the crack propagation behaviour is no longer fully described by a single value K_{Ic} but is better characterized by a $K_J-\Delta a$ curve (R-curve) (Fig.30) [16].

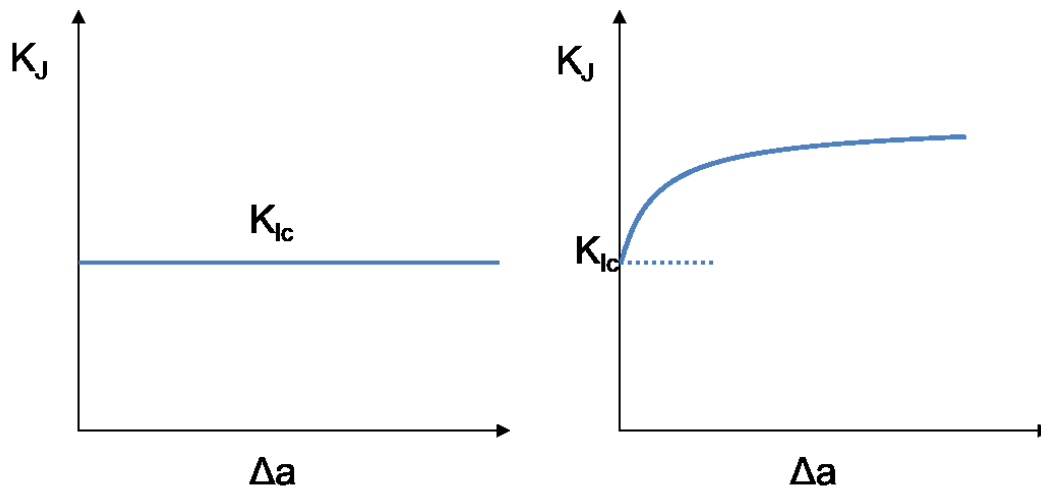


Fig. 30 Flat or rising R-curve behaviour. Adapted from [16].

The first observation of increasing R-curve behaviour was done by Hübner and Jillek in polycrystalline alumina [17]. Rising R-curves were found later in many other ceramics such as SiC [18], Si_3N_4 with elongated grains [19] and different partially stabilized zirconia with MgO, CeO or Y_2O_3 [20–22].

In this study the R-curve behaviours of SiC/PMMA and Al_2O_3 bio-inspired composites were studied using single edge bend (SEN(B)) specimens loaded in four point bending mode according to ASTM E1820 [23]. All the tested specimens were pre-notched with a diamond blade and the notch sharpened with a razor blade keeping the ratio $a/W \approx 0.5$. The tests were conducted in a servo-hydraulic machine Instron (model 5500) with a 5kN loading cell at a testing speed of 0.01mm/min. At the centre of the notch a linear variable differential transformer (Solartron, LVDT) with a resolution of $1\mu\text{m}$ was employed to follow the displacement during the loading process (Fig.31). The LVDT is an electromechanical transducer that can convert the rectilinear motion of the sample into a corresponding electrical signal. After every loading-unloading step the crack length was measured with SEM, optical microscopy and X-ray microtomography.

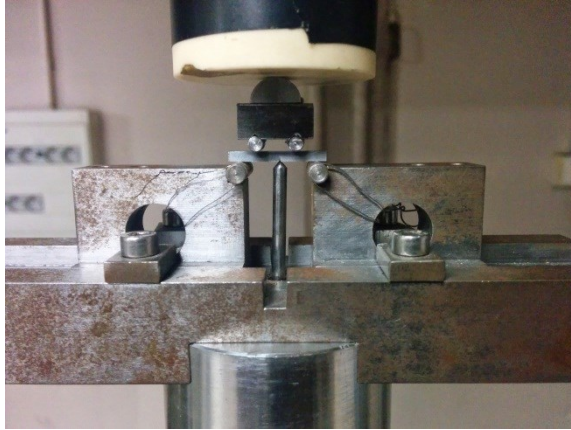


Fig. 31 Set up for R-curve measurement with the LVDT.

During the loading of the sample, as the crack started to propagate within the microstructure, a change in the compliance was observed. After unloading, the sample recovered the elastic deformation but a significant plastic deformation was observed (Fig.32). The plastic contribution to the work of fracture was evaluated as the area under the loading curve as reported in the following J-integral calculation.

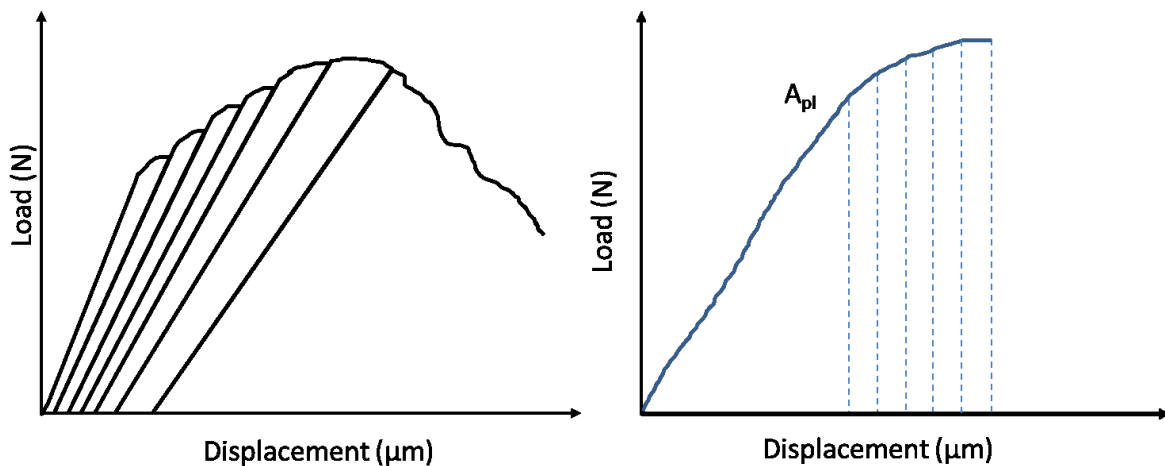


Fig. 32 Example of loading curve for R-curve measurements. The sample was loaded and unloaded several times as change in the compliance of the material was observed, meaning that the crack was growing within the microstructure. At every step the crack length was measured and the sample relocated carefully in the same position inside the testing machine to allow the crack to grow more. From the area under the load-displacement curve the elastic and plastic contribution could be analysed.

A J-integral approach was used to calculate the K_J at every single crack propagation, the following equations were employed [23]:

$$J = J_{el} + J_{pl} \quad (3.18)$$

where J_{el} is the elastic component of the J-integral and J_{pl} the plastic one. J_{el} can be evaluated by the following relationship:

$$J_{el} = \frac{K_{(i)}^2(1-\nu^2)}{E} \quad (3.19)$$

where $K_{(i)}^2$ is the fracture toughness evaluated at each a_i crack length; ν is the Poisson's ratio and E the Young's modulus. The elastic moduli E were calculated with the rule of mixtures for composite materials. $K_{(i)}$ is given by:

$$K_{(i)} = \sigma Y \sqrt{a_i} \quad (3.20)$$

$$Y = 1.99 - 2.47 \left(\frac{a_i}{W} \right) + 12.97 \left(\frac{a_i}{W} \right)^2 - 23.17 \left(\frac{a_i}{W} \right)^3 + 24.8 \left(\frac{a_i}{W} \right)^4 \quad (3.21)$$

where σ is the stress applied, Y is a geometrical factor and W is the thickness of the sample.

The plastic contribution to the J-integral can be calculated as:

$$J_{pl} = \frac{1.9A_{pl}}{Bb_0} \quad (3.22)$$

where A_{pl} is the area under the force versus displacement curve (Fig.32) and b_0 is the uncracked ligament ($W-a_0$). J-integral measurements were done satisfying all criteria reported in the ASTM E1820 [23], K_J fracture toughness was back-calculated using the $J-K$ equivalence:

$$K_J = (J \cdot E)^{1/2} \quad (3.23)$$

3.9 Thermal diffusivity and thermal conductivity

Thermal diffusivity was measured by laser flash analysis (LFA) method, introduced for the first time by Parker et al. [24]. The LFA experiments were conducted using a LFA 427

(Netzsch, Selb, Germany) instrument which consists of a furnace, sample holder and IR detector, a laser system and a data acquisition system connected to a computer (Fig.33). This equipment allows the measurement of the thermal diffusivity up to 2000°C with a measuring range between 0.1W/mK up to 2000W/mK. During the experiment the lower surface of a plane parallel sample is heated by a short high energy pulse. The pulse is absorbed on the surface of the sample and a change in temperature could be detected on the upper surface monitored with an infrared detector. The thermal diffusivity is calculated from the specimen thickness and the half of time required for the rear surface to reach its maximum value:

$$a = 0.1388 \cdot \frac{d^2}{t_{1/2}} \quad (3.24)$$

where a is the thermal diffusivity, d is the sample diameter and $t_{1/2}$ is half of the time that the sample need to reach the maximum temperature. The voltage and the duration of the laser pulse employed ranged between 400 to 450V and 0.5 to 0.8ms respectively depending on the analysed material. Examples of the input and output signals from the laser impulse are reported in Fig.34. In both case correction fits are considered. For the output signal a Cowan fit was chosen because models better the experimental points. The Cowan correction model assumes one dimensional conduction heat transfer in the specimen. It only considers radiation from the top and bottom of the surfaces neglecting the radiation loss from the circumference (Fig.34).

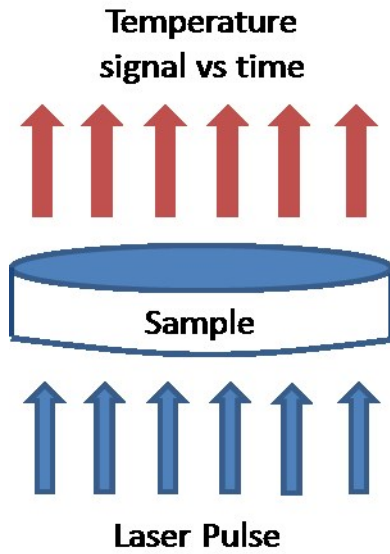


Fig. 33 Laser flash analysis employed to analyse the thermal diffusivity of tested samples.

Square specimens of 10x10mm with a thickness of 1mm were cut from the materials. The specimens were coated with a graphite emulsion to help increase the energy absorbed on the laser side and to increase the temperature signal on the detector side. Measurements were made from room temperature to 1500°C and three pulses were recorded at each chosen temperature. Thermal conductivity, k , was calculated using the following equation:

$$k = a \cdot C_p \cdot \rho \quad (3.25)$$

where a is the thermal diffusivity, C_p is the specific heat capacity and ρ is the density of the specimen.

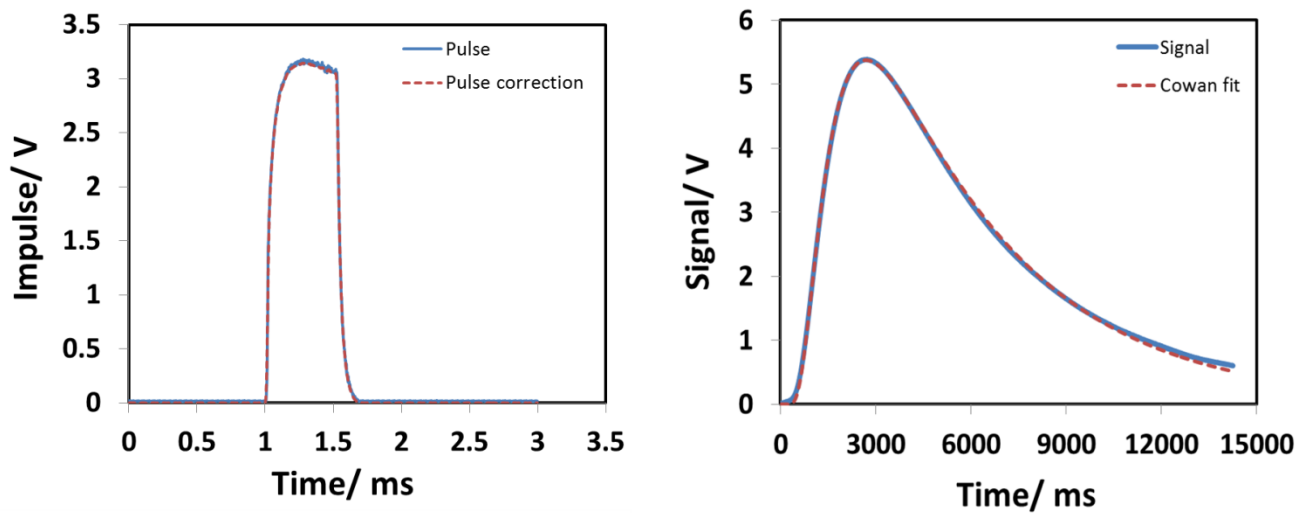


Fig. 34 Examples of curves from the initial laser pulse and the signal detected after the laser crossed the analysed material. Correction curves are automatically elaborated by the software employed.

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4 Porous Silicon Carbide (SiC) Scaffolds

4.1 Introduction

The advance of key technological fields like transportation, building, energy or healthcare depends on the development of novel lightweight porous materials capable of providing exceptional mechanical performance under demanding environments, from high temperatures to corrosive media. Applications such as catalysis supports, filters, separation membranes, thermal insulators, reinforcement of composites, require porous structures able to combine structural stability with high surface area, control of internal fluid flow and tailored thermal or electrical conductivities. Among ceramic materials, silicon carbide presents outstanding mechanical, thermal and chemical properties (such as thermal shock and corrosion resistance) making it a promising candidate for many of these applications, in particular those that involve use under extreme environments [1,2]. The fabrication of porous SiC ceramics requires manufacturing techniques able to provide the required control over the material structure from micro to macro levels and this includes the development of efficient sintering strategies to fabricate strong, stable structures. This is particularly challenging as the presence of a strong covalent bond between the Si and the C atoms that provides the outstanding properties of SiC as a structural material, at the same time results in a very low sinterability due to the low self-diffusion coefficient between the two components, thus making necessary the use of sintering aids [3].

The sintering routes normally used to produce dense SiC are solid [4,5] (SSiC) and liquid phase sintering (LPS) [1,3]. The two processes involve different densification mechanisms, thus requiring different additives, and processing parameters in terms of temperature and firing time. In liquid phase sintering generally different percentages of rare earth oxide elements such as Al_2O_3 and Y_2O_3 have been employed [1,3,6]; in solid phase sintering the most used additives are B and C [5,7] but other formulations are possible such as using AlN, Al_4C_3 - B_4C -C etc. [8]. During LPS the mixture of the additives with the passivating silica layer that coats the SiC particles forms a liquid at the sintering temperature. Matter transport

occurs by atomic diffusion through the liquid phase and densification is derived from the capillary pressure of the liquid film located between the fine solid particles. The liquid phase forms a glassy phase in the final product. Pressureless liquid-phase sintering allows sintering at lower temperature (1800°C to 1950°C) and better mechanical properties have been achieved at room temperature using oxide additives as sintering aids [3,9]. These results can be related to the fact that the glassy phase filling the pores between the particles leads at better densification, thus decrease the number of flaws and defects inside the structure. Increase of fracture toughness up to 100% and flexural strength up to 70% have been achieved in dense SiC sintered by LPS compared with SSiC [10]. However in other studies it has been reported that the presence of these phases at the grain boundary lowers the thermal strength and chemical stability of SiC, thus lowering the working temperature to around 1500°C [11]. It has been also demonstrated that the presence of glassy phases can lower the resistance to slow crack growth [12].

During the solid state sintering of SiC different mechanisms are involved compared to LPS. Atom diffusion occurs at the surface, through the volume or at the grain boundaries without liquid formation. It has been suggested that the addition of C and B to SiC powder reduces the grain boundary to surface energy ratio generating in this way the necessary driving force for diffusional mass transport that favour the sintering [4]. Moreover, it has been hypothesized that C has a de-oxidation effect by reacting with the native silica layer that covers the SiC grains, while B segregates to the grain boundaries reducing their energy [7]. However, much higher temperatures are needed to complete a solid phase sintering of SiC (2000-2100°C). Nevertheless due to the low sinterability of SiC, non-conventional sintering routes such as SPS and the application of pressure have also been largely used to obtain dense SiC minimizing the grain growth and achieving high-density [13,14]. The final microstructures and mechanical properties are strongly affected by the additive formulation, the sintering conditions and the local atmosphere, being always necessary to find a compromise between sintering and grain growth.

As reported by Jennifer Winn [15] and Pujar et al. [6] a significant increase of the densification of compact SiC powder during liquid phase sintering has been achieved by placing the samples in a $\text{Al}_2\text{O}_3/\text{SiC}$ powder bed. It has been suggested that the addition of alumina to the sintering bed generates a sufficient partial pressure of volatile metal sub-

oxides in the sintering atmosphere preventing or limiting the loss of sintering aids, and therefore allowing higher densification. A similar approach has been used in this study to obtain strong SiC porous structures.

The consolidation of complex porous SiC architectures is in fact even more challenging, as it is not possible to apply pressure to promote densification. Some of the available options to produce SiC macroporous structures are based on the use of polymeric pre-ceramic precursors [16,17], wood-derived structures or by the reaction of carbon foams with Si sources [18,19]. These approaches overcome the sintering limitations but provide poor control of the architecture at multiple scale lengths. Previous attempts of using freeze casting, sacrificial templating or robocasting of SiC suspensions [1,20,21] have led to limited densification of the walls and considerable shrinkage. Despite all these efforts, it is still necessary to improve these processing routes in order to produce macroporous SiC structures with controlled morphological features at multiple scale lengths, while optimising the sintering conditions of such structures to obtain high-density walls and high mechanical properties.

Several top-down and bottom-up manufacturing techniques and assembly strategies are being developed in order to design complex and multifunctional devices with controlled microstructure and properties [22–25]. Freeze casting of ceramic suspensions has been shown to be one of the most promising top-down approaches for complex shaping and microstructural control at multiple length scale. Freeze casting uses the complex structure of ice to create monolithic and hybrid materials that exhibit unique bio-inspired hierarchical structures and very promising properties [22]. It is based on the directional freezing of a colloidal suspension at controlled speed to promote the growth of lamellar ice. The growing ice crystal expels the ceramic particles, arranging and compacting them in a lamella between adjacent ice crystals [26]. The control of the freezing process allows tailoring the morphological features of the lamellar structure over a range of size-scales, with the final porous structure being a replica of the original ice crystals.

The aim of this work has been to manufacture high-performance SiC scaffolds with lamellar architectures by freeze casting. These scaffolds can be used to fabricate composites as shown later in chapter 6. In order to develop a sintering route that enables optimum sinterability of SiC grains while preserving the lamellar porous architectures their

consolidation and densification have been investigated by analyzing the effect of temperature, time, and atmosphere under pressureless solid and liquid-phase sintering. The correlation between structure and functional properties are investigated and characterized by combining SEM, TEM, and XRD with mechanical testing, and thermal conductivity measurements.

4.2 Materials and methods

4.2.1 Slurry preparation

For the preparation of SiC scaffolds with lamellar structures α -SiC colloidal suspensions were prepared by mixing 9 and 20vol% of α -SiC particles (ABCR-H.C Starck, Germany) with average particle size (d_{50}) of 450 nm and a specific surface area (BET) of 23-26m²/g in distilled water. For some particular experiments a mixed particle size distribution was used. Smaller β -SiC particles with average size (d_{50}) of 40nm and a specific surface area >80m²/g (**SkySpring Nanomaterials**, USA) were mixed with the normal α -SiC employed in ratio of 30/70 respectively. For the stabilization of freeze casting suspensions the additive formulation was: 1.4wt% of TMAH (Tetra-methyl-ammoniumhydroxide, Sigma-Aldrich, USA) as dispersant, 1.4wt% PVA as binder (poly-vinyl-alcohol, PVA 22000, VWR, Belgium), both related to the particle content, and 4wt% of sucrose (related to the water content) as ice shaping agent (Anala R Normapur, VWR, Belgium) [27].

For liquid phase sintering, 8wt% of Al₂O₃ (Baikalox B-series SMA6, Baikowski, France) and Y₂O₃ (Grade C- ABCR – H.C. Starck) powders (60/40 weight ratio) related to the amount of SiC powder were added to the suspension [1]. For solid phase sintering, 0.35wt% of Boron (Merck KGaA, related to SiC amount) was added and the additives (PVA and sucrose) acted as the carbon source. The used compositions are reported in Table 1. The suspensions were ball milled at 300rpm (Capco test equipment, 12VS, UK) for 20h with SiC balls (10mm in diameter) and afterwards de-aired for at least 30 minutes with a vacuum pump to remove air bubbles.

Table 1 Additives and sintering aids in wet processing of macroporous SiC scaffolds.

	Processing additives	Solid Sintering Aids (SS)		Liquid sintering aids (LPS)
		Boron	Source of C	
Freeze casting	1.4wt% TMAH (dispersant) 1.4wt% PVA (binder) 4wt% sucrose (related to the water content) @pH 10	0.35wt %	PVA+ sucrose	8wt% of an oxide mixture (6/4 wt% $\text{Al}_2\text{O}_3/\text{Y}_2\text{O}_3$)

The suspensions were then directionally frozen using a freeze caster imposing cooling rates at the cold finger of 5 and 15°C/min. The freeze-casted scaffolds were freeze-dried for 24 hours (Freezone 4.5 by Labconco, USA) and subsequently sintered.

4.2.2 Rheology

The flow properties and viscosity of SiC suspensions were measured in a Discovery Hybrid Rheometer HR1 (TA Instruments). The flow experiments were carried out with a cone-plate ($\varnothing=60$ mm, cone angle $\theta=2^\circ$, truncation=58 μm) and a solvent trap cover. The viscosities of the suspensions were evaluated imposing a shear rates ranging from 0.1 to 1000 s^{-1} . All the tests were run at room temperature.

4.2.3 Sintering

A sintering study was carried out in order to determine the optimum sintering conditions to fabricate strong structures while preserving the lamellar architectures and avoiding exaggerated inter-lamellar grain growth. Pressureless sintering at different conditions (Table 2) took place either in a conventional or SPS graphite furnaces. Liquid and solid phase sintering were compared in both furnaces. These sintering studies were conducted with scaffolds obtained with 20vol% solid loading.

The sintering was also analyzed by following the shrinkage of dense pellets of the bulk powders mixed with the sintering aids in the SPS under vacuum, and in a dilatometer (Netzsch DIL402C) under Argon. For the SPS pellets the powders were cold pressed in a 20mm diameter graphitic die at 32MPa (HPD 25/1 FCT System, Germany). These pellets were subsequently sintered under vacuum at a heating rate of 200°C/min and a minimal constant pressure of 20MPa up to 2000°C. Cylindrical pellets of 15mm length and 5mm in diameter were isostatically pressed (~ 300MPa) and tested in argon in the dilatometer up to 2000°C with a heating rate of 20°C/min using a graphite rod and furnace. In both cases the displacement of the plunger vs. temperature during heating, is used to identify the temperature range at which densification takes place.

The porous scaffolds were pressureless sintered under vacuum during 8 minutes in the SPS. The heating and cooling rates were 200°C/min and 150°C/min respectively. In the conventional graphite furnace, the scaffolds were fired in an inert atmosphere (Ar) with a heating rate of 6°C/min up to 600°C, held for 2 hours for de-binding, followed by a heating ramp at 20°C/min up to the maximum temperature (Table 2), cooling rates were fixed at 20°C/min. To enhance densification a two-step sintering approach was also tried both in SPS and conventional graphite furnace [28].

In order to study the effect of the powder bed during the sintering [15] some LPS scaffolds were placed on top of a powder bed composed of SiC and alumina powder (96wt% SiC + 4wt% Al₂O₃ inside of a closed graphite crucible. The amount of packing-bed powder was fixed at 5 times the weight of the green body).

Table 2 Summary of sintering conditions used in this study

Liquid phase sintering						
Furnace	Method	Activation Temp. (°C)	Temp. (°C)	Holding time	Aids	Powder Bed
Graphite	Conventional	--	1800	2 h	A+Y	--
		--		3 h		--
		--	1850	2 h		--
		--	1900			--
		--	1800			96%SiC 4%Al ₂ O ₃
	Two-steps	1900	1750			--
		1900	1800			--
SPS	Conventional	--	1800	8 min	A+Y	
		--	1800	8 min	A+Y	96%SiC 4%Al ₂ O ₃
Solid phase sintering						
Graphite	Conventional	--	2000	1h	B+C	--
SPS	Conventional	--	1870	8 min		
		--	1920			
		--	1970			
	Two-steps	2057	1870	--		
		2112	1920	--		

4.2.4 Structural and mechanical characterization

The microstructure of the materials was analysed via scanning electron microscopy (SEM, Leo Gemini 1525). Microstructural features such as lamella and pore sizes were evaluated directly on SEM images of the microstructures (~200 measurements were considered). Transmission electron microscopy (TEM, Fei Titan 80/300) was used to analyse LPS samples; STEM-HAADF and EDX to identify different phases within the structure. The Archimedes method (Sartorius, YDK01, Goettingen, Germany) was used to determine their density and porosity. Phase composition analysis was performed by X-ray diffraction (XRD, PAN-analytical, Almelo, Netherlands). Scan data were collected with CuK α ($\lambda=1.54178$ Å) radiation at a step size of 0.1° and 150s for step.

Compression and bending tests were performed on a universal testing machine (Zwick/Roell 1474) with a load range up to 100kN. The compression test was done following the ASTM C133 [29] standard with crosshead speed of 1.3mm/min. In order to homogeneously distribute the load during the compression tests, a stainless steel semi sphere was placed at the top of the samples. The 4-point bending tests were performed following the ASTM C1161 [30] at crosshead speed of

0.2mm/min. For each material, 10 to 20 specimens measuring approximately $5 \times 5 \times 5 \text{ mm}^3$ (for compression) and $20 \times 2 \times 3 \text{ mm}^3$ (for bending) were cut from a ceramic part with a diamond disk and grinded to ensure parallel surfaces.

The thermal diffusivity of the samples was measured using a Netzsch LFA 427 - Laser Flash Apparatus, at temperatures between 30°C and 1500°C. A short energy pulse heated up the bottom surface of the sample, while the temperature on the upper surface was measured and monitored with an infrared detector. The specimens were coated with graphite emulsion. A laser voltage of 450V and a pulse width of 0.8ms were used. The thermal diffusivity was measured in argon atmosphere, using a heating rate of 10°C/min. Between 3 and 5 measurements for each temperature were carried out. The “Cowan+pulse correction” diffusivity model was used for the processing of the experimental data. The thermal conductivities were calculated with Proteus®Software, using the acquired data of thermal diffusivity, specific heat and density of the samples.

4.3 Results

4.3.1 Freeze casting of porous SiC structures

SiC suspensions with concentrations of 9 and 20vol% and stabilized with TMAH exhibited nearly Newtonian behaviour with very low apparent yield stress ($<0.2 \text{ Pa}$ for both cases) and viscosities of 0.003 and $0.012 \text{ Pa}\cdot\text{s}$ (at 100 s^{-1}) respectively (Fig.35b). The stability of the suspensions was studied with sedimentation tests at different times (1 min, 1h and 1day) (Fig.35a). Both suspensions were stable within 1 hour but some sedimentation occurred after 1 day, especially for low concentrated suspensions.

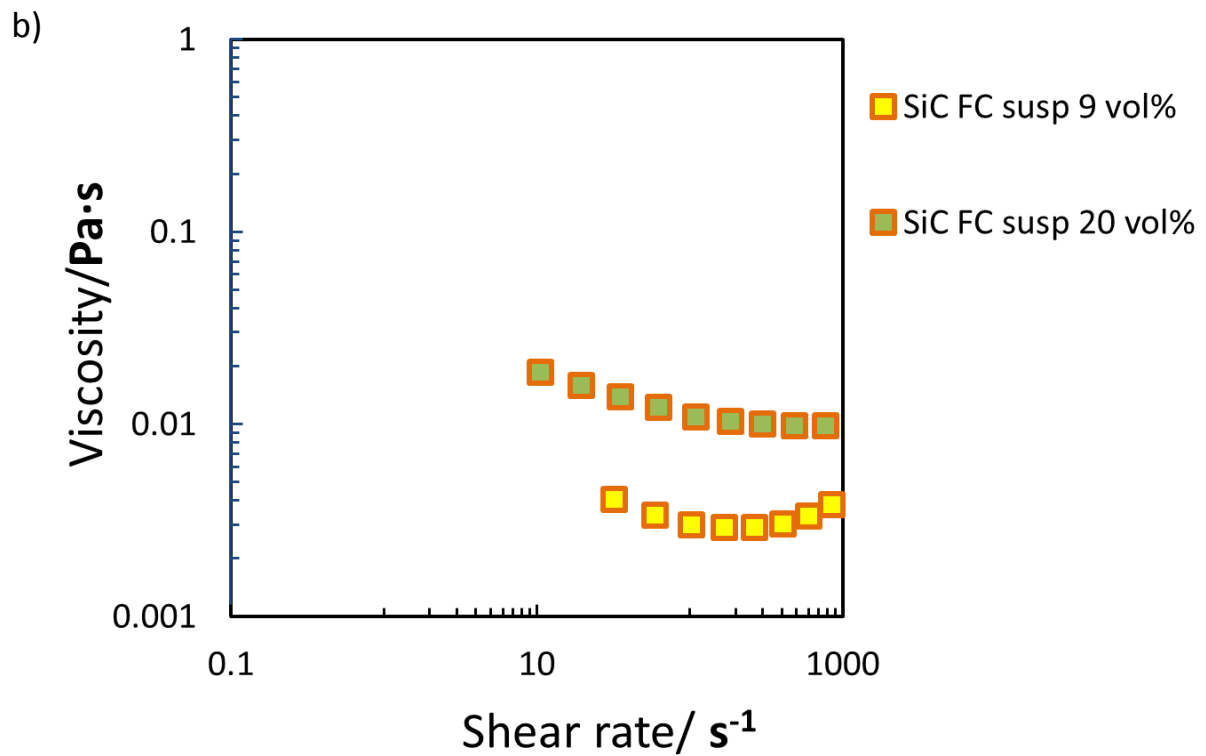
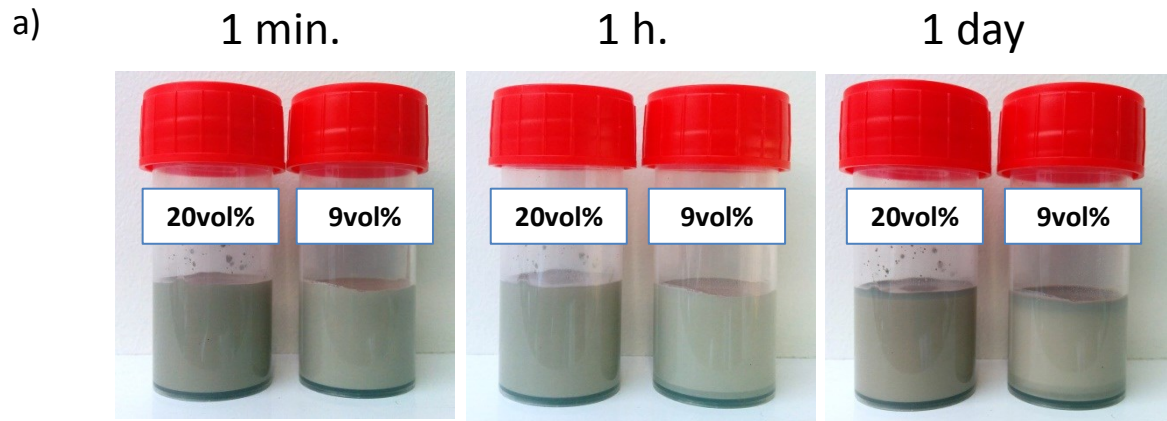


Fig. 35 a) Sedimentation study of SiC nanoparticles suspensions. Time points at 1 min., 1hr., 1 day. b) Rheological behaviour of SiC suspensions, viscosity vs. shear rate graph shows that freeze casting suspensions are nearly Newtonian.

Freeze casting of SiC suspensions generated lamellar structures highly interconnected by thin bridges and characteristic surface roughness in their walls. The freezing speed influences the developing microstructure. The faster the freezing speed the finer is the final microstructure (Fig.36b) which is in agreement with the tendency found previously in other

studies [26]. The freezing rate imposed at the cold finger is directly related to the speed of the advancing ice-front inside the SiC ceramic suspensions, that also varies with the suspension properties (for example solid loading and thermal conductivity). A transparent mould made of Perspex was used to follow the ice-front tip growth in the 20vol% suspension (Fig.36a) [31]. The speed of the freezing front varied between 13 and 27 $\mu\text{m/s}$. At the higher freezing speed 15°C/min the employed freeze caster imposed a precise cooling rate down to -100°C. At lower temperature ($T < -100^\circ\text{C}$) the actual experimental freezing rate was lower than the programmed one. At -100°C the samples were almost completely frozen, therefore the ice crystals already impose within the scaffolds their shaping effect.

The manipulation of the freezing rate between 5 and 15°C/min led to a change of the average lamella and pore size (d_{50}) from 30 to 9 and 37 to 12 μm , respectively.

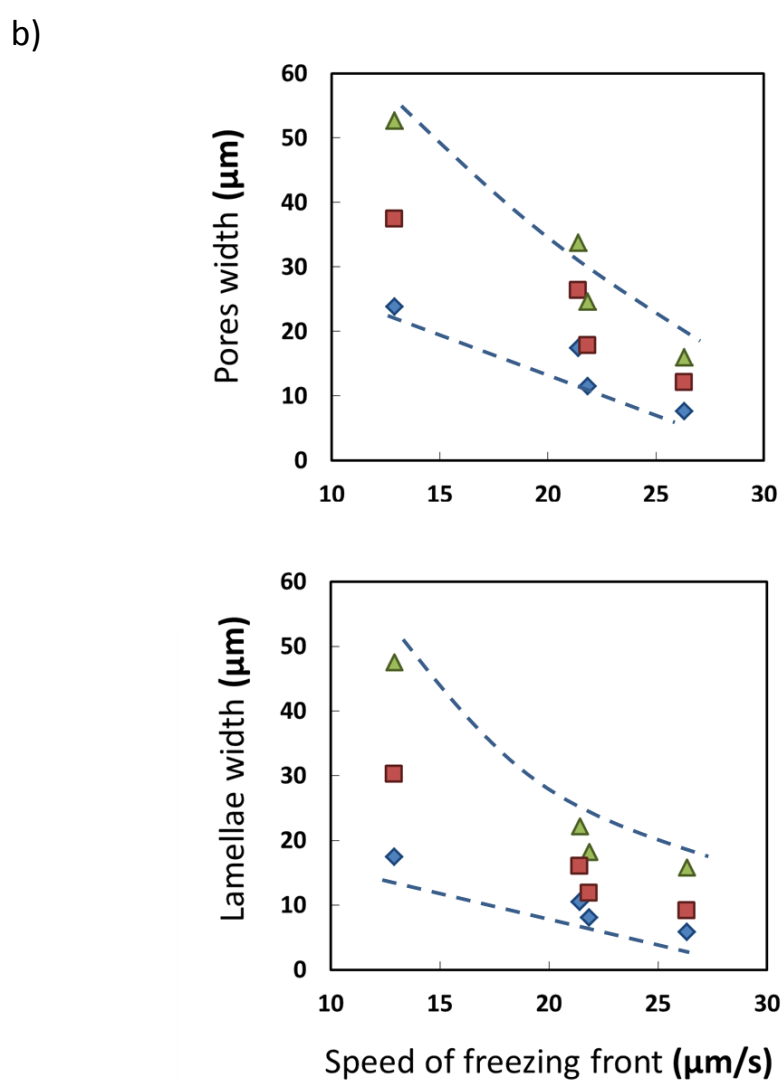


Fig. 36 a) Perspex mould used to measure the freezing speed; b) Effects of freezing front speed on lamellae and pore size. The measurement was performed on an SSiC sample with 20vol% of ceramic loading sintered at 1950°C after epoxy infiltration. The analysis was not repeated on the sample obtained with optimum sintering conditions. The values d10 d50 and d90 are related to the cumulative distribution of lamella thickness. 10% of the walls have a thickness $\leq$ of d₁₀; 50% of the walls have a thickness $\leq$ of d₅₀; 90% of the walls have a thickness $\leq$ of d₉₀.

Green lamellar scaffolds with relative density ranging from 0.1 to 0.2 prepared from suspensions with a 20vol% and 9vol% solid loading respectively were used to analyze sintering. Although the SiC powder used has a wide particle size distribution (Fig.37) their faceted shape does not facilitate optimum packing in the lamellae walls causing low green densities. As an alternative SiC suspensions with mixed particle size distributions (particles with average size of 450nm plus particles with average size of ≈ 40 nm, in a ratio of 70/30wt %) were also freeze-casted. This provided better particle packing in the walls of the green structures, but also affected the freezing pattern leading to less aligned structures with more domains (Fig.38).

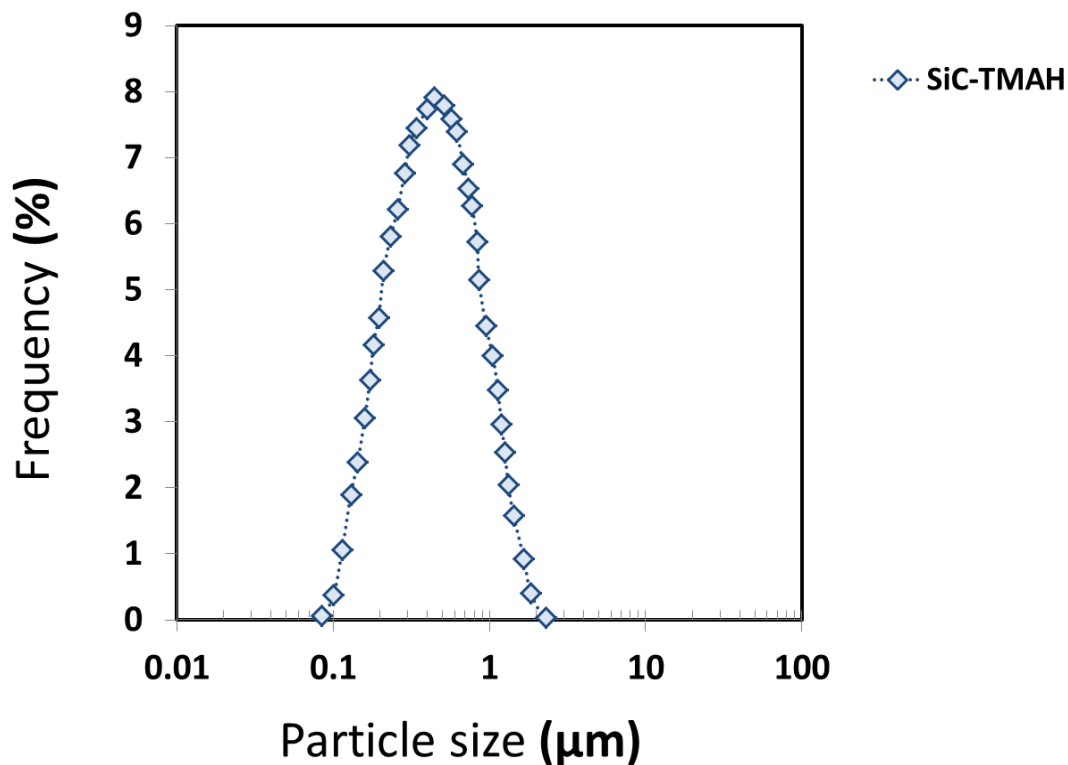


Fig. 37 Particle size distribution of 450nm SiC dispersed with TMAH after 1 day of milling.

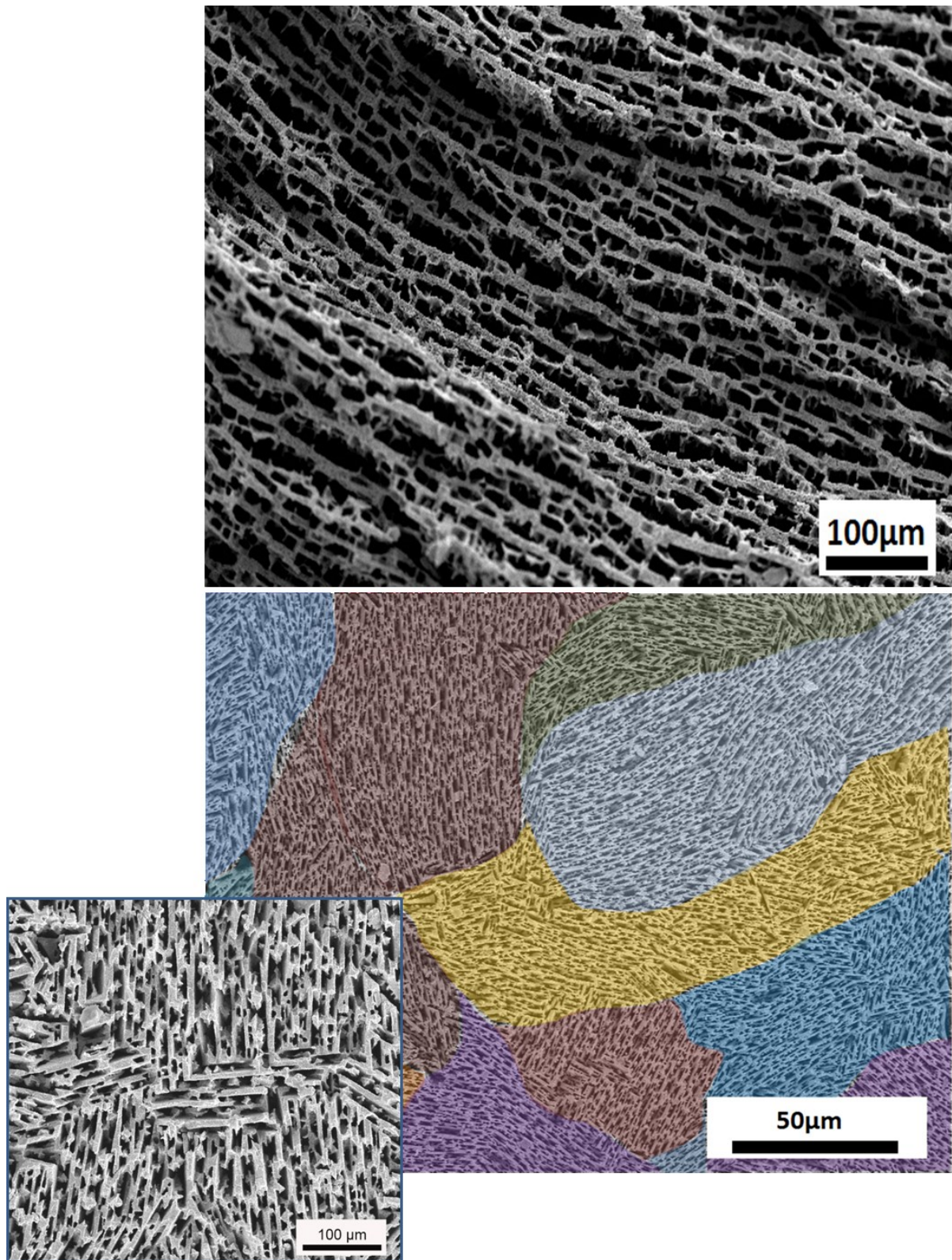


Fig. 38 On top, sample obtained with single particle distribution and below microstructure of a sample obtained with a mixed particles size distribution. The two pictures have different magnification, 100x and 50x respectively. In the latter case, better densification is achieved but many domains are formed during freezing. The pictures shown are of the samples after sintering.

4.3.2 Sintering

Solid phase sintering of porous SiC either in the conventional graphite or SPS furnaces resulted in very limited wall densification. Temperatures of 2000°C and above led to exaggerated grain growth (Fig.39). Firing in a conventional graphite furnace led to the formation of hexagonal SiC platelets up to 20 µm in length in the lamellae walls that grow in the spacing between them (Fig.39). The lack of sintering between the platelets resulted in highly interconnected porosities (relative densities up to 0.18 with 76% open pores) and poor consolidation. The highest density achieved was 0.71 g/cm³ (0.22 relative density).

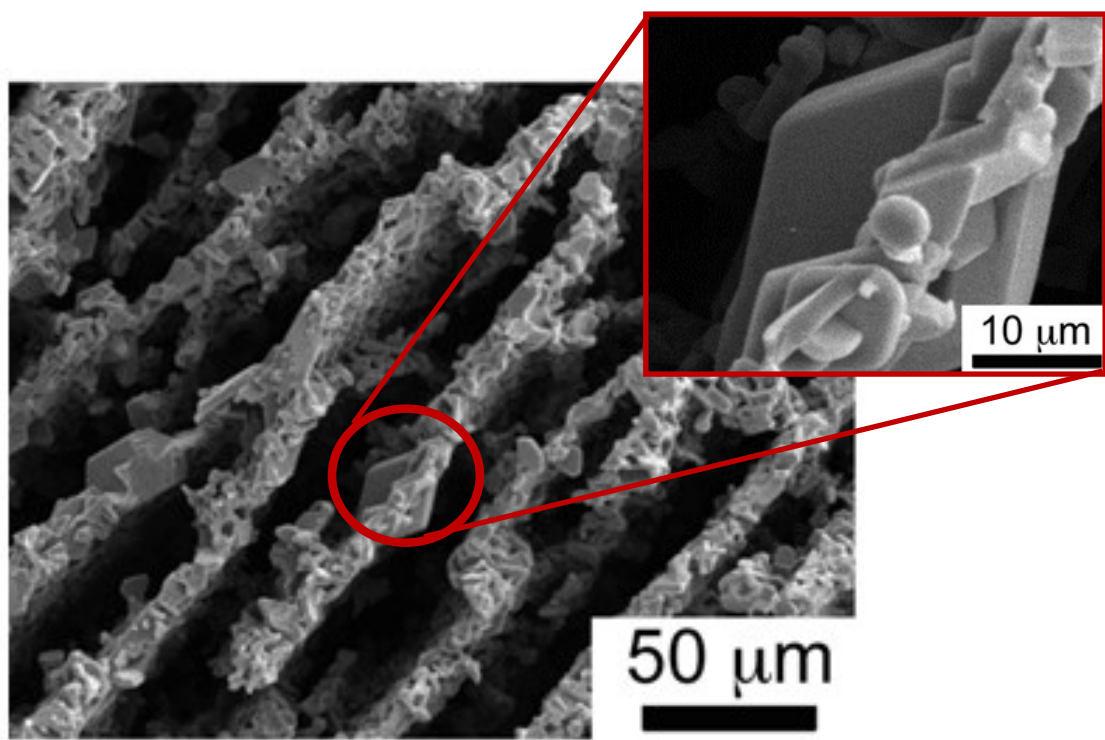


Fig. 39 SSiC in conventional graphite furnace at 2000 °C.

In order to try to reduce grain growth and enhance lamellae densification an attempt was made to identify the optimum solid state sintering temperature by monitoring the movement of the piston while bulk powders were sintered in the SPS under the initial working pressure of 20MPa. The powders sinter at around 1920°C (Fig.40). A sintering window of ±50°C above and below this temperature was fixed to investigate the temperature effects on the final microstructure. However, although SPS prevented grain growth, low densification was reached inside the lamellae walls for all temperatures

(Fig.41). Moreover the samples showed some structural inhomogeneity and often loss of lamellar organization.

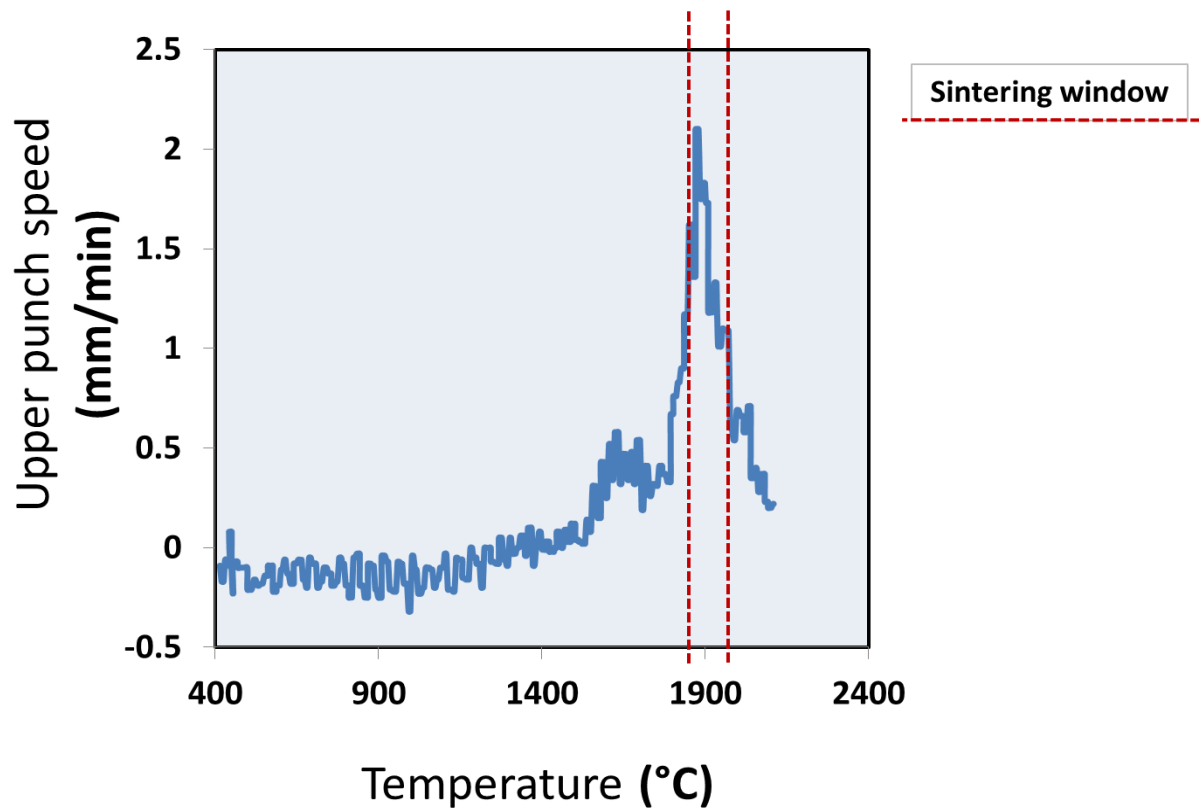


Fig. 40 Densification of powder pellet in SPS. The movement of the piston is reported versus the temperature. Significant movement was recorded at the temperature at which the powder sinters.

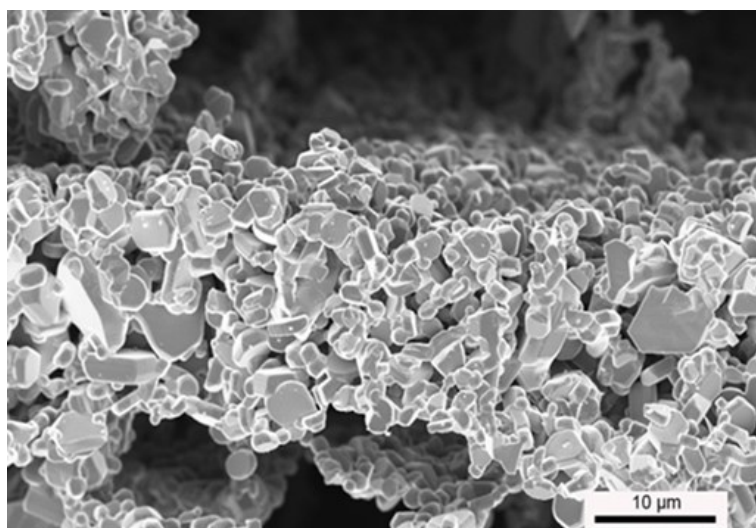


Fig. 41 SSiC in SPS at 1970 °C.

A two-step sintering approach in the SPS was tried [28] to enhance diffusional processes at the SiC grain surfaces in order to activate their sinterability while preventing grain growth. The green SiC scaffolds were first subjected to a temperature peak (at 10% more of chosen sintering temperature for 10s) and subsequently cooled down to the sintering temperature for 8 minutes (Table 2). This sintering approach did prevent grain growth but did not result in significant densification of the lamellar structure. The mechanical strength after SPS sintering was not significantly higher compared to the green state (relative and absolute density of 0.21 and 0.68g/cm³ respectively, similar to the green state). SiC freeze casted scaffolds sintered at 1920°C by SPS (with activation at 2112°C) showed some improvement in the sintering between particles but in concurrence with grain growth.

Liquid phase sintering has been considered as alternative route. Dilatometry showed that the sample started to densify at a temperatures below 1600°C (melting temperature of the sintering additives) and total densification was achieved above 1800°C (Fig.42). Improved consolidation and limited grain growth were achieved with liquid phase sintering in a conventional graphite furnace (Table 2). Samples sintered at 1800°C for 2h with a heating rate of 15°C/min under Ar flow, showed a good degree of consolidation at macroscopic level but structural analysis revealed a high volume of pores in the walls (relative and absolute density of 0.29 and 0.94g/cm³ respectively). Increasing the sintering temperature to 1900°C led to significant grain growth, with big hexagonal SiC platelets extended between the lamellae and walls (Fig.43) (relative and absolute density of 0.31 and 1.0g/cm³ respectively).

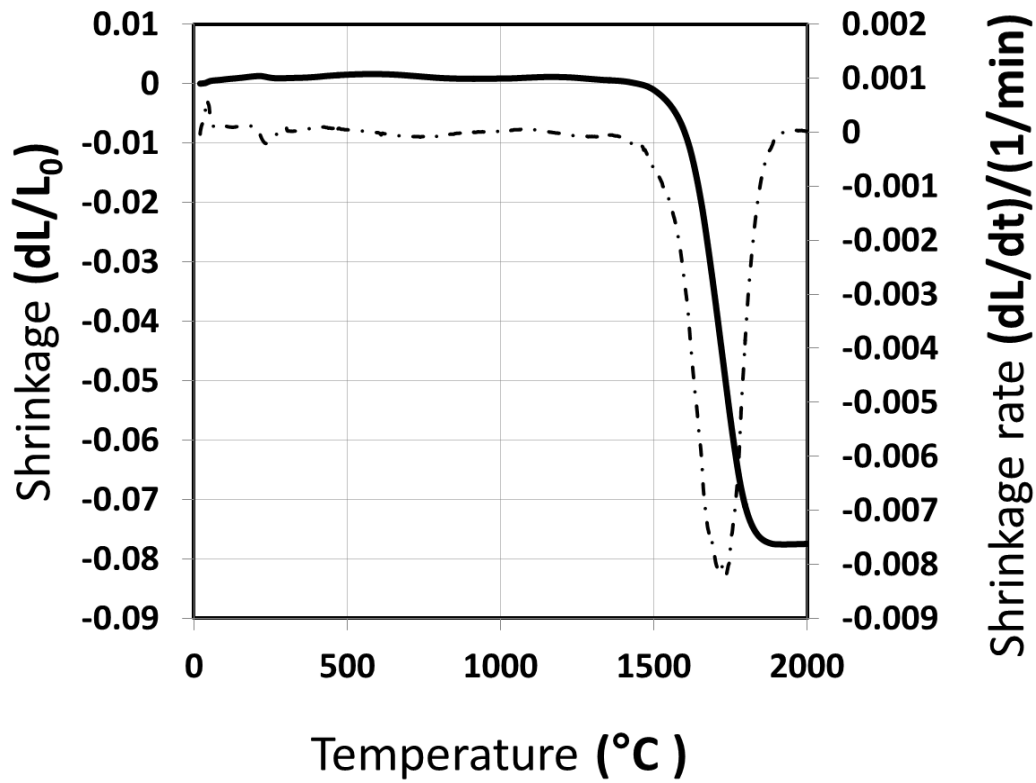


Fig. 42 Dilatometer of LPS SiC.

By increasing the firing time at 1800°C up to 3h, grain growth was limited but no significant improvement in densification was achieved (relative and absolute density of 0.33 and 1.08g/cm³ respectively).

Two-step sintering, with an activation peak at 1900°C (Table 2) led to some improvement in the densification (relative and absolute density of 0.38 and 1.14g/cm³ respectively).

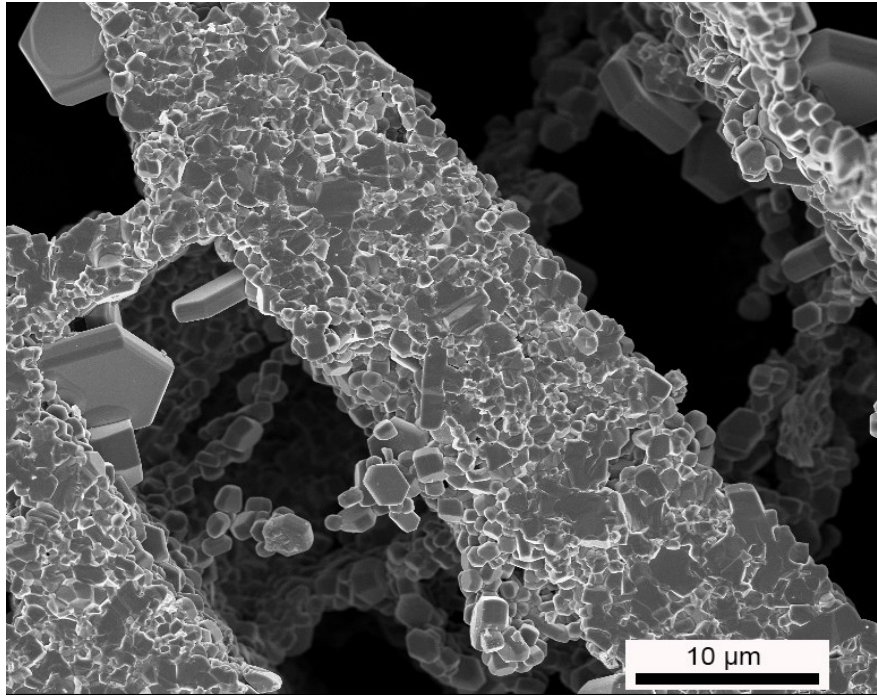


Fig. 43 LPS in conventional graphite furnace at 1900 °C.

Higher and significant densification was achieved instead when 4wt% of alumina was added in the SiC powder bed used during the firing process. Higher amounts of alumina in the powder bed did not significantly improve the sintering. Porous structures sintered following this route (1800°C for 2h, on top of a SiC powder bed with 4wt% of Al_2O_3) showed the highest densification while keeping the lamellar structure at microscopic level (Fig.44). At the macro scale, samples have good mechanical integrity and can be easily cut and polished. The lamellae in the freeze casted scaffolds are highly dense, with a relative density of 0.44 (absolute density of $\sim 1.4\text{g/cm}^3$), while the whole structure is preserved.

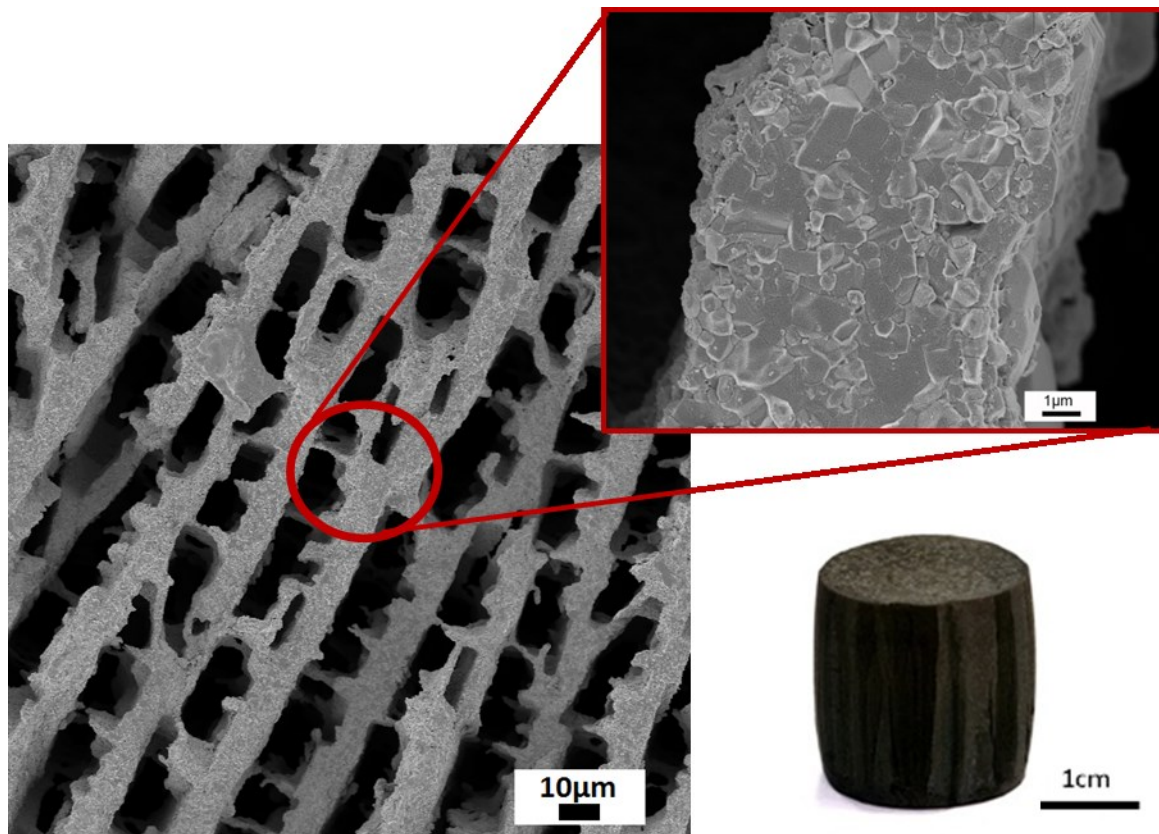


Fig. 44 LPS of a 20vol% scaffold at 1800 °C using 4wt% of Al₂O₃ in the powder bed.

4.3.3 Structural characterization

The freeze casted scaffolds obtained from SiC suspensions with 9vol% solids (Fig.45), frozen at 5 and 15°C/min, showed a final relative density of 0.24 (0.76g/cm³) and 0.26 (0.81g/cm³) respectively. An increase of the solid loading up to 20vol% increases the relative density to 0.43 (1.38g/cm³) and 0.44 (1.42g/cm³) that correspond to a residual porosity of 56.6% and 55.7% in samples frozen at 5 and 15°C/min respectively. Samples with 9 and 20vol% solid loading shrink an average of 26% and 23% respectively in the freezing direction (related to the initial green dimensions). Faster freezing rates resulted in thinner lamellae and smaller pores for both suspensions (Table 3).

Table 3 Lamella and pore average sizes at changing solid loading and freezing rate. Values obtained by image analysis.

	Lamella size (μm)		Pore size (μm)	
	5°C/min	15°C/min	5°C/min	15°C/min
9 vol%	3.6 ± 1.0	3.1 ± 0.8	15.5 ± 4.9	13.0 ± 3.9
20vol%	12.3 ± 2.2	9.4 ± 1.5	14.9 ± 2.6	12.7 ± 3.3

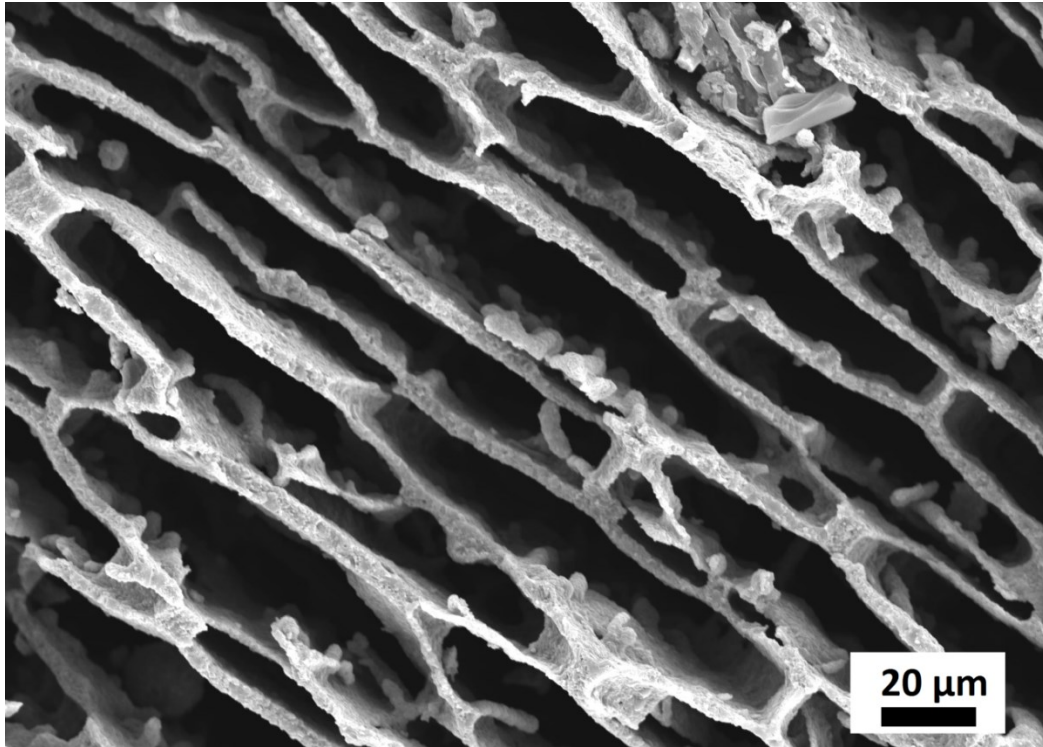


Fig. 45 LPS of a 9vol% scaffold at 1800 C using 4wt% Al₂O₃ in the SiC powder bed.

4.3.4 Composition

XRD analysis was done on the best sintered scaffold. Hexagonal 6H-SiC was identified along with secondary phases, such as Y₃Al₅O₁₂ (YAG) and Al₂O₃ (Fig.46). These results match with those obtained by transmission electron microscopy. TEM images revealed different secondary phases (with a size of 100-600nm and irregular shape) homogeneously distributed in between the SiC grains. Two different phases were identified by EDX: the first and more frequently found contains Al, Y and O with an atomic ratio Al/Y~1.7 (the brightest phase in the HADDF image, Fig.47a), and the second containing Al and O (with lower contrast in Fig.47a). Micro-diffraction patterns of the two phases confirmed that they are

single crystalline $\text{Al}_5\text{Y}_3\text{O}_{12}$ and Al_2O_3 respectively, in agreement with the XRD results. The grain boundaries between these secondary phases and SiC grains were clean and had an ordered structure (Fig.47b). At SiC grain boundaries, no thick equilibrium glassy film was found though small degree of disorder was observed (Fig.47c). EDX experiment shows that these types of grain boundaries are rich in Al and Y but deficient in Si. Finally glassy pockets rich in Al and O were found at some the triple junctions between the secondary phase and SiC grains (Fig.47d).

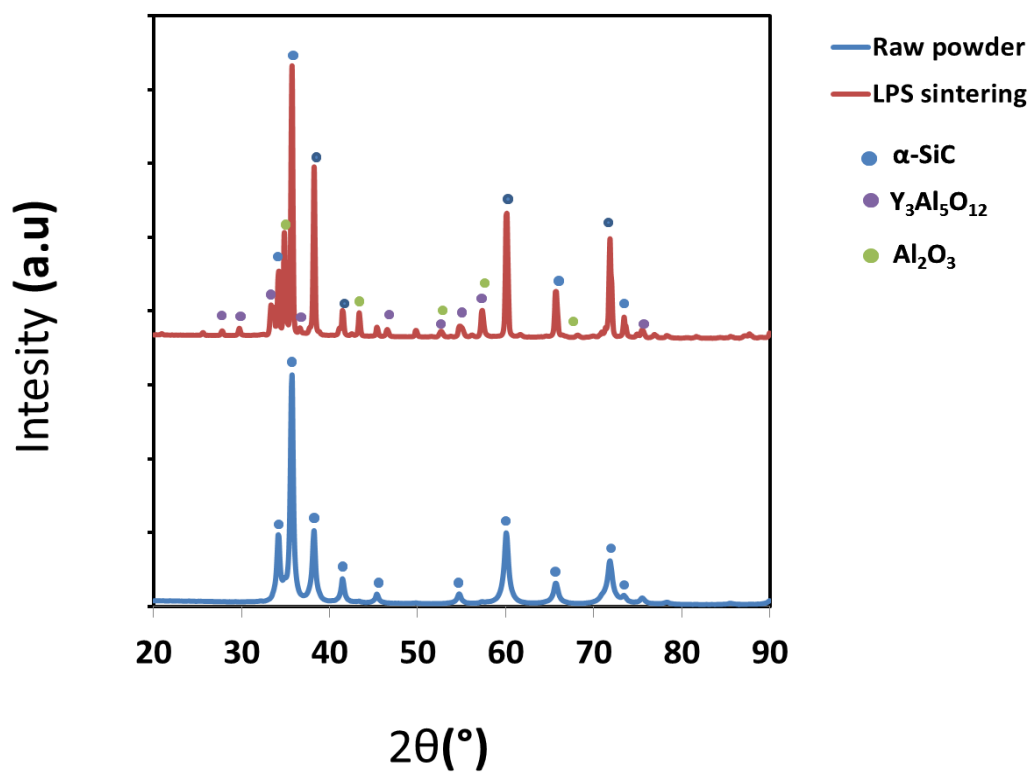
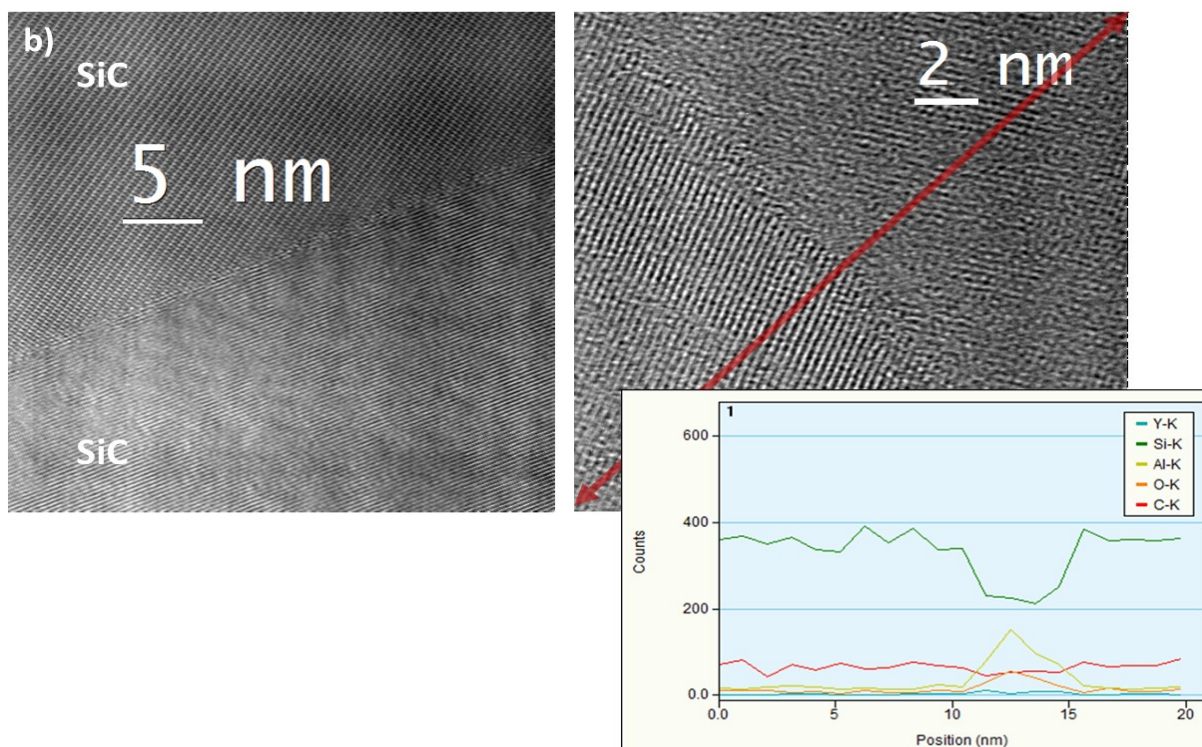
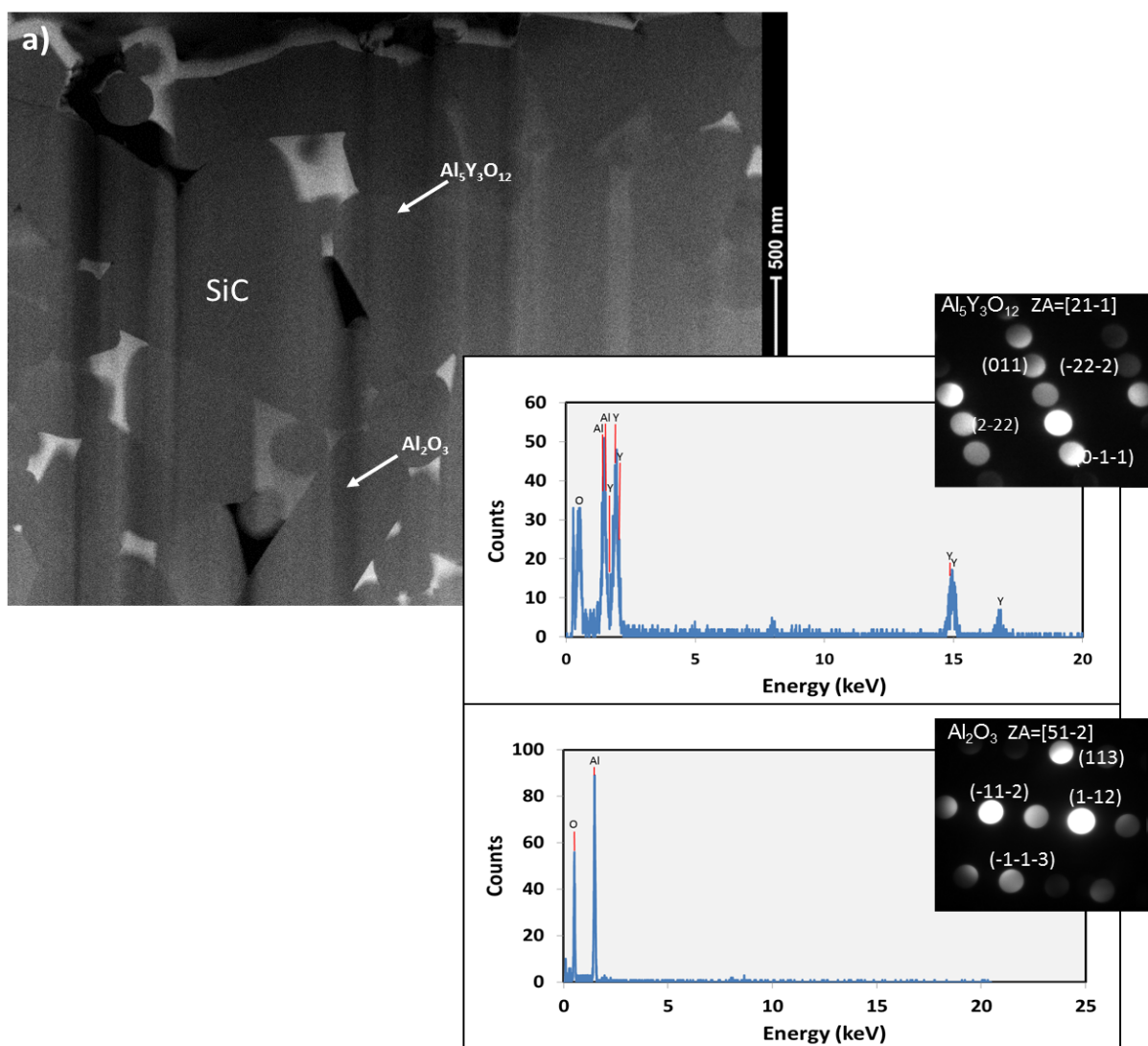


Fig. 46 XRD spectrum of raw SiC powder and LSP scaffold.



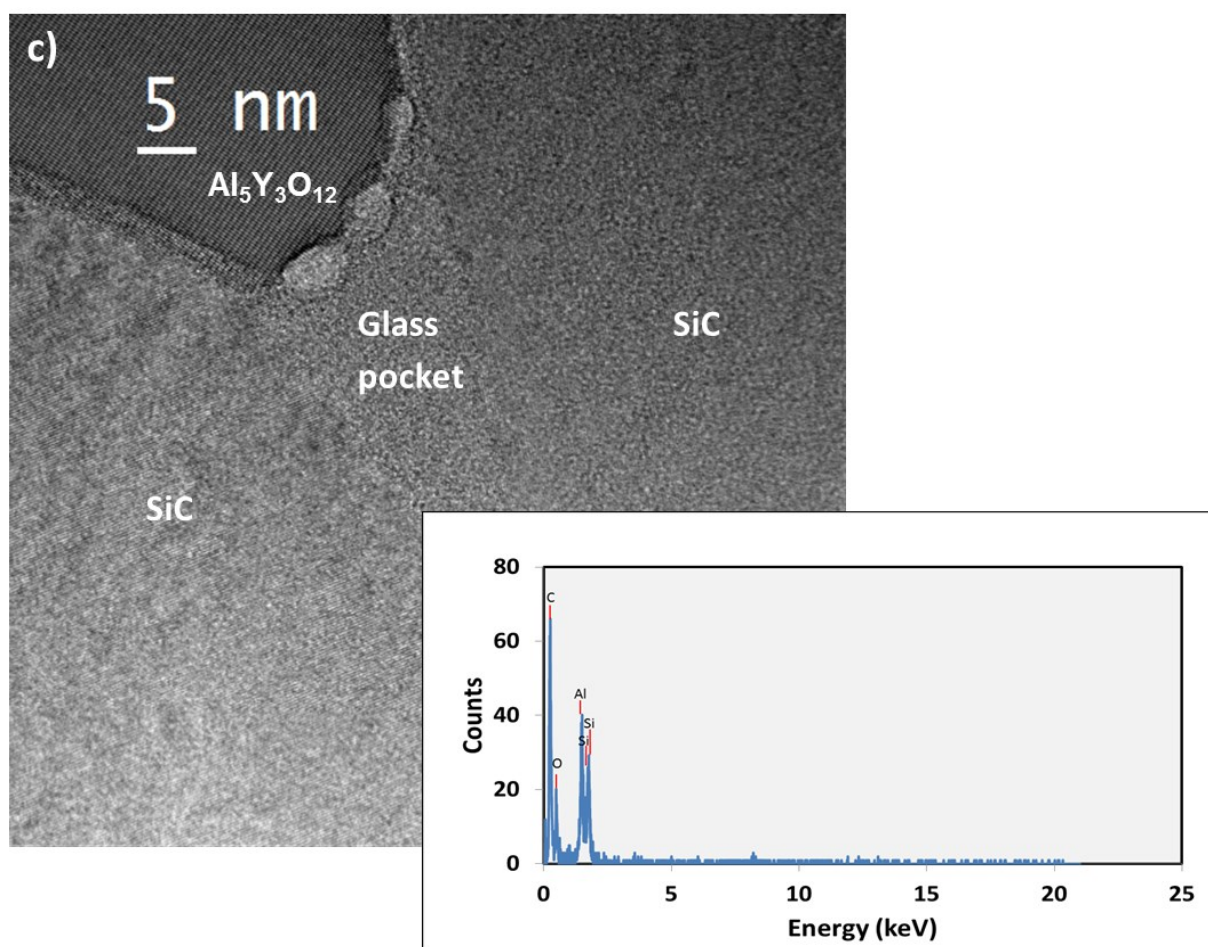


Fig. 47 TEM images of LPS silicon carbide. The analysis was done by Dr. Na Ni. a) STEM-HAADF image where the contrast is proportional to the atomic mass of the phase. Darkest grains are SiC and brighter phases are secondary phases with the brightest ones containing Al-Y-O and the less bright one Al-O. EDX and indexed micro-diffraction patterns for these two phases are shown. b) HRTEM micrograph of a typical grain boundary between the SiC and the secondary phase ($\text{Al}_5\text{Y}_3\text{O}_{12}$); c) HRTEM of a typical SiC grain boundary and corresponding EDX elemental line profile obtained in STEM across the same grain boundary; d) The glass pocket at SiC and $\text{Al}_5\text{Y}_3\text{O}_{12}$ triple junction. The EDX obtained from this glassy phase is shown.

4.3.5 Mechanical properties

Table 4 summarizes the mechanical properties for the freeze cast samples obtained under optimum sintering conditions. Loading direction and processing settings affected the crushing strength of freeze casted structures. Faster freezing rates (from 5 to 15°C/min) and higher solid contents led to higher values of compressive strength. Also, lamellar structures prepared from suspensions containing double particle size distribution exhibited higher crushing strengths up to 280MPa.

Table 4 Summary of mechanical properties of freeze cast SiC samples

	Freeze casting				
	9vol%		20 vol%		20vol% (double particle size)
	5°C/min	15°C/min	5°C/min	15°C/min	5°C/min
Compressive strength (MPa)	22±3	33±6	107±13	135 ± 23	264±15
Flexural strength (MPa)	10±2	13±3	40±16	37±18	N.A.

The stress initially increased with the strain up to the maximum crushing strength. Afterward the scaffold started to gradually fail, consequently the stress progressively decreased, but the structure failure was not catastrophic (Fig.48).

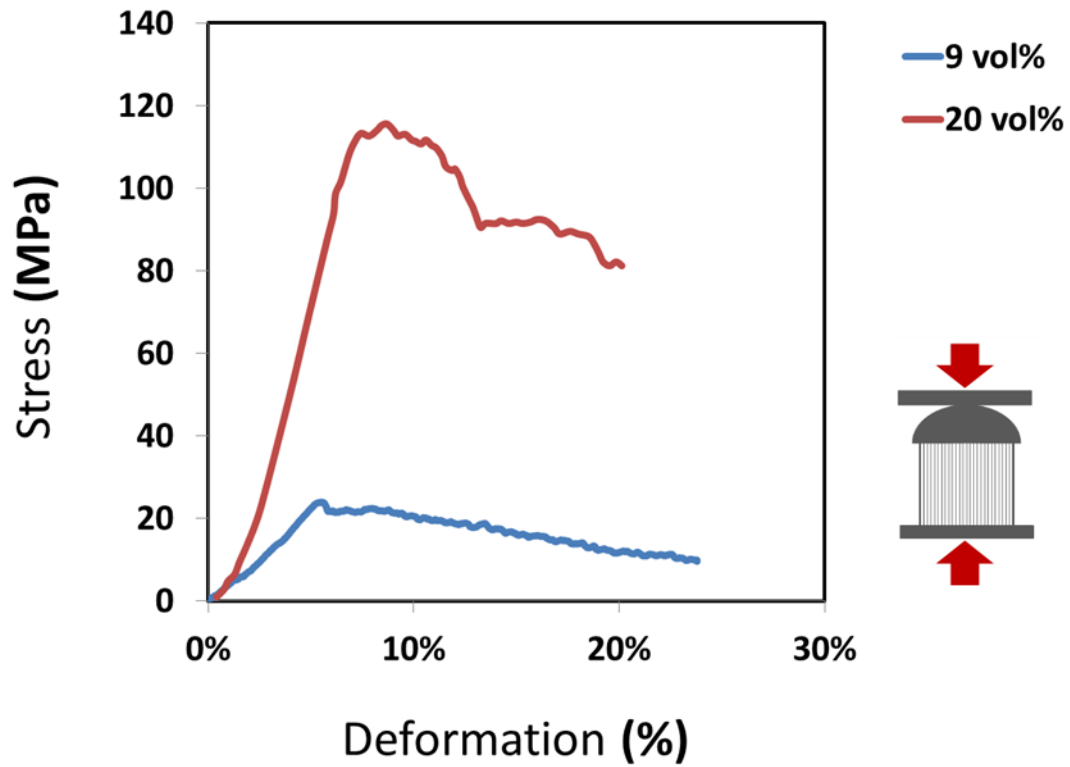


Fig. 48 Crushing strength of LPS scaffolds. Stress and deformation curve for samples obtained with 9 and 20vol% are reported.

A less significant dependence with the freezing rate was observed for bending strengths. Stress-deformation curves show a short linear elastic region before critical crushing showing values similar to other materials found in literature [18]. Nevertheless, flexural strength for freeze casted scaffolds with lower solid content is not reported for inconsistency of the mechanical test. In these cases, due to their high porosity, the bars crushed in the contact points with the loading fixture rods, and the resulting deformation zone acted as starting points of cracks that lead to the failure of the samples (Fig.50). The bending curve is nevertheless reported (Fig.49) to show the significant deformation recorded.

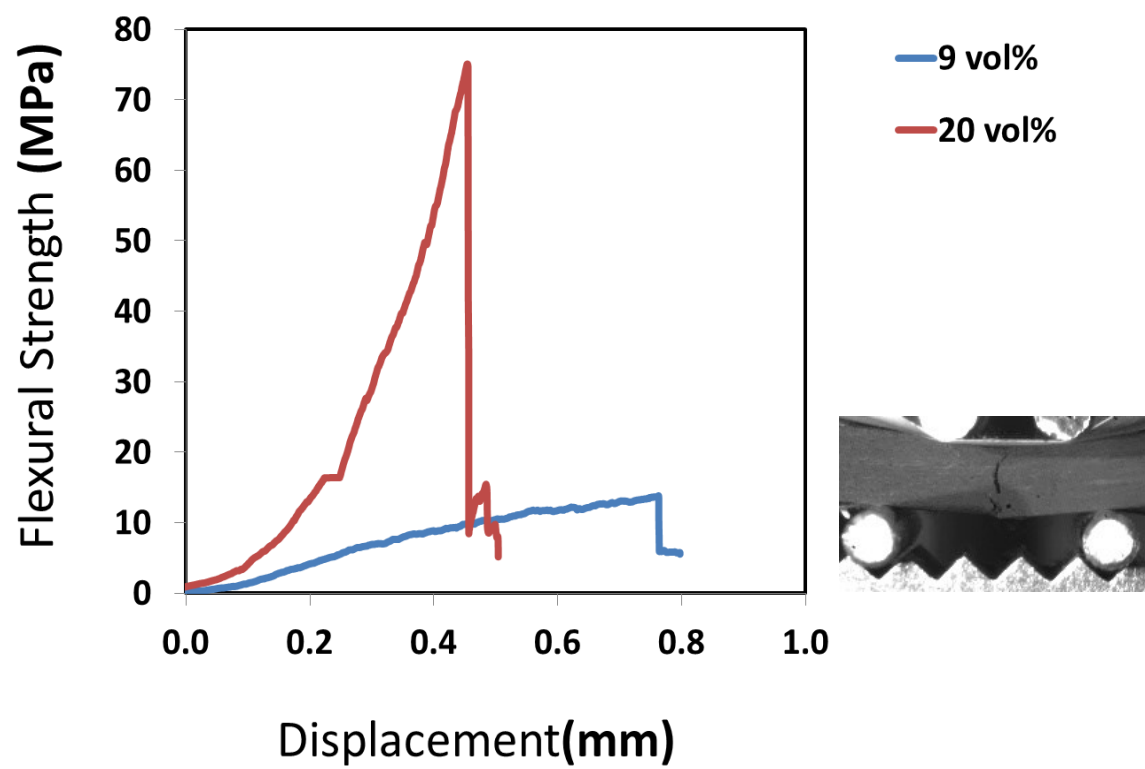


Fig. 49 Bending test curve in 4PB of SiC bars.

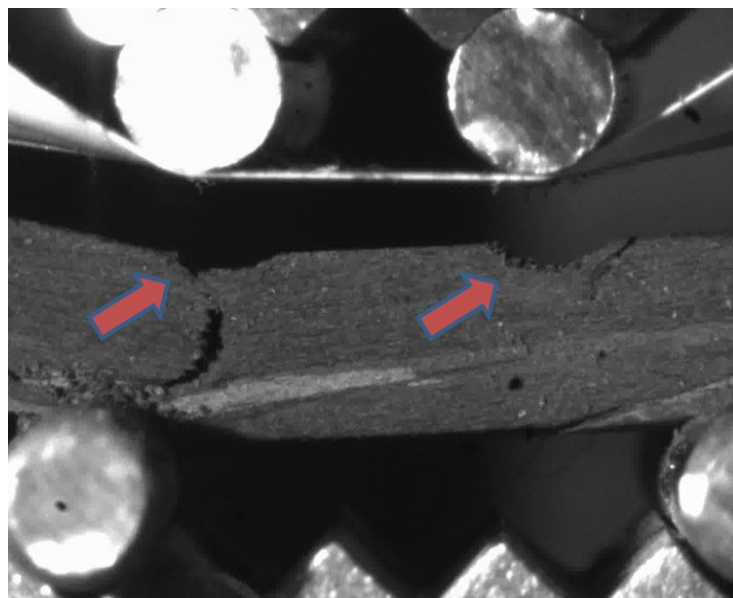


Fig. 50 Low solid loading sample deformed under bending test.

4.3.6 Thermal conductivity

Scaffolds prepared with different solid loadings and freezing rates were measured along the two main anisotropic directions (parallel and perpendicular to the freezing direction). In general, thermal conductivity values decreased with increasing porosity due to the air trapped into the porous structures (Fig.51). A slight increase of thermal conductivity was observed for scaffolds frozen at faster rates. A significant decrease is observed when the thermal conductivity was measured perpendicular to the freezing direction. For all samples the thermal conductivity showed a gradual decrease with the temperature up to 1500°C. Calculations were performed using a specific heat (C_p) given by the following equation [32]:

$$C_p = 1.267 + 0.049 \cdot 10^{-3}T - 1.227 \cdot 10^5 T^{-2} + 0.205 \cdot 10^8 T^{-3} \quad (4.1)$$

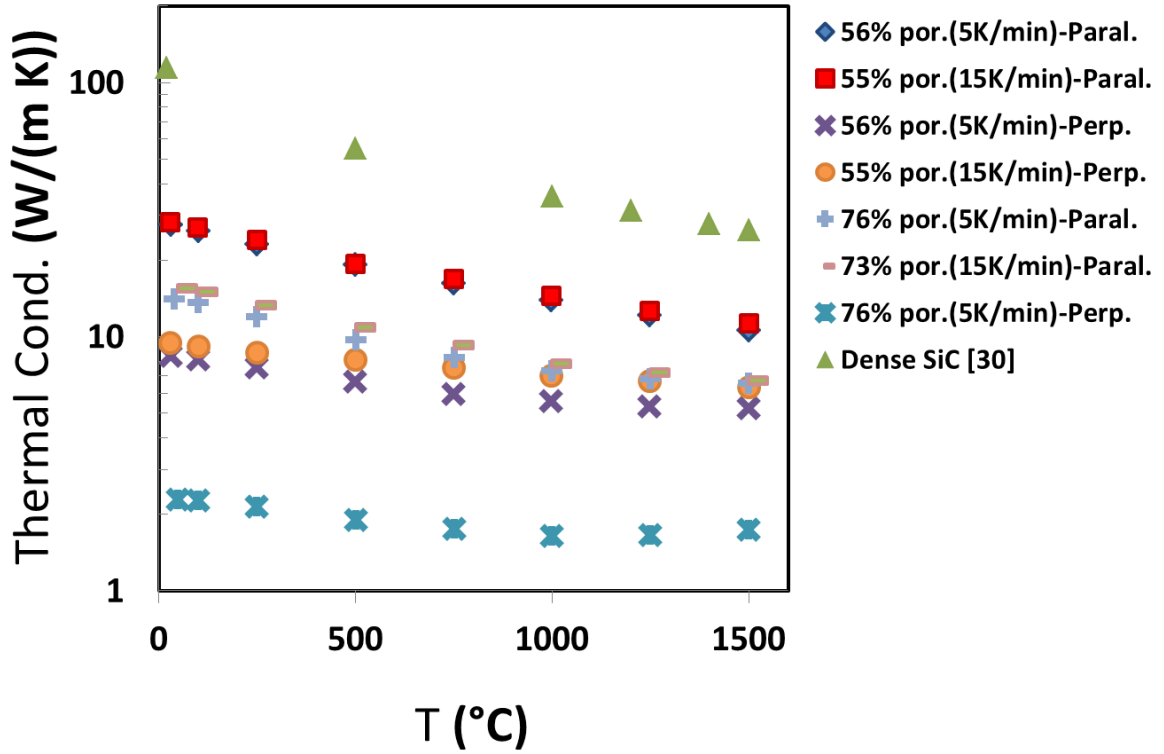


Fig. 51 Thermal conductivity of porous freeze casted LPS silicon carbide scaffolds. Measurements in the parallel and perpendicular direction of the freezing speed are reported. Error bars are included but too small to be visible. The thermal conductivity with the temperature for dense silicon carbide has been obtained from reference [30].

4.4 Discussion

4.4.1 Rheology

Well-dispersed and stable suspensions with low viscosity are necessary to facilitate the ice growth through the suspension and to avoid sedimentation. The rheological behaviour of SiC-TMAH suspensions was optimal for the ice-templating process that always took place within 1 hour. The limited sedimentation observed in the less concentrated suspension is probably due to a lower steric stabilization (lower amount of particles within the suspension). Using the equations (1.3) and (1.5) presented in Chapter 1, describing the sedimentation phenomena occurring within a colloidal suspension, for silicon carbide ($\rho_p = 3,21\text{g}\cdot\text{cm}^{-3}$) in 0°C water ($\rho_L=0,99\text{g}\cdot\text{cm}^{-3}$ and $\eta=1.793\text{mPa}\cdot\text{s}$) the maximum radius for laminar flow is $40.5\mu\text{m}$. The silicon carbide particles used in this study have a diameter of $0.4\mu\text{m}$,

they are therefore in laminar-flow system and their sedimentation velocity is around $0.43\mu\text{m/s}$. This result means that, without taking into account interactions with other particles, a particle will take around 30min to move of 1mm, therefore in our case the suspensions can be considered stable.

4.4.2 Microstructure

Freeze casting allows the creation of hierarchical structures with a certain level of microstructural control by manipulating the slurry concentration, freezing rate and additive formulation as already reported in previous studies. A decrease in solid loading leads to an increased porosity while the freezing rate determines the lamellae wavelength. Faster freezing speeds result in thinner lamellae and smaller pores, thus increasing the frequency of the lamellae wavelength. Our findings are in good agreement with previous work [20] (Fig.52).

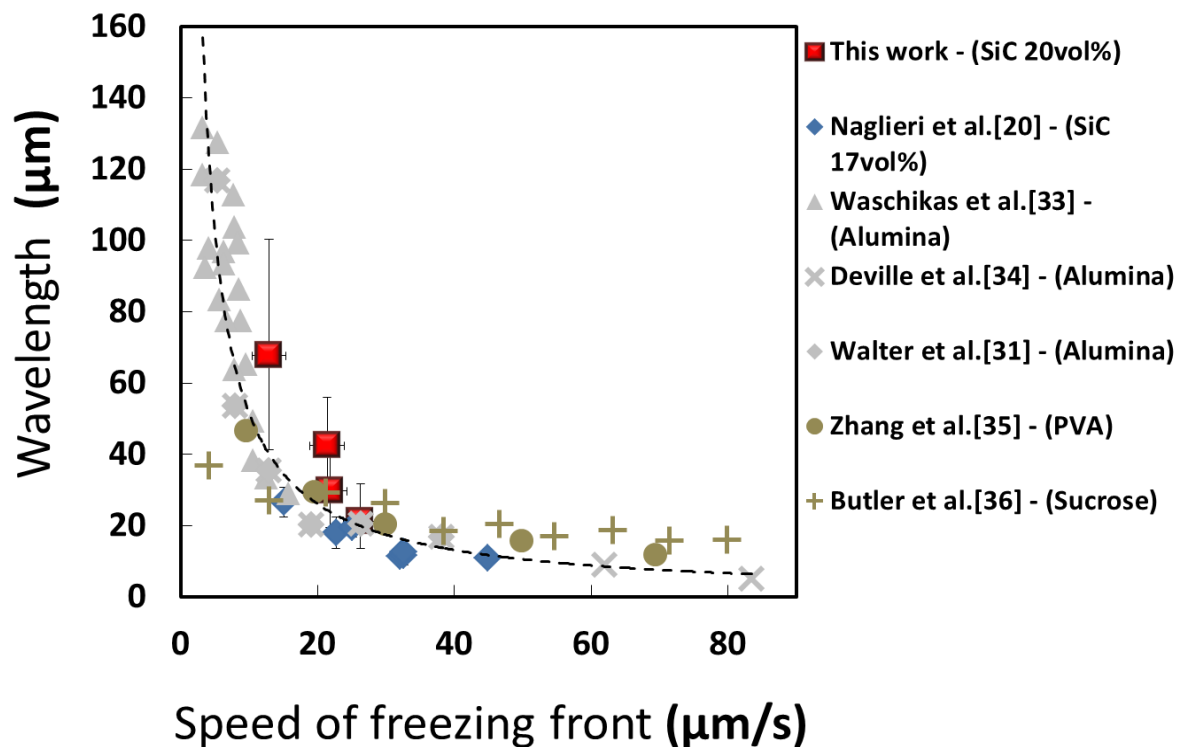


Fig. 52 Wavelengths of freeze casted SiC scaffold compared with other studies. The wavelength of a freeze casted sample is considered the sum of the thickness of a lamellae and the following pore space. The exponent of the power law is -0.98. References [20,31,33–36].

Moreover, as reported in previous studies, the structures can be considerably manipulated at low freezing front speed (below $20\mu\text{m/s}$), where minimal changes on the imposed freezing speed significantly influence the final wavelength obtained. This on the other hand makes it more difficult the control on the final microstructure. As the freezing front speed increases the variation of the wavelength with the freezing rate slows down substantially and it seems difficult to reach wavelength much inferior to $\sim 20\mu\text{m}$ while using microscopic particles.

4.4.3 Sintering

The sintering conditions play a very important role on consolidating the SiC particles into a strong structure while preserving the original architecture. Limited sintering results in poor cohesion and weak structures, but large densification could damage the porous architectures, making necessary to find a compromise between them. Different processing methods for the fabrication of porous materials usually rely on different sintering routes. Partial sintering is one of the most frequently used and simple technique to produce porous SiC with porosity below 65wt% and with pores size going from 0.1 to $10\mu\text{m}$ [18]. For this method usually no additives and low sintering temperatures are employed to only partially sinter coarse SiC particles generating uniformly distributed residual porosity. The replica method can be used to fabricate highly porous scaffolds with porosity ranging from 60 up to 98% and cell size from $100\mu\text{m}$ up to millimeters [18]. Different studies showed that changing the amount of additives or sintering temperature different porosity percentages can be obtained. The replica methods do not usually enable good microstructural control. Sacrificial template methods, as the one employed in this study, use a template as pore forming agent that is subsequently removed during sintering. With this technique is possible to obtain a good control over the porosity, pore size and pore morphology. The porosity obtainable with this process can range from 15 up to 95% with pore sizes ranging from 1 to $700\mu\text{m}$ [18]. In this case the sintering conditions have to be properly tailored to preserve the microstructure imposed during processing. To overcome the problem of sintering usually faced when silicon carbide is used whichever is the technique employed, new processing routes have been introduced using pre-ceramic polymer precursors or wood-derived carbon foam. The advantages of these processes are that usually require low sintering temperature ($1000\text{-}1200^\circ\text{C}$) and do not need sintering aids. However these processes show some

disadvantages. In the case of wood derived scaffolds the structure is strongly anisotropic [37] and residual carbon and silicon are often generated [38]. Meanwhile the use of pre-ceramic polymer precursors often leads to large shrinkage during the conversion that produces defects and cracks within the foams [16]; this shrinkage increases when increasing the firing temperature at which the polymer is converted into ceramic. Finally in both cases, the processes needed to achieve the final products are extremely complex and involve many different steps. In this study two different sintering routes were used, solid and liquid phase sintering. Solid state sintering in a graphite furnace leads to poor densification and exaggerated grain growth at temperatures above 2000°C. Despite limiting the grain growth, solid state sintering in the SPS leads to inhomogeneity and loss of the porous architectures. Scaffolds prepared in the SPS showed heterogeneities on densification and multiple cracks, probably due to the high speed of the process not optimized for delicate porous structures. A preliminary thermal treatment to burn out the processing additives (i.e. PVA, TMHA and sucrose) prior the thermal cycle in the SPS would help to avoid damaging the structure. However, as in solid phase sintering the organic additives are the source of carbon to aid the sintering, it is necessary to carry out this pretreatment inside the SPS. The fast heating rates are too extreme to burn out the organics without damaging the structure. Another factor that leads to a poor wall densification (Figs.39-41) may be related to the inter-particle porosity in the green state (Fig.53) due to the poor packing of the particles. The SiC particles have a faceted and irregular shape, what makes it difficult the packing when they are compacted by the ice growth.

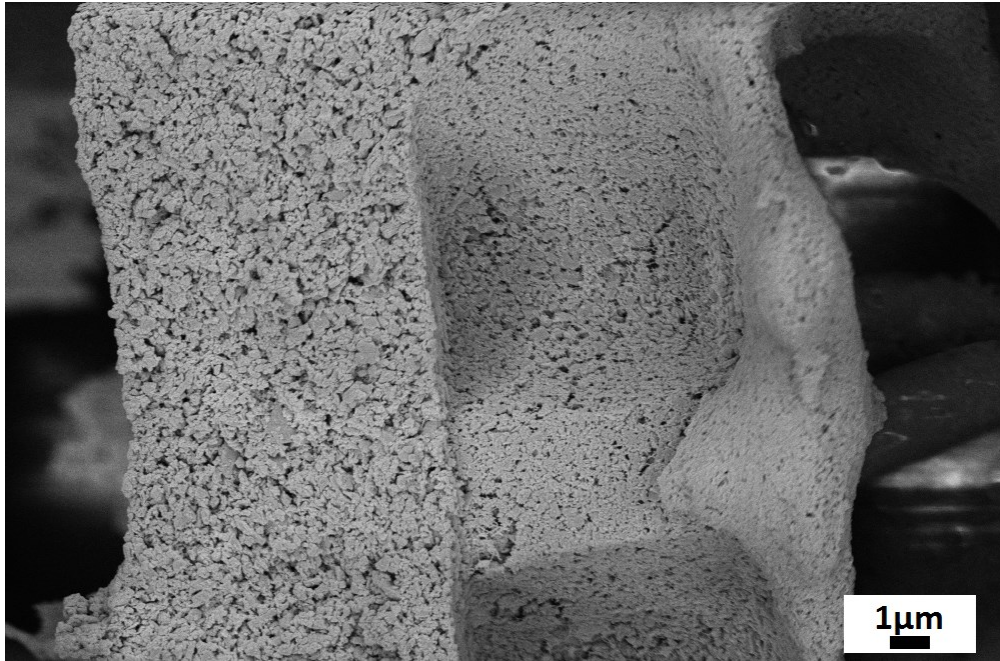


Fig. 53 SiC freeze casted green body. The irregular shape of the particles hampers good packing in the green state.

The addition of Al_2O_3 and Y_2O_3 has been reported to be the more effective way to liquid phase sinter SiC particles. As reported by W. Chi et al. [39] the amount of sintering aids and the sintering temperature strongly affect the final density of liquid-sintered porous structures along with its mechanical properties. The sintering aids are usually kept between 4 and 10wt%. Fukushima et al. [1] first sintered SiC freeze casted scaffold at 1800°C for 2h adding 4wt% of additives. They freeze casted SiC slurry containing 10vol% of ceramic phase and after sintering they obtained scaffolds with residual porosity ranging between 86.5% and 86.8% (depending on the freezing temperature) and compressive strengths oscillating between 5 and 16MPa. In this study using a similar solid loading of 9vol%, scaffolds with a residual porosity around 75-76% and a maximum crushing strength around 30MPa have been obtained. Even though the scaffolds in both studies are obtained using slurries with similar ceramic loading, this difference of 10vol% in residual porosities and 0.15 in relative density between the two materials, could be related to a lower degree of lamellae densification obtained in the Fukushima's study. More recently Naglieri et al. [20] freeze cast SiC particles adding up to 10wt% of additives and firing the structures at higher temperatures (1850 and 1900°C) and holding for different times. In this study they also showed that sintering conditions strongly influence the porous morphology where bigger

grains are obtained at higher temperatures, but they do not report densities or compressive strengths. In this study an approach similar to Fukushima et al. [1] has been chosen, increasing the percentage of oxide up to 8wt%. Liquid phase sintering at 1800 °C for 2h (using a SiC powder bed) resulted in a good degree of lamellae densification reaching a density of 0.938 g/cm³, which represents 32.6% of improvement with regards to the best results obtained with solid state phase sintering (0.71 g/cm³). Higher sintering temperatures of 1850 and 1900 °C lead to higher densification, up to 1.0 g/cm³ (max density), however significant grain growth occurred, with hexagonal grains that extended between the lamellae (Fig. 43). An increase of firing time up to 3 h leads to an improvement in density to 1.082 g/cm³, representing an improvement of 15.3%. Under these conditions, grain growth is limited but remaining inter-granular (within the lamellae) porosity was still present. An activation peak at 1900°C (Table 2) was applied in order to enhance the sintering while avoiding grain growth. Further improvements in the lamellae densification were obtained with this approach resulting in scaffolds with up to 1.143g/cm³ density. It has been suggested by Chen and Wang for the solid phase sintering of Y₂O₃ [28] that the role of the activation step can be associated with a suppression of grain-boundary migration while the grain-boundary diffusion is maintained. In case of liquid phase sintering the activation step could have a different role. The liquid having lower viscosity at high temperature could easily penetrate between the grains and fill tiny pores, in this way it can rearrange and compact the particles more effectively and help the densification. By quickly decreasing the temperature after the activation, the liquid would be confined between the grains, while reducing solution-precipitation phenomena, grain growth is retarded [40]. The samples exhibit good densification, and limited grain growth, however some scattered grains up to 8µm grew on the cellular ceramics (Fig.54).

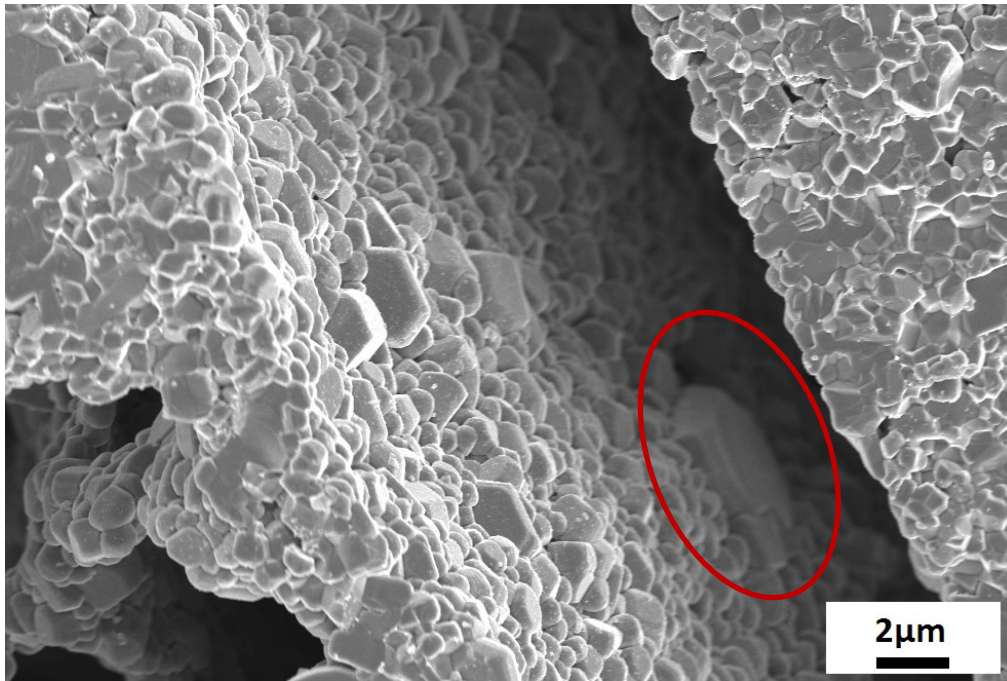


Fig. 54 Two-step LPS scaffold. Good densification of the lamellae can be observed however big grain can still be observed within the microstructure (red circle).

Alumina addition to the sintering bed increases the relative density by allowing the diffusion of oxide species into the sample. The use of Al_2O_3 in a closed crucible and the high temperatures generate volatile metal sub-oxides with sufficient partial pressure to prevent, or limit, the volatilization of the sintering aids, and therefore enhancing densification. Another factor that plays a key role in the HP is the crucible dimension. A small cylindrical container (10x10cm) enhances the sintering by increasing the pressure and creating a local atmosphere rich in Si, C, Al, and O thus preventing the evaporation of the sintering aids away from the sample. This approach of using a doped powder bed has been employed to obtain dense SiC structure but it is the first time that has been used to sinter porous SiC scaffolds.

XRD and TEM results provide the composition of the final scaffolds and show that under these sintering conditions there is the formation of different crystalline and vitreous phases typical of liquid phase sintering between SiC grains identified as $\text{Al}_5\text{Y}_3\text{O}_{12}$ and Al_2O_3 as reported in previous studies [9,41,42].

4.4.4 Mechanical properties

The crushing strengths of the freeze casted scaffolds (measured in the freezing direction) show similar or slightly higher values to those of similar SiC porous scaffolds with the same percentage of residual porosity produced using other techniques (Fig.55).

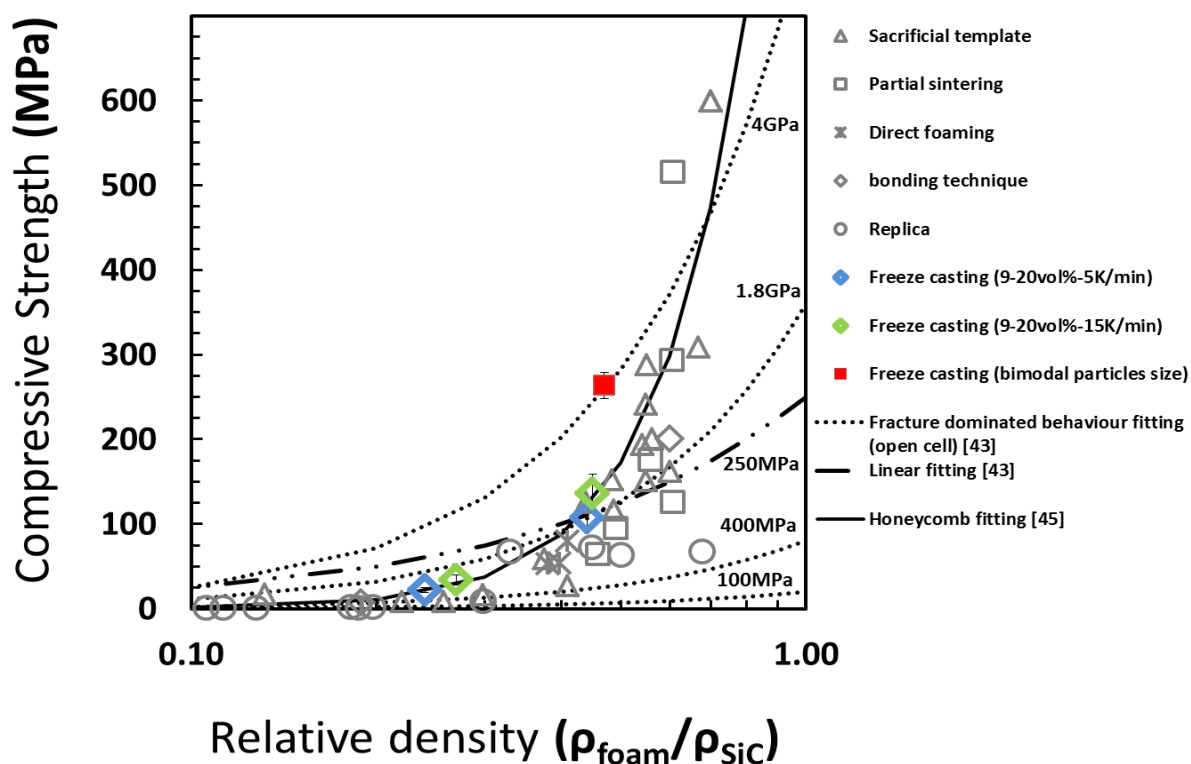


Fig. 55 Comparison of compressive strength vs relative density of freeze casted sample and other SiC macroporous scaffolds produced with different techniques. In order to calculate the relative density a ρ_{SiC} of 3.21g/cm³ has been considered. The fitting models for open-cell foams in fracture dominated behaviour, for honeycombs loaded out of plane and a linear fitting are reported [43]. Different curves for the fracture dominated behaviour fitting are reported considering different strengths σ of the SiC struts, from 100MPa up to 3GPa. Data for different techniques are from [18].

Stress-strain curves of compressive tests revealed that scaffolds resist up to the maximum strength after which it starts to fail gradually. The upper and bottom parts starts to crack as the lamellae tend to fail progressively under the applied load. The entire structure resists in these conditions for a certain amount of applied strain (usually around the 10-15%) after that a crack propagates vertically provoking the failure of the scaffold. Freeze casted scaffolds with finer structures obtained by faster freezing tend to be stronger probably due

to the smaller probability of forming large defects in the lamella walls reducing the tendency of crack formation and propagation until failure. Much higher compressive strength up to 263MPa has been achieved with the scaffolds fabricated using a bimodal particle size distribution. The porosity of the sample slightly reduces down to 53% with a final density of 1.51 g/cm³ that represent a noteworthy improvement if compared with the freeze casted scaffold obtained with a similar solid weight and porosity of 55%. The higher mechanical strength of the bimodal distribution scaffold could be related to the different silicon carbide *polytypes* alfa and beta employed, that has been reported favour the development of a complex microstructure with elongated grains [12,44]; or simply because using a double particle size distribution, achieving a better packing between the particles and therefore a better sintering, less defects and pores are left inside the lamellae increasing the crushing strength of the whole structure.

Different models are reported in Fig.55 to evaluate which one better fits the experimental data. The following equations have been employed for the different models [43,45]:

- open-cell in fracture dominated behaviour :

$$\sigma_{foam} = \sigma_{wall} \cdot 0.2 \cdot \left(\frac{\rho_{foam}}{\rho_{SiC}} \right)^{3/2} \quad (4.2)$$

- honeycomb loaded out-of plane:

$$\sigma_{foam} = 6 \cdot E_s \cdot \left(\frac{\rho_{foam}}{\rho_{SiC}} \right)^3 \quad (4.3)$$

- Linear fitting:

$$\sigma_{foam} = \sigma_{wall} \cdot \left(\frac{\rho_{foam}}{\rho_{SiC}} \right) \quad (4.4)$$

The values of σ_{wall} obtained with the open-cell and the linear model (reducing the square of the residuals) are respectively 1.89GPa and 233MPa. Both models seem not perfectly fit the experimental data, whereas the honeycomb fitting proposed by Deville et al. [45] appears to perfectly work considering a E_s for the silicon carbide of 231MPa. However, the derived value of the elastic modulus is three orders of magnitude lower than the usual elastic modulus for dense SiC (~400GPa [46]). Contrarily, the linear model gives a value for the strength of a single lamella strut that is more reliable. The morphology of these SiC freeze casted scaffolds can be more closely modelled as parallel plates loaded in compression

instead than proper honeycombs. However, as reported by Deville et al. [47] buckling is the dominant failure mode for freeze casted structures. Applying the equation for Euler buckling, $F = \pi^2 EI / (KL)^2$ [48], where E is the elastic modulus (400GPa), $I = bh^3/12$ the moment of inertia (b and h the dimension of the cross area, respectively 20 μ m and 100 μ m), $K=1$ for hinged ends and L the length of the beam (5mm), the strength of ~135MPa for a single lamella failing in buckling has been evaluated. However the presence of numerous bridges between the lamellae, along with different domains with different lamella orientations does not simply allow the scaffold to fail in buckling and therefore the actual failure strength might be higher than the theoretical one.

A clear crushing point could be identified for the bending tests. This could support the theory that the best tool to quantitatively compare different porous materials is using the bending test [49]. Also in this case was observed that faster freezing rates for the 20vol% samples lead to a slight increase of flexural strength. Lamellar structures obtained from 20vol% suspensions exhibit crack initiation and propagation in the stress region (i.e. just in the middle of the span on the side under tension). However, distortion of the regions under the contact with the loading bars was observed for the samples with high porosity obtained from low solid loading suspensions. The samples were under localized compression instead and the crack nucleation always occurred in that specific area. Therefore those results have been not taken into account, being the test not adequate to characterise the mechanical performance of highly porous materials. The flexural strength of the freeze casted samples in the direction perpendicular to the freezing direction is comparable to most of the SiC macroporous materials produced with other techniques with the same range of porosity. From literature only samples produced from a nano-infiltration transient eutectic process (NITE-SiC) obtained from a decarburization process of a mixing of SiC and carbon powder showed higher flexural strength [50]. However the reported data have been obtained with three points bending test that can give overestimated values (Fig.56).

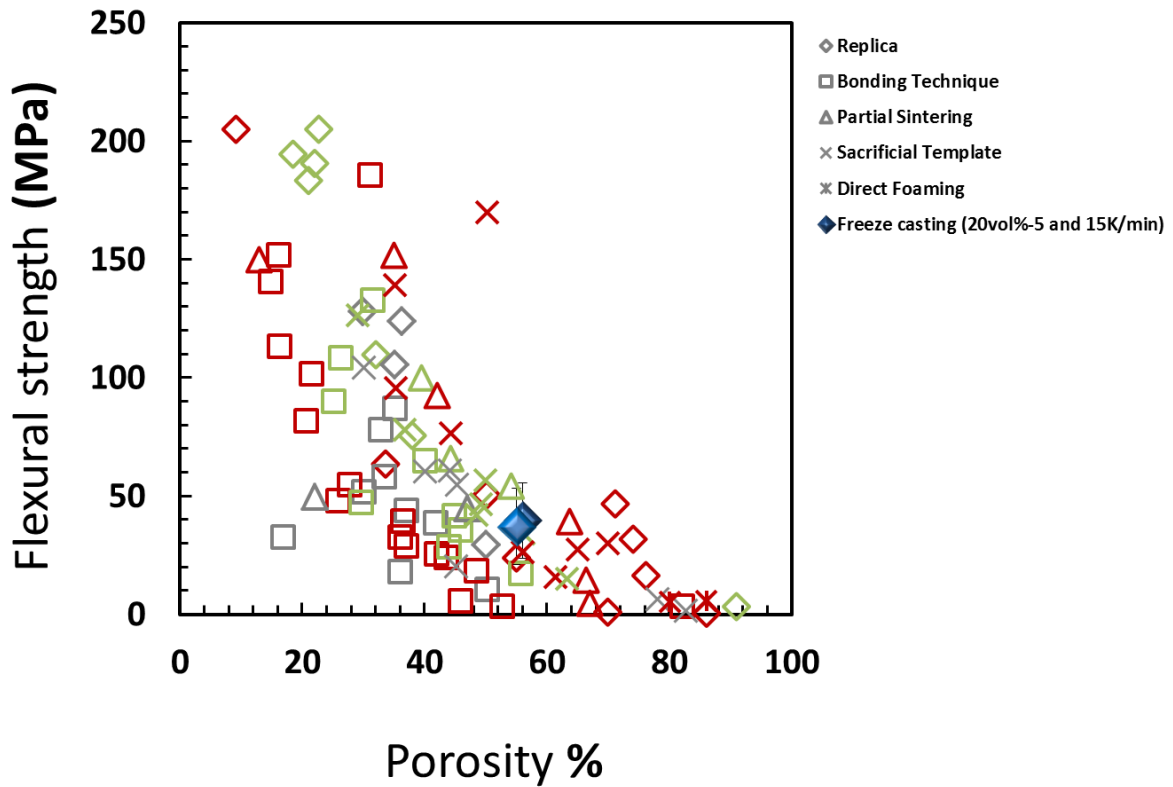


Fig. 56 Comparison of flexural strength vs porosity of freeze casted scaffolds produced in this study and other SiC macroporous sample produced with different techniques. Data reported in red and green are obtained with 3PB and 4PB tests respectively. The grey points are not specified. Adapted from [18].

4.4.5 Thermal conductivity

Thermal properties are also intimately related to structural features. Freeze casted structures show higher thermal conductivity in the longitudinal direction (parallel to freezing rate), due to the heat transfer along the dense lamellae. The dense lamellae facilitate a continuous medium that facilitates heat transfer. The conductivity drops when measuring the freeze casted scaffolds in the perpendicular direction to the freezing front. The differences between samples with same solid loading but obtained with different freezing conditions may be related to the number of lamellae per unit of transversal area. Samples frozen at higher freezing speed showed slightly higher thermal conductivity of those frozen at 5°C/min for both solid contents. A decrease of the thermal conductivity is observed for all the samples when increasing the temperature up to 1500°C being the thermal conductivity at high temperature of very porous materials governed by radiation [51]. However overall,

the thermal conductivity remains stable up to high temperature making these scaffolds suitable for high temperature applications. Similar values of thermal conductivity can be found in literature for SiC macroporous scaffolds produced with different processing techniques [18]. If we consider the simple model proposed by Ashby [52], where the thermal conductivity of a foam can be considered as the thermal conductivity through the solid walls and the air entrapped between the pores, the thermal conductivity can be calculated using the following equation:

$$\frac{\lambda_{foam}}{\lambda_s} = \frac{\lambda_g}{\lambda_s} + \left(\frac{1}{3} - \frac{\lambda_g}{\lambda_s} \right) \left(\frac{\rho_{foam}}{\rho_{SiC}} \right) + \frac{2}{3} \left(\frac{\rho_{foam}}{\rho_{SiC}} \right)^{3/2} \quad (4.5)$$

where λ_{foam} is the thermal conductivity of the scaffold, λ_s is the thermal conductivity of the bulk material, λ_g is the thermal conductivity of the entrapped gas, ρ_{foam} is the density of the foam and ρ_{SiC} the density of the dense SiC.

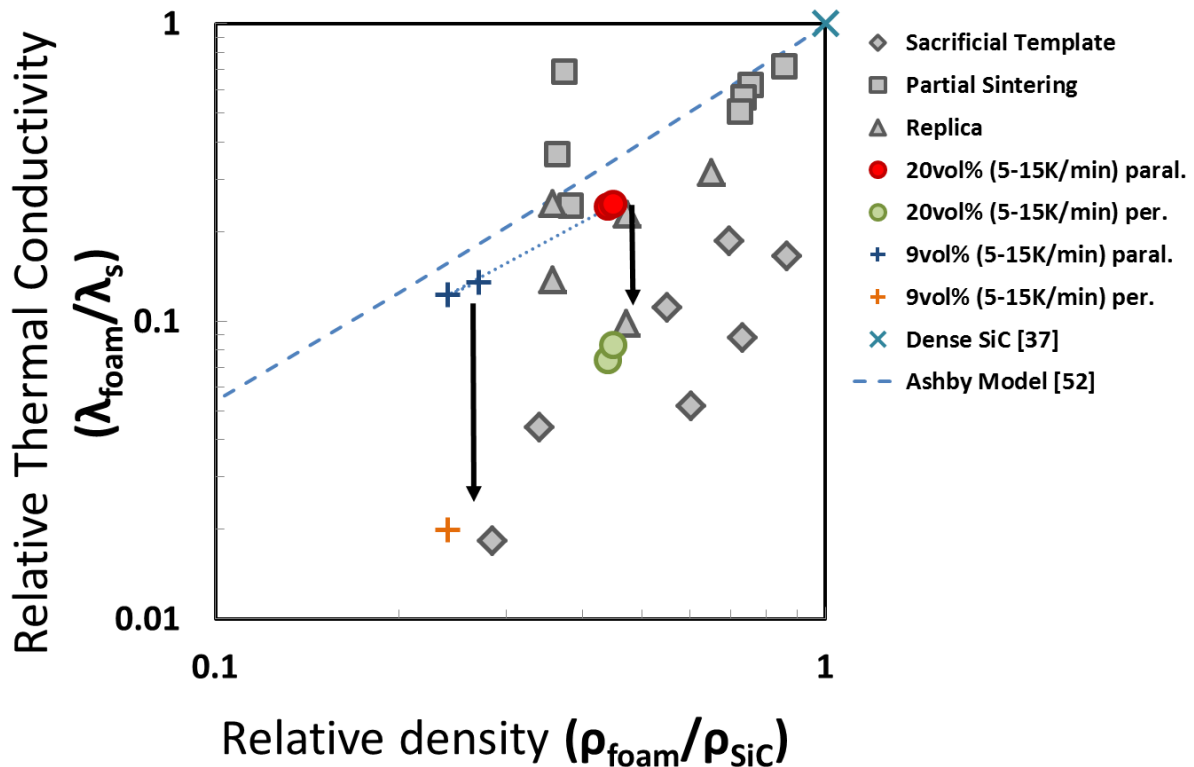


Fig. 57 Thermal conductivity vs porosity freeze casted scaffolds and SiC scaffolds produced with other techniques. For the model calculation a λ_s of 114 Wm-1K-1 for SiC [37] and a λ_g of 0.025 Wm-1K-1 for dry air at room temperature have been considered [51]. Partial sintering data are obtained from [2], replica values from [53] and sacrificial templates ones from [50,54]

Despite the fact the Ashby model is for isotropic foams, for the freeze casted scaffolds the thermal conductivity in the direction parallel to the freezing direction seems to follow a similar trend predicted by the model where at increasing of the porosity the thermal conductivity also decreases. The thermal conductivity in the direction perpendicular to the freezing direction decreases faster as the porosity increase compared to the model probably due to the less effective heat transfer within this configuration.

4.5 Conclusions

Freeze casting provides SiC scaffolds with lamellar structures that can also be tailored by manipulating the processing and freezing conditions. The technique provides the possibility to tune the architecture generating different porosities and mechanical behaviours. Liquid phase sintering in a controlled atmosphere promotes the formation of dense walls without losing the microscopic porous lamellar architecture. With the chosen sintering route strong lamellar SiC scaffolds have been produced that can be employed for the fabrication of layered ceramic/polymer composite as shown in Chp.6. Data show that there is a clear relationship between processing conditions, microstructure, sintering and mechanical performance. This enables tuning the processing to optimize functional properties for specific applications. In particular these structures could be used in applications with structural demands under extreme environments, such as filter or barriers for high temperature applications.

4.6 References

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5 Ultra-light and strong SiC net-like structures

5.1 Introduction

The progress of many advanced technologies from transportation to catalysis or tissue engineering requires the designing and engineering of new strong porous multifunctional materials [1–5]. The demand is driving the development of new manufacturing techniques that could build complex porous architecture with characteristic features spanning from the nano to the macro scale [2]. Highly porous (porosity >90%) ceramic structures that could combine functional capabilities with mechanical performance have attracted the attention of numerous scientists in different fields [6–10]. Specifically the imitation of hierarchical design principles found in nature can be applied to create resistant lightweight engineering materials. The challenge for these production techniques is to fabricate strong structural lightweight materials while preserving the pore size in the microscopic scale. The specific properties of ultralight materials are in fact defined by the unit-cell geometry and architecture design together with the properties of the solid constituents [6]. Emulsification or direct foaming have been the most exploited technologies in ceramic industry to produce highly porous ceramics with macroscopic dimensions [2]. The microstructures achieved with these processes usually exhibit large pores sizes (typically above 100 μm) and the structures tend to be weak [11]. The degradation of the mechanical response can be drastic as density decreases [5]. Many examples of low-density materials showing this trend have been reported recently; among them graphene elastomers [10,12,13], carbon nanotube [14,15] foams and silica aerogels [16–19]. Many natural materials such as diatoms, sea sponges and bone show remarkable mechanical strength although remaining lightweight and porous. It has been suggested that this ability rises from the hierarchical arrangement of different structural elements over different length scale, from the macro down to the nano scale [7]. The use of this design concept of hierarchical organization of building blocks led to an improvement on the mechanical properties of new metallic microlattices [6], TiN nanotrusses [7] and ceramic composite trusses [1,8,20]. Combining 3D laser lithography and thin film deposition these metallic and ceramic micro-lattices (often referred as metamaterials) with micro-sized pores and carefully designed unit-cell, can reach remarkable mechanical properties. Within these materials the lattices are structured to

create stretching-dominated phenomena and increase in this way their mechanical performance [5,21]. However the strength and stiffness of the walls or struts is crucial to determine the final properties of a porous structure. These should be free of defects to improve mechanical efficiency [22]. The main limitation of this approach is that only samples of small dimensions ($10\text{-}10^3\mu\text{m}$) have been produced to date and with limited variety of materials (Al_2O_3 , Ni and TiN). A step forward will be the ability of producing strong lightweight structures with useful dimensions using flexible, low-cost manufacturing processes for high-volume fabrication.

Silicon carbide, displaying a unique combination of thermal, chemical, electrical and mechanical properties is a very attractive material for the fabrication of low-density structures for advanced technological applications [23,24]. Commercial uses of porous SiC structures have already been exploited by many industrial applications such as in water filters, porous burners, diesel particulate filters, metal matrix composites, polymer matrix composites, high-temperature/high-voltage semiconductor electronics, membranes, hot gas filters, and molten metal filters [24]. However, these are “traditional” porous materials with porosities still below 80%. The development of even lighter porous SiC structures that can also be stiff and strong would be particularly beneficial for many of these applications. One of the current challenges is to develop processing technologies that will address structural control along with wall quality and smart design concepts.

In this study ultra-light (porosity >90%) and strong SiC porous scaffolds have been produced through the controlled assembly of thin, strong micro-fibres into a complicated hierarchical structure via freeze casting. The hierarchical organization, the high porosity, along with the bulk characteristics of SiC allowed producing mechanically robust scaffolds with a unique combination of properties: thermal insulation, electrical conductivity and low acoustic impedance.

5.2 Materials and methods

5.2.1 Starting materials and processing

Colloidal suspensions of SiC fibres in water were prepared by mixing 1.5, 3 and 7 vol% SiC fibres with a diameter of $\sim 1.5 \mu\text{m}$ and length of $\sim 18 \mu\text{m}$ (Alfa Aesar, product specification). Chitosan solutions (1wt%) were prepared by dissolving chitosan flakes (Sigma Aldrich) (0.5g) in 50ml of an aqueous solution of acetic acid (Sigma Aldrich, Reagent Plus, $\geq 99\%$) (0.05M). SiC fibres were added to the chitosan suspension, ultra-sonicated for 30 min. and mixed for 24h with a Turbula (T2F-Glenmills, Switzerland) shaker mixer. Along with the SiC fibres, 15wt% (with respect to the SiC) of Al_2O_3 (Baikalox B-series SMA6, Baikowski, France) and Y_2O_3 (Grade C- ABCR – H.C. Starck) in a ratio of 6/4 were added to promote sintering. After mixing for 24 hours, the suspensions were de-aired with a vacuum pump for at least 30 minutes to remove air bubbles and frozen directionally by placing them on a Cu cold finger whose temperature was decreased at a constant rate of $15^\circ\text{C}/\text{min}$ [25]. The frozen scaffolds were dried for 24 hours (Freezone 4.5 by Labconco, USA) and subsequently sintered in an inert atmosphere (Ar) with a heating rate of $20^\circ\text{C}/\text{min}$ up to the maximum temperature (1800°C); cooling rates were fixed at $20^\circ\text{C}/\text{min}$.

5.2.2 Characterization

The apparent density and porosity of the sintered scaffolds were measured by Archimedes' method (Sartorius, YDK01, Gottingen, Germany) in water. The flow behaviour and viscosities of SiC fibres suspensions were measured in a Discovery Hybrid Rheometer HR1 (TA Instruments). The flow experiments were carried out with a parallel plate ($\varnothing=40 \text{ mm}$) at room temperature with a solvent trap cover to prevent solvent evaporation and with a gap ranging between 500 to $800 \mu\text{m}$. The viscosity was measured imposing a shear rate oscillating from 0.1 to 1000 s^{-1} . The microstructure of the materials was analyzed via scanning electron microscopy (SEM, Leo Gemini 1525).

The flexural strength of single fibres was measured by *in situ* micro- three point bending test by Giorgio Sernicola [26]. The fiber was placed on a trough, which edges were acting as supports, previously milled via focused ion beam on a silicon substrate. The fiber was loaded

using an Alemnis nanoindenter equipped with a Synton-MDP diamond wedge tip moved in displacement control. The Alemnis was setup to displace the tip at a speed of 2nm/s until failure of the fiber. The load was recorded by a Honeywell 50g load cell sitting under the specimen stub. The test was conducted in an Auriga Zeiss SEM; high resolution live images allowed a fine alignment of the tip over the specimen and a video of the test was recorded for further offline analysis.

Compression tests were performed on a universal testing machine (Zwick/Roell 1474) with a load range up to 100kN. The compression test was done following the ASTM C133 [27] standard with a crosshead speed of 1.3mm/min. In order to homogeneously distribute the load during the compression tests, a stainless steel semi-sphere was placed at the top of the samples. For each composition, 5 to 10 specimens measuring approximately $5 \times 5 \times 5 \text{ mm}^3$ were cut from a ceramic part with a diamond disk and grinded to ensure parallel surfaces.

Elastic moduli were calculated at CSIC in Madrid by Dr. Alvarez-Arenas. Elastic moduli were evaluated from the measurement of the ultrasonic phase velocity in the samples in the frequency range 0.1-0.9 MHz assuming a Poisson's ratio of 0.3. To preserve the integrity of the sample and avoid introducing any modification in their response, air-coupled ultrasonic techniques was used avoiding the use of coupling fluids between transducers and samples and/or any direct contact between them. Two different air-coupled ultrasonic techniques were used depending on the sample size, both operating in through transmission mode and at normal incidence. In both cases, wide-band and high sensitive piezoelectric air-coupled transducers [28] a PANAMETRICS 5077 pulser/receiver and a DPO5054 Tektronix oscilloscope were used. First, ultrasound velocity in $20 \times 20 \times 20 \text{ mm}^3$ samples was obtained from conventional time of flight measurements in the three main directions. Afterward slices of dimensions of approximately $20 \times 20 \times 1 \text{ mm}^3$ were cut along the three main directions to test them in resonance to get a resonant frequency of the slice thickness mode about 0.25 MHz following the method explained by M.D.Fariñas et al. [28].

Ultrasound velocity (v) is related with the density (ρ), bulk (K) and shear modulus (G), or Young's modulus (E) and the Poisson's ratio (ν) [26,29]:

$$\nu = \sqrt{\frac{K + \frac{4}{3}G}{\rho}} = \sqrt{\frac{E(1-\nu)}{(1+\nu)(1-2\nu)}} = \sqrt{\frac{G(4G-E)}{3G-E}} \quad (5.1)$$

The thermal properties of the samples were measured using a Netzsch LFA 427 - Laser Flash Apparatus, at temperatures between 30 °C and 1500 °C. A short energy pulse heated up the bottom surface of the sample, while the temperature on the upper surface was measured and monitored with an infrared detector. The thermal diffusivity was measured in Ar atmosphere, using a heating rate of 10°C/min. Between 3 and 5 measurements for each temperature were carried out. The “Cowan+pulse correction” diffusivity model was used for the processing of the experimental data. The thermal conductivities were calculated with Proteus® Software, using the acquired data of thermal diffusivity, specific heat and density of the samples. The electrical conductivity ρ was measured as the inverse of the resistivity R obtained with the two point technique:

$$\rho = \frac{Rwh}{l} \quad (5.2)$$

w , h and l are the dimensions of the bars used for the test (10x10x10mm³). Copper contacts and silver paint were used to improve the electrical contact between the samples and the anodes.

5.3 Results

5.3.1 Microstructure

Freeze casting (also known as ice templating) of ceramic suspensions is one of the most promising paths to shape complex structures with controlled microstructural features at multiple scale lengths following a top-down approach. It uses the complex structure of ice crystals as templates to create monolithic and hybrid materials that exhibit unique hierarchical organization and very promising properties. The freezing of colloidal suspensions in a particular direction at controlled speeds (imposing a specific thermal gradient) promotes the growth of lamellar ice crystals.

The growing ice crystals expelled the ceramic fibres as they grow, arranging and compacting them in lamellas between adjacent ice crystals (Fig. 58a). The control of the freezing process allowed tailoring the morphological features of the lamellar structure over a range of size-scales, being the final porous structure a replica of the original ice crystals (after sublimation). Higher freezing rates, imposing different kinetics of ice-crystal growth, decreased the pores size from 50 to 15µm while the lamellae thickness remained constant in the order of the fibre diameter (Fig.58b). Adjusting the processing parameters and the freeze casting conditions porous structures with high porosity and small average pore size have been produced.

Freeze casting of silicon carbide short fibres suspensions (with approximately a diameter of 1.5µm and average length of 18µm) enabled obtaining SiC scaffolds with very high porosity and robust mechanical properties. A good flocculation of the fibres in water was necessary to obtain a stable suspension for freeze casting, avoiding in this way inhomogeneity within the microstructure. Chitosan water based solutions provided very good stabilisation and flocculation of SiC fibres avoiding segregation over large range of time (Fig.59a) and leading to homogeneous slurries with low viscosities (Fig.59b).

The flocculation obtained using chitosan-based suspensions was likely due to the interactions of hydroxyl and amine groups present in the repeating unit of the chitosan chain, through hydrogen bonding with the silanol groups formed on the SiC surface in presence of moisture or water [30]. These non-covalent interactions along with the electrostatic forces between the chitosan chains and the SiC surfaces facilitate electro-steric stabilisation of the fibres producing weakly flocculated suspensions. Although the use of chitosan increased the viscosity, rheological analyses showed that it remained low enough to allow the formation of lamellar ice crystals (the apparent viscosity for the suspension with higher solid loading 20wt% is well below 100Pa·s) (Fig.59b). Approximating a single fibre to a small cylinder and considering only two forces acting within the suspension, the gravitational force and the opposing force generated by the Archimedes' principle, the resulting force acting on the cylinder is:

$$F = (m - \rho_L V)g = (\rho_P - \rho_L)g\pi r^2 \cdot l \quad (5.3)$$

where ρ_p and ρ_L are the densities of the particles and liquid respectively, r and l are the radius and the length of the corresponding cylinder and m and V the mass and volume of the particle. The frictional force predicted by Stokes' law for a non-spherical object can be written as [31]:

$$F_S = 3\pi\eta v_p d_e K \quad (5.4)$$

where d_e is the equivalent diameter of a sphere having the same volume as the cylinder and K is a correction factor. Equating the two previous equations, the terminal velocity of the particles v_p is:

$$v_p = \frac{(\rho_p - \rho_L)gr^2 \cdot l}{3\eta d_e K} \quad (5.5)$$

Considering $\rho_p = 3.21 \text{ g}\cdot\text{cm}^{-3}$ $\rho_L = 0.99 \text{ g}\cdot\text{cm}^{-3}$ for densities of SiC [32] and water respectively [33], $r = 0.75 \mu\text{m}$ and $l = 18 \mu\text{m}$ radius and length of the fibre (Alfa Aesar, product specifications), $\eta = 1.793 \text{ mPa}\cdot\text{s}$ for the viscosity of water and a $K = 1$ [33], their sedimentation velocity is $10.38 \mu\text{m/s}$, that is two order of magnitude higher than for the nanoparticles employed in Chapter 4.

After freeze-drying, the green bodies were fired to sinter the fibres and strengthen the structure. Another important challenge was to develop an adequate sintering route that allowed consolidating the structure and obtaining ultralight but strong SiC scaffolds. Due to the limited sinterability of SiC the use of sintering aids is necessary during pressureless sintering. As reported in Chapter 4, Al_2O_3 and Y_2O_3 were added to the suspensions up to 15wt% (of the SiC content) [34]. The additives in combination with the SiO_2 present on the SiC surface melted at lower temperature producing a liquid phase sintering between the fibres that enhanced the bonding between them (Fig.60d). As reported in Chapter 4, to avoid the evaporation of additives at high temperature the atmosphere was controlled placing the sample in a closed graphite crucible, on a SiC/ Al_2O_3 powder bed.

The sintered structure showed a network/lattice-like structure with extremely interconnected porosity and hierarchical architecture (Fig.60a) with aligned porous fibres layers. During the freezing process some fibres were trapped by the growing ice crystals and they positioned perpendicular to the freezing direction forming bridges between the

lamellae (Fig.60c). The number of fibres trapped tended to increase at higher solid loading and as result the structure of denser lattices became more isotropic with a more cellular architecture (Fig.60b). The density and the pore architecture of the scaffolds could be tuned changing the solid loading and the freezing rate, as already reported by previous study [35]. Reducing the solid loading of the initial suspension from 7 to 1.5vol%, the porosity increased from 92% up to 98%.

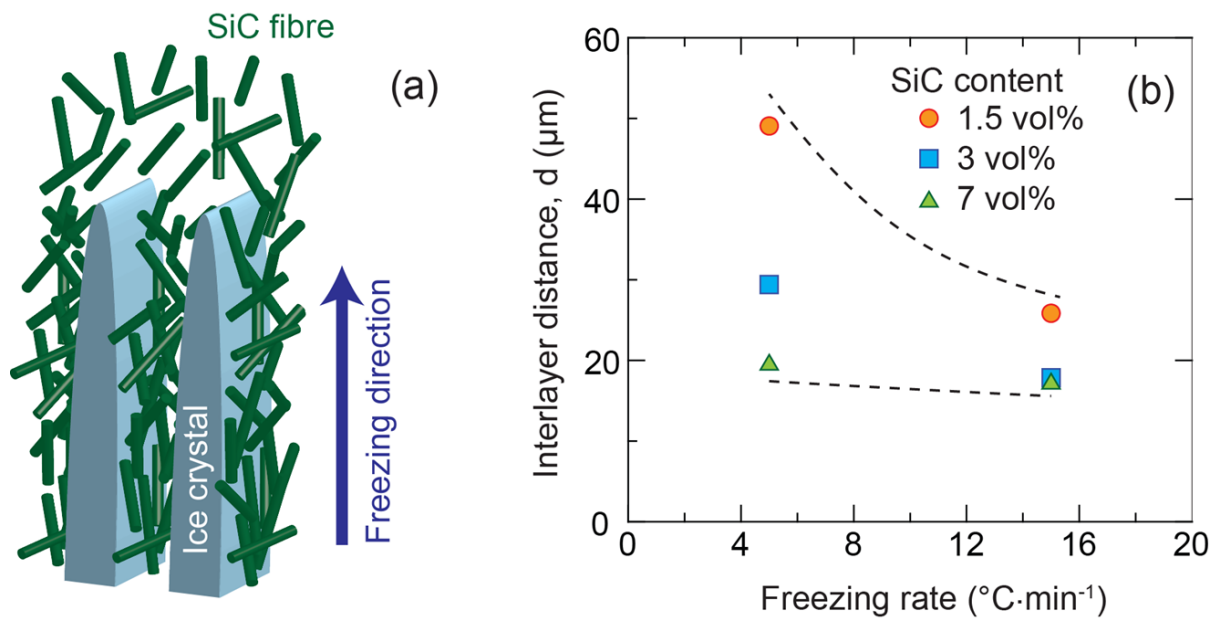


Fig. 58 a) Model of freeze casting of SiC fibres. During the freezing the ice crystals growing in a preferential direction expel the fibres that accumulate between two adjacent ice crystals. b) The structure can be tuned changing the solid loading of the initial suspensions and the freezing speed imposed. Adapted from [26].

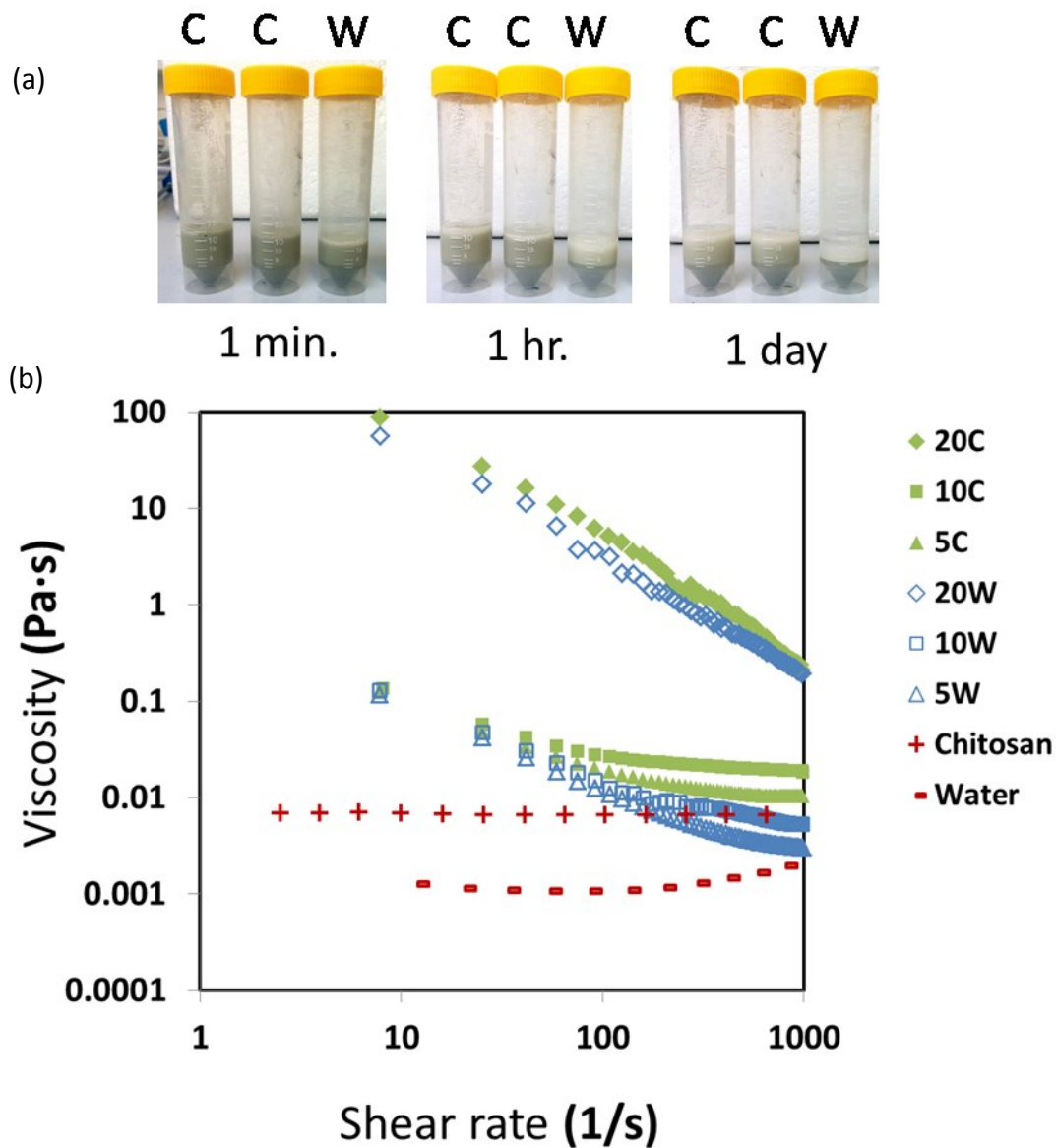


Fig. 59 Rheological properties of studied suspensions. a) Sedimentation study comparing the stability of water-based suspension using TMHA (W) with chitosan based one (C) with similar solid loading (10wt%), over three sedimentation times. Chitosan-based suspensions show to be stable over long range of time. b) Viscosity vs Shear rate of fibres suspensions using normal colloidal dispersant and chitosan at different solid loading (wt%). In the graph are also reported the viscosity of the solutions without fibre loading.

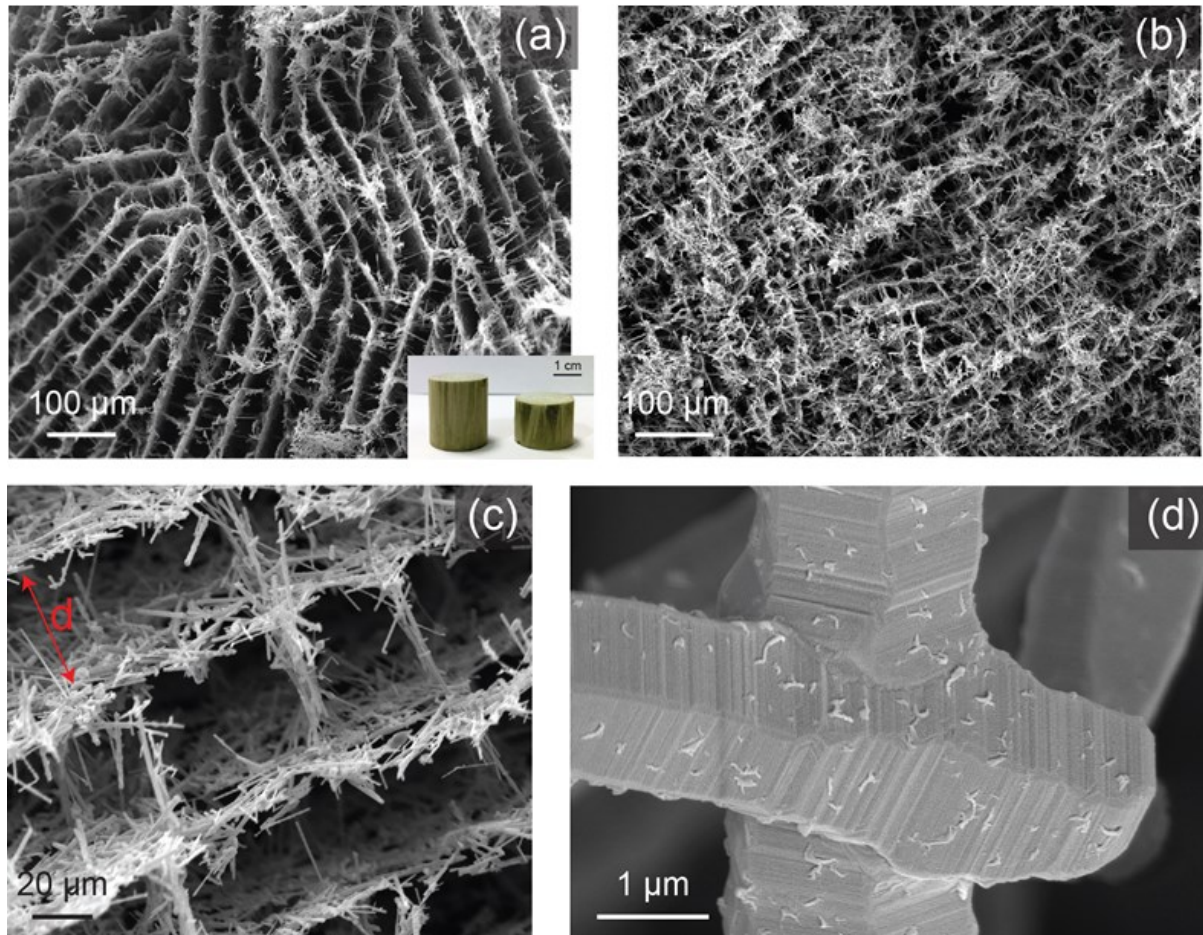


Fig. 60 Figure a) Scanning electron micrograph showing the network-like structure obtained using a suspension containing 5wt% fibres (98% final porosity). b) More isotropic structure obtained using 20wt% fibre suspensions (92% final porosity). c) Detail of the the structure shown in (a). The walls are thin (1-2µm) and formed by entangled fibres. Some fibres arrange perpendicular to the lamellae forming bridges between them. d) Junctions between fibres showing the good densification obtained by liquid phase sintering. Adapted from [26].

5.3.2 Mechanical and functional properties

Compression tests revealed a brittle behaviour of the SiC-network structures. The stress/strain curve shows that after the linear elastic part and after reaching the maximum strength, the curve reaches a plateau that is associated with the brittle crushing of the cells. In the plateau it is possible to observe dips that can be associated to failure events in subsequent levels. After each dip the strength is recovered until densification is reached after 50% of strain (Fig.61a). In-situ compressive tests have confirmed this behaviour. It was possible to observe that after reached the maximum crushing strength, the scaffold did not fail completely, but the junctions between fibres at the top and the bottom of the scaffolds, those in contact with the plates of the testing machine, started to break and accumulate. As

the load was transmitted to the following layer of cells the strength was recovered. The observed dips in stress at the plateau correspond with these failure events. However the bulk of the structure remained stable and is still able to sustain the load.

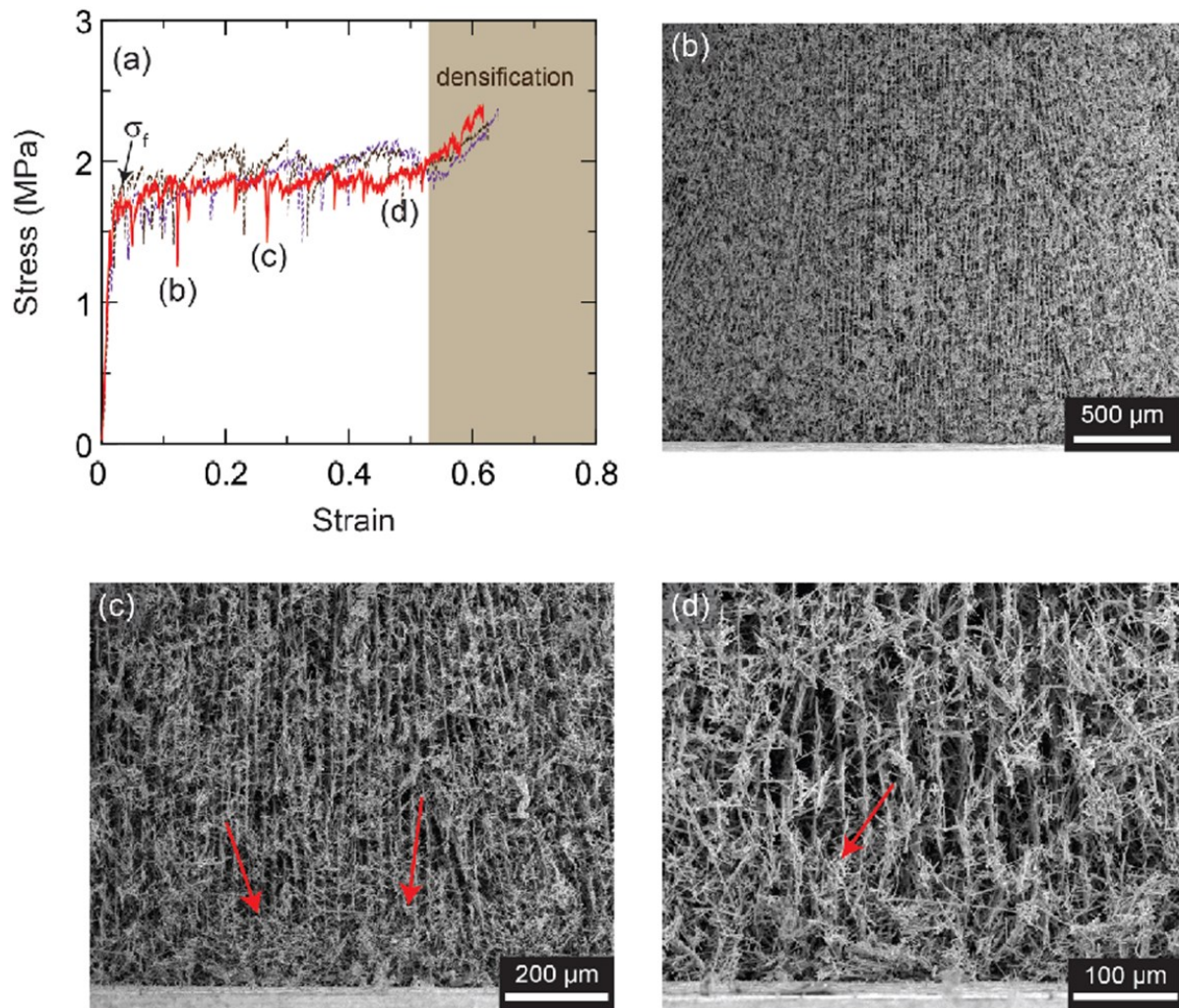


Fig. 61 a) Stress-strain curves of brittle SiC lattices with a porosity of 94%. (b-d) in-situ SEM compression test (corresponding to red line) shows how failure occurs at the junction between fibres at the top and bottom of the sample while the centre remains intact and can still hold the load. Red arrows indicate where the failure process starts that lead to the fibres accumulation. Adapted from [26].

Combining the high porosity with the bulk properties of SiC, the resulting structures showed interesting functional properties. Besides being structurally strong they were both electrically conductive (conductivities ranging from $5.3 \cdot 10^{-6}$ to $3.8 \cdot 10^{-4} \text{ S/cm}$) and thermally insulating (thermal conductivities of the order of $0.1\text{-}0.6 \text{ W/mK}$ (Fig.62a)). The materials, as many other porous structures obtained by freeze casting, were clearly orthotropic where

the two dimensions perpendicular to the freezing direction showed similar properties and dissimilar compared to direction parallel to the freezing path. The anisotropy was observed in the mechanical properties, thermal conductivity and acoustic impedance, especially scaffolds with high porosity. In terms of thermal conductivity the structures showed higher thermal insulation in the direction perpendicular to the freezing direction that can be up to ~ 3 times higher for samples with a porosity of 97%. A relevant result was that the thermal conductivity of all the tested samples remains relatively stable at high temperature up to 1500°C (Fig.62a).

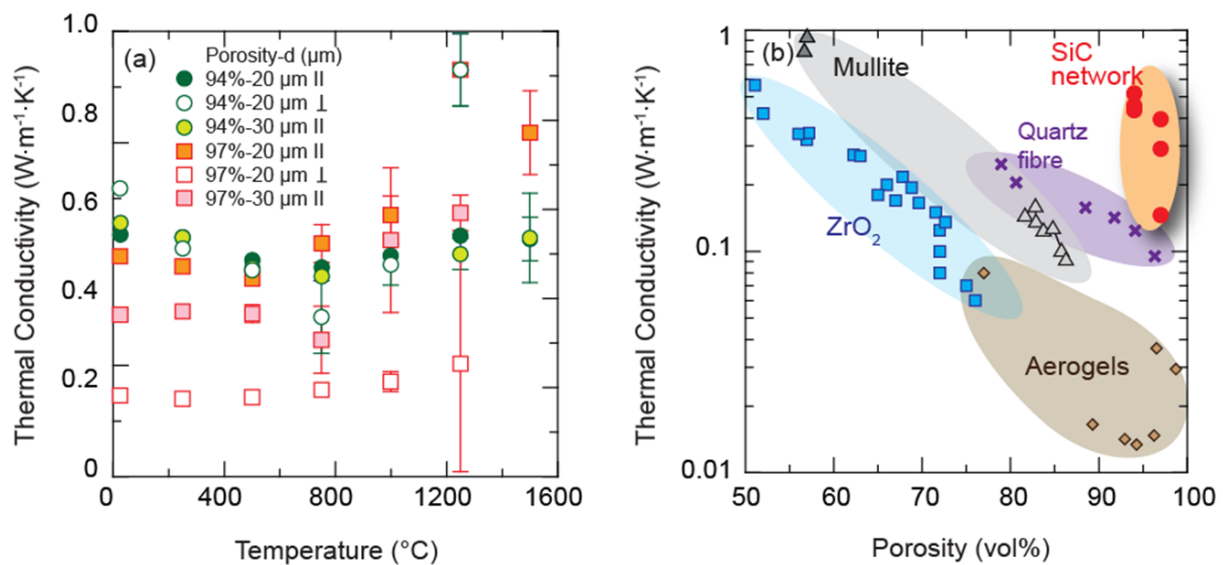
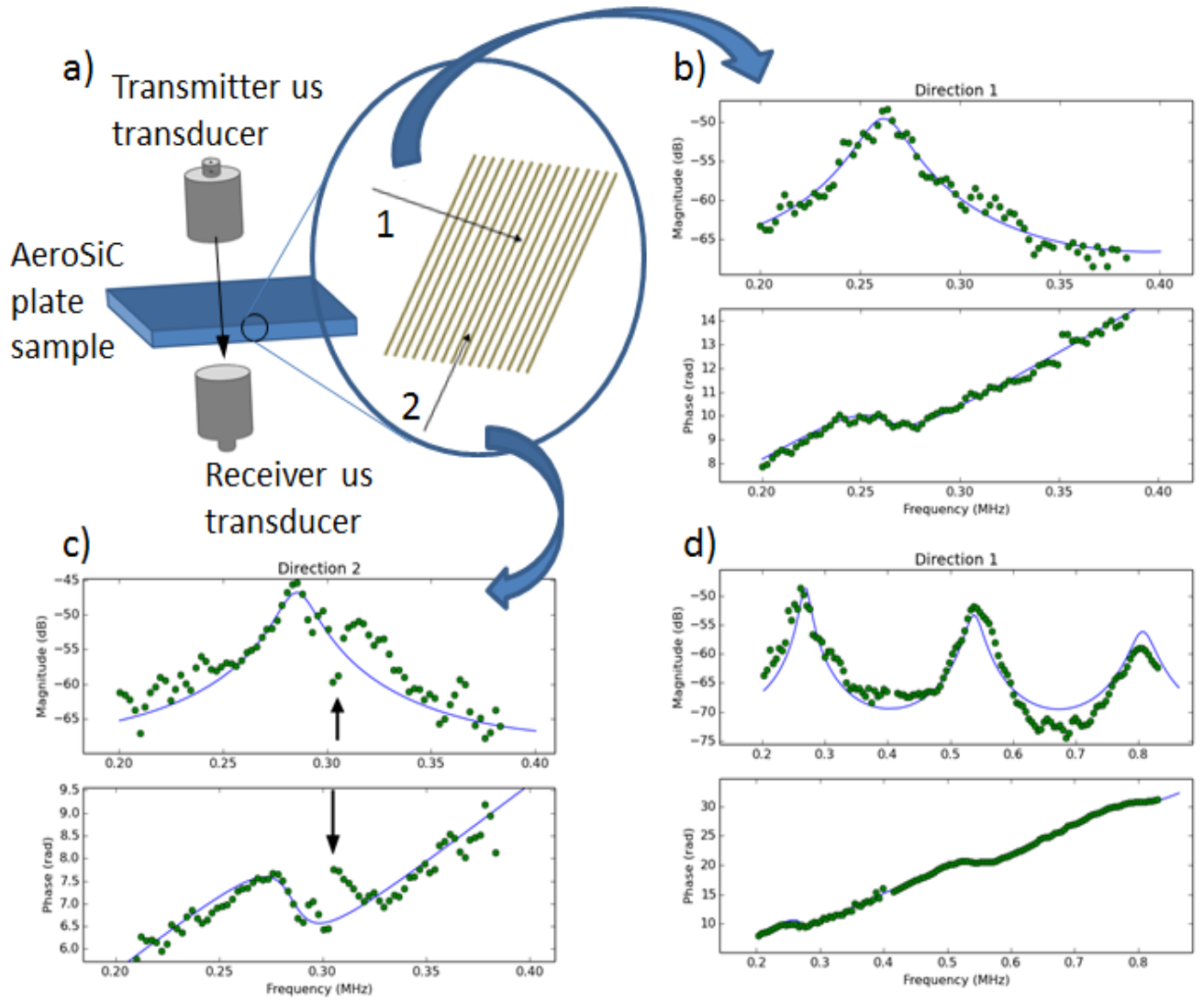


Fig. 62 a) The thermal conductivities in the direction parallel (II) and perpendicular ($\perp$) to freezing direction remain low with temperature up to 1500°C **b)** The thermal conductivity (room temperature values) of the SiC networks is similar to other porous ceramics. Aerogels have lower thermal conductivity and are lighter but they are also weaker (data from references [36–43]). Adapted from [26].

Also ultrasonic waves propagated differently within the lattice structure (Fig.63). Parallel to the layers the ultrasonic waves propagated faster, with velocities between 15% and 35% faster, than in the orthogonal direction (the anisotropy increase with decreasing the density). The ultrasound wave velocity showed low values that tended to increase with sample density (from 340 -540 m/s for $100\text{ mg}/\text{cm}^3$, up to 1100-1400 m/s for $250\text{ mg}/\text{cm}^3$). Velocity values for the less dense scaffolds were comparable to those calculated for silica aerogels with a similar technique. In addition, similar values for silica aerogels were obtained for the acoustic impedance (down to 0.03MRayl) and the ultrasound attenuation coefficient ($50\text{-}60\text{ Np}/\text{m}@300\text{ kHz}$)[28]. Furthermore, it was possible to vary the impedance

values over one order of magnitude changing the density (0.03-0.3MRayl). The acoustic properties make this material an appropriate candidate to be used as impedance matching membranes for wide-band-air-coupled piezoelectric transducers or for the production of acoustic metamaterials [44]. They show properties similar to the currently used aerogel but with better machinability and mechanical stability. Fig. 63 summarizes the results for the thickness resonances in the transmission coefficient along the two different directions. While for propagation along direction 1 (plate thickness 2.6 mm) the material exhibited a behaviour very close to the expected one for an homogeneous material (Fig.63b), along the direction 2 (plate thickness 1.9 mm) a sharp interference was always observed that produces a remarkable distortion of the spectra of the first thickness resonance (in the case shown, at 310 kHz, see arrows) (Fig.63c). This interference can be explained by the appearance of two different guided waves that propagate along the two different and simultaneous paths of propagation that the material offers in this direction: along the layers and along the spaces between them. Along the direction 1 the first three orders of the thickness resonances have been also measured (Fig.63d). For this direction, the structure behaves as an homogeneous material in a very wide frequency band; on the contrary, for propagation in the direction 2 the spectra becomes distorted as frequency increases and no higher order resonances are observed.



ULTRASOUND SPECTROSCOPY

Fig. 63 a) Representation of the experimental set-up of the air-coupled ultrasound spectroscopy used to measure thickness resonances in the transmission coefficient of plates at normal incidence; and the two main directions of propagation of the ultrasonic wave in the material: along the layered microstructure and normal to it. b) and c) Dots: Measured magnitude and phase spectra of the first thickness resonance of the plate for plates cut along the two main directions in the material (sample 20%, 0.2 g/cc); solid line: calculated response assuming the plate as an homogenous material. d) Dots: Measured magnitude and phase of the first three orders of the thickness resonances for wave propagation in the 1 direction; solid line: calculated response assuming the plate as a homogenous material. Adapted from [26].

5.4 Discussion

As already reported in previous studies [7,45], the mechanical properties of synthetic ceramic micro-lattices can be enhanced by carefully designing their architecture and their constituent struts. The achieved deformability and high mechanical response of some

ceramic micro-lattices produced via additive manufacturing and thin film deposition are related to two main design strategies. First the possibility of depositing defect free or with limited defect size thin strut wall (typically $\sim 10\text{nm}$) and in addition, the geometry can be designed to avoid strut bending and better accommodate the load during compression. The major limitation of these processes is the extremely small dimension of the samples, few millimeters at most, that can be generated.

Following the same design strategy of using thin strut layer, reducing therefore the probability of having a defect or the defects size, strong microscopic ceramic fibres have been assembled into macroscopic (centimeters in size) structures using a bottom up fabrication approach. The bending strength of the fibres has been measured in situ using a 3-point bending test. The obtained values ranged between 1 to 3GPa, higher than those of bulk ceramic materials but analogous to those estimated for the struts of ceramic micro-lattices (Fig.64)[7,8]. The strength obtained with this testing method and using 3PB instead of 4PB could be slightly overestimated but it represents a good value for the following calculations.

The fibres tend to organize into lamellae aligned parallel to the direction of ice growth. However fiber packing in the wall is poor. The walls are therefore formed by a highly porous fiber network. Due to the combination of strong SiC fibres with a proper sintered layered structure, the materials exhibit high crushing strengths and Young's modulus in the freezing direction (parallel to the walls) even at low densities (Fig.65). The values obtained are considerably higher than aerogels and similar to microscopic ceramic lattices with comparable densities fabricated using complex techniques.

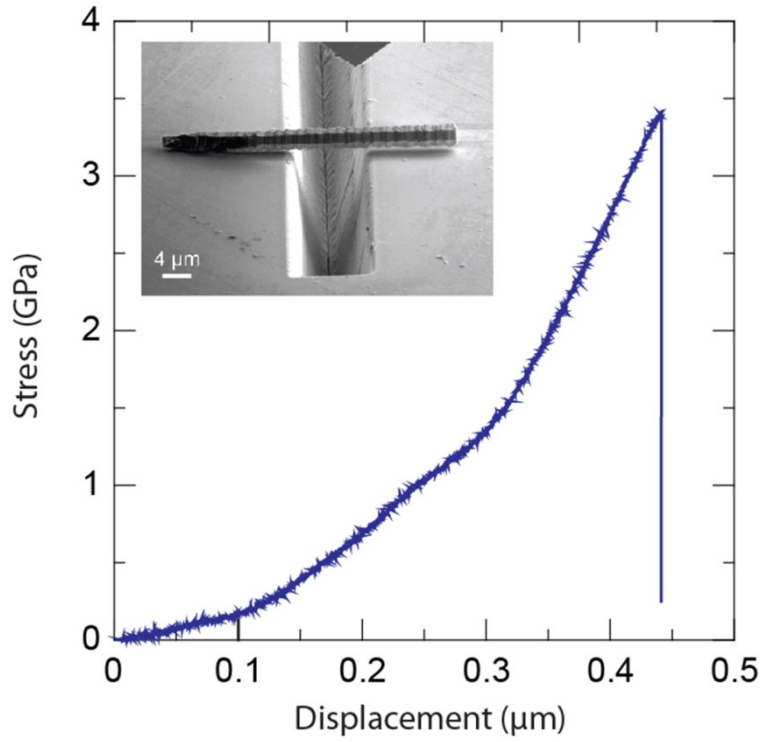


Fig. 64 Stress/displacement curve from a single fibre tree bending test performed in situ in the SEM (insert is a scanning electron microscopy showing the set-up). The initial nonlinearity of the curve is likely due to fibre movement under the indenter. Adapted from [26].

A comparison between the theoretical and the experimental strength and stiffness can be made considering a simplistic model of the material. The structures can be modelled as layered materials in which each layer can be considered, for the particular disposition of the fibres, as a honeycomb structure. The Young's modulus and strength values for hexagonal honeycombs under uniaxial loading and bending dominated behaviour can be calculated with the following scaling laws [22]:

$$\frac{E_h}{E_f} = 2.3 \left(\frac{t}{l} \right)^3 \quad (5.6)$$

and

$$\frac{\sigma_h}{\sigma_f} = \frac{4}{9} \left(\frac{t}{l} \right)^2 \quad (5.7)$$

where E_f , σ_f are respectively the Young's modulus and strength of the base fibre material (SiC in this case); E_h and σ_h the Young's modulus and strength of the honeycomb structured layer and t and l are the honeycomb cell parameters. It is well established that the ratio t/l is

proportional to the ratio ρ_h/ρ_s where ρ_h and ρ_s are respectively the density of the honeycomb and the density of the bulk material (SiC). The density of the honeycomb can be written as [22]:

$$\rho_h = \rho_s \frac{2}{\sqrt{3}} \frac{t}{l} \quad (5.8)$$

The density, the Young's modulus and the strength of the structure scale with the properties of the single wall as $\sim w/(w+d)$ where w is the wall thickness and d is the spacing between two adjacent walls. Therefore for this type of structure simplistically it is possible to say that $E \propto \rho^3$ and $\sigma \propto \rho^2$. Using this model a good agreement between the theoretical and the experimental values has been obtained. As reference the mechanical properties of the fabricated porous materials were plotted with other porous microlattices found in the literature alongside with the theoretical prediction (Fig.65). These predictions were compared also with the prediction for isotropic open cell under bending-dominated behaviour where [22]:

$$\frac{E}{E_s} \propto \left(\frac{\rho}{\rho_s} \right)^2 \quad (5.9)$$

and (case of fracture-dominated behaviour)

$$\frac{\sigma}{\sigma_s} = 0.2 \left(\frac{\rho}{\rho_s} \right)^{\frac{3}{2}} \quad (5.10)$$

In the graph the prediction for stretch-dominated cells was included. In this last case the modulus and strength will vary linearly with density [21,45]. The layered structure, with the specific pore/wall ratio obtained by freeze casting, is more efficient than the isotropic one (when compression takes place in the direction parallel to the layers) under bending mode and stretching mode comparing the theoretical predictions (dashed lines) in Fig.65. In this latter case the layered structure becomes more efficient below $\sim 95\%$ (Fig. 65c and d).

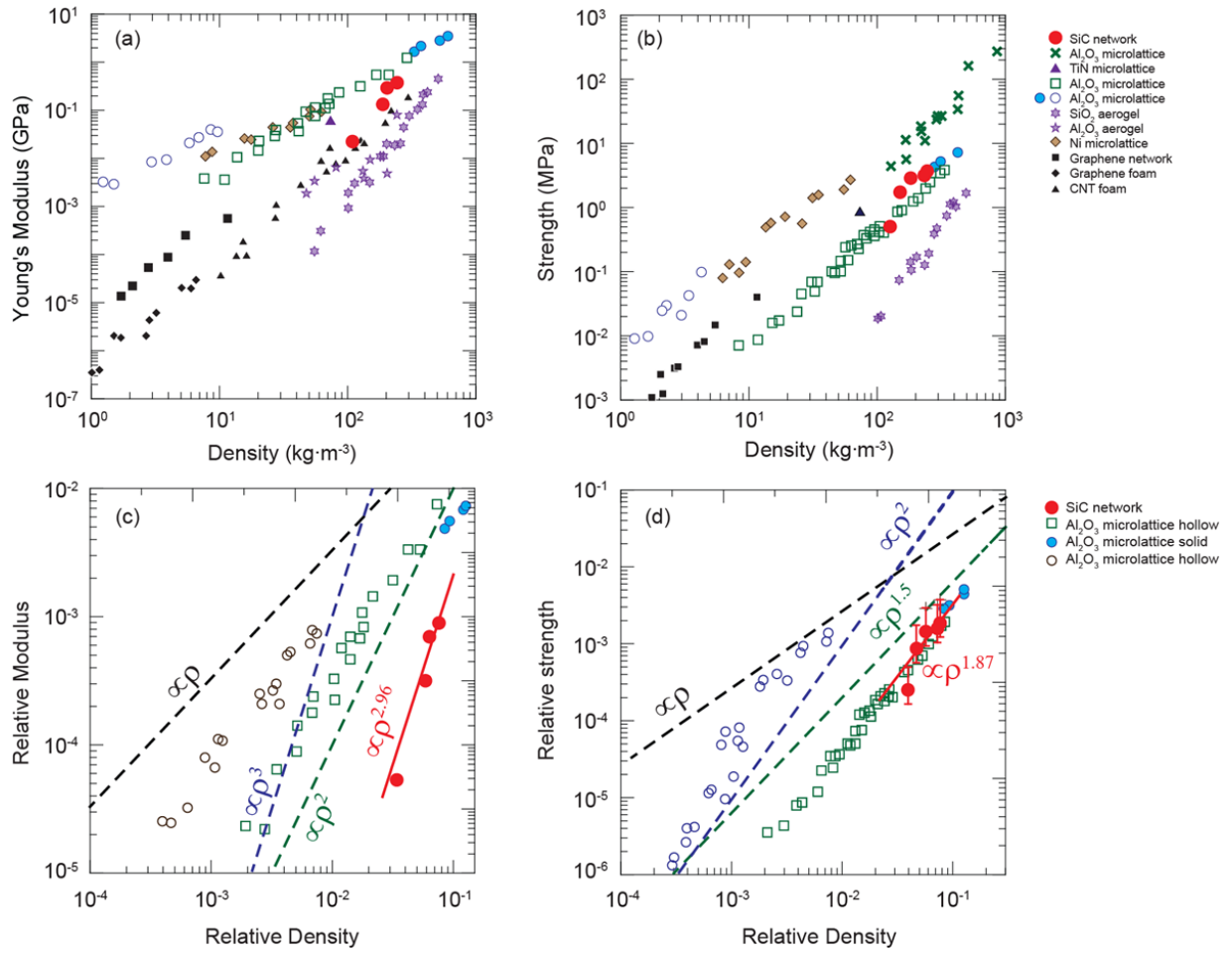


Fig. 65 Mechanical properties of the SiC lattices. (a) Comparison of the Young's modulus of the SiC lattices with other ultralight non-metallic materials (b) Comparison of the crushing strength. (c) Relative Young modulus (E/E_f) as a function of the relative density for ceramic micro-lattices. (d) Relative strength (σ/σ_f). In (c) and (d) theoretical predictions for layered and isotropic lattices (equation (5.6) to (5.10)) are plotted for comparison. In order to calculate the relative strength and toughness or the data in ref [18] a Young modulus of 164GPa and strength of 2GPa were used following the values given in the reference. The relative Young Modulus and strengths of the porous SiC structures have been calculated using $E_{SiC}=450\text{GPa}$ and $\sigma_{SiC}=2\text{GPa}$ (according to the fiber bending tests). The same values have been used to plot the expected values according to the different models (dashed lines corresponding to Equation (5.6) to (5.10)). When using a layered model, we have assumed $w/d=25$ according to the microstructural observations. Data taken from refs [1,5–8,10,12–14,16]. Adapted from [26].

The stiffness and strength of the freeze casted lattice is above that of aerogels and similar to those measured for micro-lattices, but lower than the theoretical (dashed lines in Fig.65d). The overall structure is weaker than expected from the model because, as observed in the in situ compression test, the junction between fibres is the “weak” point where the scaffold starts to fail (Fig.61). In previous studies it has been shown, through finite element simulations that under compression the maximum stresses in macro and micro-lattices are experienced by the junctions [7]. However the strength and the elastic modulus found experimentally scale with density following a power law very close to that predicted from

equations (5.1) and (5.2) (~ 3 and 1.9 respectively). Thus, although the system is a simplification of the real structures and it does not perfectly describe the architecture of higher density scaffolds that have more isotropic design (higher number of fibres entrapped between the walls), it predicts the mechanical response of the system relatively well.

Comparing with different types of materials, the mechanical properties of the SiC-network are similar to those of light polymer foams or wood (Fig. 66). The low density scaffolds show also very interesting functional properties. As reported the ultrasound propagation velocities are in the same range of those for aerogels and other highly porous natural materials such as cork. The thermal conductivities are at least one order of magnitude lower than those of conventional SiC foams with porosities below 80% [46] and comparable to some of the porous mullite and zirconia and fiber glass insulating structures (Fig. 62b). Silica aerogels show the best thermal insulator properties among man-made materials but they are significantly weaker and electrically insulating. In addition, the SiC-networks tend to remain stable with low thermal conductivity at high temperatures up to 1500°C , stability not showed usually from traditional porous thermal insulating ceramics [36]. The slight increase in thermal conductivity at high temperatures for samples with larger pores can be related to an increase in the radiative component of the thermal conductivity. Overall, the sound propagation, thermal or electrical properties are influenced by the anisotropic structure of the material. Two main paths can be distinguished, the SiC lamellae formed by tangled fibres and the gas between them. Transport along the lamellae is faster and, as expected, increases with density (as the lamellae get denser it favors better conductivity). In the normal direction to the walls sound and thermal transport “jump” from one media to the other (from wall to gas phase and so on) while electrical conductivity depends on the presence of fibres bridging the walls. In the latter direction transport properties are diminished.

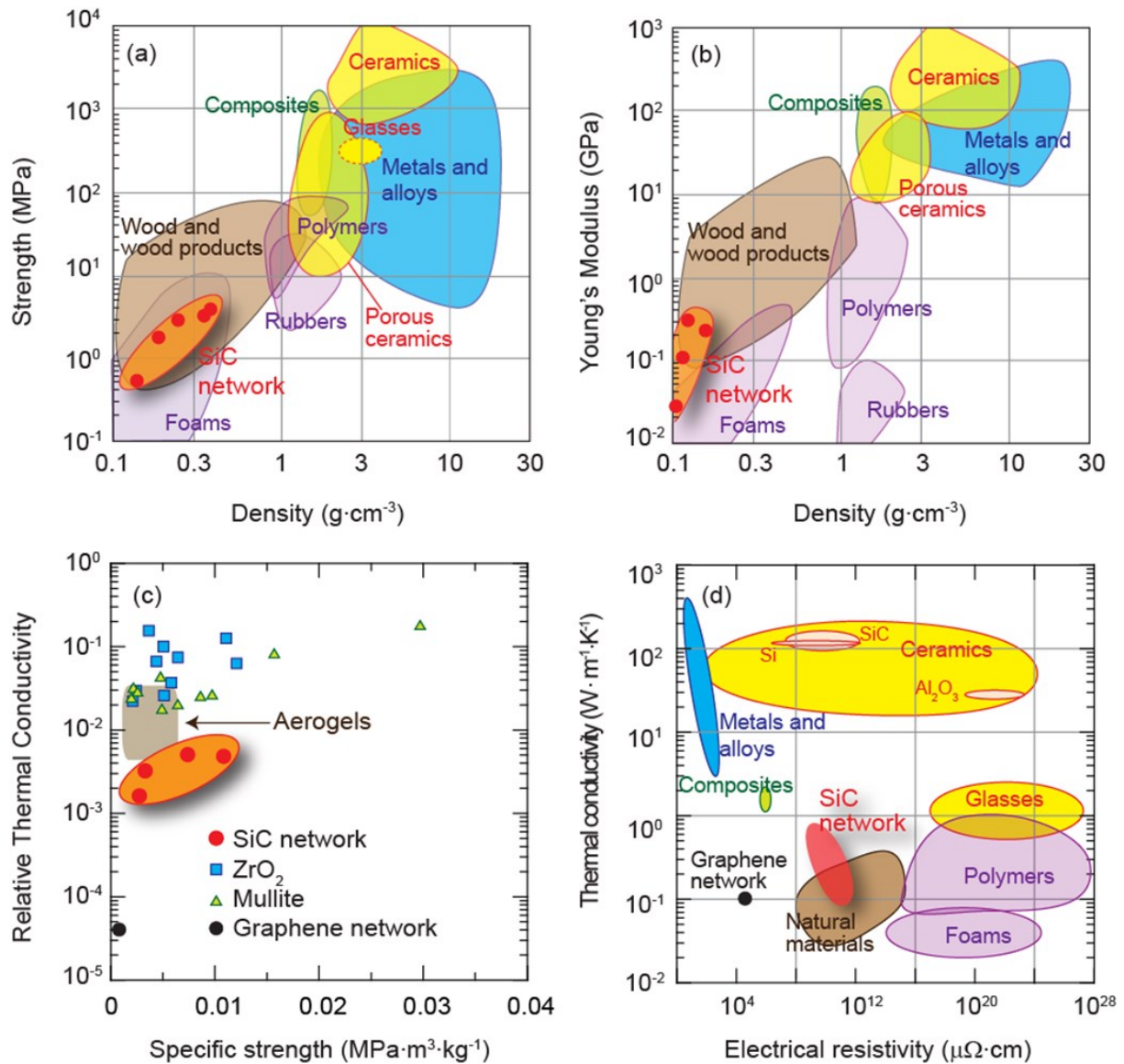


Fig. 66 a) Strength and b) Young modulus of SiC network compared to other groups of materials. The properties close to foams or wood are obtained more than to conventional porous ceramics (graphs redrawn from [29]). c) The high porosity of the SiC networks give them a very low thermal conductivity compared with the dense material while the hierarchical lamellar organization high specific strength. d) The networks offer a unique combination of low electrical conductivity (for a ceramic) with low thermal conductivity when compared to other materials. For the thermal conductivities of the dense ceramics the following values have been used (SiO₂: 1.38W/mK; SiC: 120W/mK; mullite: 6WmK; ZrO₂: 2.7W/mK; graphene: 2500WmK). Adapted from [26].

5.5 Conclusion

In summary, ultralight SiC structures with macroscopic dimension and hierarchically designed microscopic porosity have been produced. The simple wet processing method employed (freeze casting) allows producing scaffolds with different shapes and could be scaled to produce structures of practical sizes. Moreover changing the freezing conditions, it

is possible to tailor the final microstructure in terms of density and pore/wall ratio. Changing the density of the material, scaffolds with different mechanical responses can be produced. These extremely light layered SiC structures show mechanical properties similar to those of microlattices obtained with more complex methods such as additive manufacturing and atomic layer deposition. With freeze casting it is not possible to achieve the same architectural control obtained by these advanced additive manufacturing routes, therefore our structures still deform in a bending-dominated behaviour. However combining a layered architecture with strong short SiC fibres similar strength and stiffness of microlattices have been achieved. These structures show also interesting functional capabilities such as thermal insulation and electrical conductivity, making them promising candidates for thermal management, filters and catalyst supports applications designed to work at elevated temperatures or even as ceramic reinforcement in the production of composites.

5.6 References

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6 Alumina-Aluminium lamellar composites

6.1 Introduction

Ceramic materials nowadays find applications in many different advanced fields from healthcare (e.g. prosthesis for bone replacement [1], bone grafting for bone regeneration [2]) to aeronautics (e.g. thermal coating on the blades used in jet engines [3], structural parts etc.), nuclear engineering (e.g. encapsulation of nuclear waste [4]), power generation [5], electronics etc. They are often preferred to metals and polymers for their better corrosion and wear resistance, enhanced chemical and thermal stability, high flexural strength and hardness that make them suitable for demanding applications. However, the performance of ceramic materials is often limited by their brittle behaviour and low fracture resistance. The achievement of both strength and toughness is an essential requirement for most structural materials but these properties are often mutually exclusive [6]. The possibility for a material to achieve a significant deformation when loaded is one of the toughening mechanisms, frequently referred as intrinsic (that acts in front of the crack tip), to achieve high fracture resistance and is the main toughening mechanism for metallic materials. Any attempt to increase the strength translates into a decrease of plasticity and thus toughness. Strong materials such ceramics with limited deformation tend to be brittle but toughness can be generated relying on other types of mechanisms that are not related to intrinsic plasticity. Extrinsic toughening mechanisms, acting behind the crack tip and shielding locally the stress, are the primary source of toughness in ceramic materials.

Several toughening strategies have been engineering to maximize the fracture toughness of monolithic ceramics such as crack deflection, grain or fibre bridging [7]. However the fracture toughness values achieved so far [7,8] are much lower than those of metals. Ceramic matrix composites (CMCs) are ideal candidates to overcome this problem. In the past decades, the idea of toughening brittle materials using ductile or strong reinforcements has been diversely explored to produce composites with superior traits. Reinforcements used are: discontinuous such as whiskers, short fibres, particles, and platelets or continuous such as long fibres or laminates. Several factors can affect the mechanical performance of CMCs: the interfacial adhesion between phases, the reinforcement morphology (shape and

size), volume fraction and distribution [9]. For example, at equal amount of reinforcing phase the use of laminates has been shown to be one of the most efficient toughening strategies [10–13]. The metallic ductile phase tends to remain intact and bridge the opening crack increasing the crack-propagation resistance of the material. The use of laminates or reinforcement with high aspect ratios, increases also the probability of intersection with a propagating crack. However it is becoming increasingly clear that, in order to optimize the contribution from both the matrix and the reinforcing phase it is extremely important to reach a precise control on the material properties and microstructural organization at multiple length scales [8].

This kind of architectural control is well exploited by Nature that produces damage tolerant materials that can be at the same time strong and tough. Many natural materials rely on the actuation of both intrinsic and extrinsic toughening mechanisms within the same structure. The design concepts found in Nature that allow both types of mechanisms to act are based on the production of composite materials with highly hierarchical microstructures [14,15]. Bone, seashells, teeth are clear examples of these structural motives. Natural materials are indeed composites where the inorganic phase (with different mineral content depending of the function) is cleverly interlayered with an organic phase that acts as the compliant phase. These composites have characteristic structural features on multiple length scales from molecular to macroscopic dimension that give the final structure a mechanical performance much higher than those of the single constituents.

In the last decades many attempts have been done to replicate such structures in artificial materials [16–19], but the man-made Nature-inspired materials are still far from perfectly replicating the complex and intricate hierarchical structure of natural ones [20]. Conventional ceramic processing techniques (slip/tape-casting, hot pressing, chemical vapour deposition etc.) cannot replicate faithfully the hierarchical organization at many different length scales, requiring therefore an implementation of the actual design motives and fabrication processes. One of the first attempts to mimic nacre-like structure was done by Clegg et al. [21], where stacking up laminas of SiC interlayered by a graphite layer increased the work of fracture of the material by a factor of over 100. Subsequent tries to reproduce nacre-like materials have been usually limited to the bonding of thick ceramic layers ($\sim 200\mu\text{m}$) with metallic ones [10,12,22]. More recently a new class of bio-inspired

composite materials with superior mechanical properties, using novel processing techniques such as freeze casting (ice-templating) [16,17,19,23] or magnetically assisted slip casting (MASC) [24], has been developed combining a ceramic hard phase with a ductile phases (metal or polymer) acting as “lubricant”.

Aluminium alloys are attractive materials to produce CMCs due to their low density, their good corrosion resistance and high thermal and electrical conductivity. The main challenge is to find “top-down” fabrication methods that allow the fabrication of metal/ceramic structural composites that are both low-cost and damage-tolerant. The most common fabrication routes used for ceramic/metal composites production have been powder metallurgy and molten metal routes [25]. The former one does not allow the production of complex ceramic networks being necessary to start from the mix of ceramic and metal powders [26]. Moreover a good dispersion of the powders it is not always easy to achieve and aggregates are often produced. Infiltration of porous ceramic preforms is an attractive route to produce interpenetrated composite materials for the wide variety of types, morphologies and metal volume contents that can be selected allowing the production of tailored microstructures. However, in the molten metal route – squeeze casting, gas pressure infiltration and high pressure die casting infiltration - the application of pressure is usually required and they may suffer from premature failure of the ceramic preforms [25]. Due to the poor wettability of metal on ceramic preforms conventional melt infiltration methods in fact require external pressure. In this way the molten metal is forced to flow into the porous ceramic preform that has to be strong enough to withstand the applied pressure. Therefore these conventional techniques cannot be taken in consideration for highly porous preforms. More recently, innovative techniques have been developed such as pressureless infiltration process (reactive infiltration) also known as Lanxide process [27] and electrodeposition like the one developed by Pappacena et al. [28]. Specifically, pressureless infiltration is an attractive technique due to its cost effectiveness and near-net-shape capability [29]. The process is capillarity driven. However, the types of metal or metal alloys are restricted. Only a few composite materials can be produced by this method and the most common are Al alloys infiltrated into ceramic preforms. As reported by Aghjanian et al. [30] an Al-4wt% Mg alloy can spontaneously infiltrate completely an alumina preform. The presence of Mg in the alloy and the use of a nitrogen atmosphere during the infiltration

are critical to complete the process. According to numerous studies, the addition of magnesium in aluminium increases the wettability of the molten aluminium on the ceramic substrate [31,32]. It seems that the role of Mg in the alloy is mainly to reduce the surface tension and promote a chemical reaction with the ceramic particles. Whereas, the role of the nitrogen in the process is not completely clear, but it has been supposed that it helps to further reduce the surface tension and thus enhance the wettability of the molten aluminum on the ceramic part [30]. It has been also suggested that the Mg in the alloy partially evaporates and reacts with N_2 and forms a coating of Mg_3N_2 on the ceramic preform. This compound reacts with the molten Al which is then reduced to AlN recycling the Mg. This reaction between Mg_3N_2 and Al seems reduces the contact angle between the Al and the ceramic [29] allowing pressureless infiltration. Mg plays also a role in gettering O_2 in the N_2 atmosphere thus reducing the possible formation of a passivating alumina layer on the metal surface. The amount of Mg required to initiate the process is dependent on several parameters including particle size, infiltration temperature, pore size, dwell time and infiltration atmosphere. Termination of infiltration is associated with the removal of Mg from the melt front due to the formation of an alumina/spinel layer.

In this study, freeze cast alumina preforms have been used due to their excellent mechanical strength that makes them suitable to a liquid metal infiltration process and for the possibility in tuning architecture at multiple scales. Two different alumina particles morphologies have been used in the fabrication of the preforms, spherical nanoparticles and platelets [33]. By manipulating the suspensions solid loading and freezing rate, we are able to produce layered preforms with different residual porosity and microstructural features. In order to fabricate bio-inspired ceramic/metal composites (CMCs), the porosity of the freeze cast scaffold has been filled with an Al-4wt% Mg alloy that acts as a second soft phase producing bulk ceramic-metal layered composites. Freeze casting allows the fabrication of composites with a ceramic loading that can vary from 30% to 60% in weight, when in conventional CMCs reinforced with particles or fibres typically the ceramic content varies either from very low (5-30%) [34] or very high (60-80%), due mainly to the lack of commercially available preforms. Launey et al. [16] have shown that layered metal/ceramic composites can exhibit excellent combinations of strength and toughness. In their study an Al-Si eutectic alloy was selected to infiltrate a freeze casted alumina preform for its lower

melting point and viscosity and also because it showed a low contact angle on Al_2O_3 (around 50° in vacuum) [35] allowing pressure infiltration at relatively low pressures. The presence of Si, however, makes the alloy more brittle than pure aluminium. In this study a pressureless infiltration process has been used that allow infiltrating Al-4Mg, an extremely ductile aluminium alloy, even in the more porous preform, with ceramic layer thickness down to $4\text{-}5\mu\text{m}$. Traditionally laminate structures have been produced by alternately cold pressing layers of ceramic and reinforcement and subsequently hot pressing them to produce different types of bonding (diffusion, reaction, deformation etc. [11]). With this process many laminates of different materials have been produced such as: Nb/Nb₃Al [13]; Al/ Al_2O_3 , Ni/ Al_2O_3 , Cu/ Al_2O_3 [12,36]. However using this approach coarse microstructures have been produced with ceramic layers ranging from 50 to $500\mu\text{m}$. With this approach the ceramic layers are two or three orders of magnitude smaller than traditional ceramic-layer composites produces with conventional ceramic processing and even smaller than those produced by Launey et al. [16].

6.2 Materials and methods

6.2.1 Microstructure

Freeze casting of water based alumina nanoparticles and platelets/nanoparticles suspensions was used to produce lamellar alumina scaffolds as reported in other studies [16,17,33,37,38]. The alumina nanopowder used were BaikaloX B-series SMA6 (Baikowski, France), with a nominal particle size of $0.3\mu\text{m}$, a specific surface area of $7\text{m}^2/\text{g}$ and no more than 70ppm of impurities (Baikowski, product specifications). Suspensions of solid content of 30 and 50wt% were prepared and subsequently frozen in the freeze casting set up shown in Chapter 2, at a cold-finger cooling rate of 5 and $15^\circ\text{C}/\text{min}$. The alumina platelets had a diameter and a thickness of $5\text{-}10\mu\text{m}$ and $300\text{-}500\text{nm}$, respectively (AlusionTM, Antaria Limited, Bentley, Western Australia). To promote sintering between the platelets, water based suspensions with a total solid loading of 30wt% were produced using a bimodal distribution of platelets and nanoparticles in a ratio of 70:30. When platelets were used suspensions were frozen at $5^\circ\text{C}/\text{min}$ to promote a better alignment within the lamellae. In

both type of suspensions, Dolapix type CA (Zschimmer and Schwarz GmbH and Co., Germany) was used as dispersant, polyvinyl alcohol (PVA) 22000 (VWR, Belgium) as binder and sucrose type Anala R Normapur (VWR, Belgium) as freezing additive. Slurries with only alumina nanoparticles were ball milled at 300rpm (Capco test equipment, 12VS, UK) overnight with alumina milling media (alumina balls of 10mm in diameter). Before being frozen, the slurries were de-aired with a vacuum pump at least for 1hr to remove entrapped air bubbles. The preparation of the slurries containing the alumina platelets was more complex. To avoid any damage to the platelets during the milling step, only the alumina nanoparticles used as sintering aid were ball milled overnight. Once the milling balls were removed, the alumina platelets were added and the suspension was sonicated for at least 30min and mixed in a planetary (Turbula mixer) mixer overnight. A de-gassing step was also applied. After de-gassing all the suspensions were directionally frozen at specific freezing rate to promote ice crystal growth. Patterning of the cold finger was used to better align the ceramic lamellae [39]. The frozen samples were then freeze-dried (Freezone 4.5, Lobconco, USA) and the obtained green bodies sintered in a conventional furnace (Ultratherm, Pyrotherm Ltd, UK) in air. The temperature was raised at 1°C/min up to 1000°C and held for 1 hour to burn out of the binder. Afterwards the temperature was increased at 5°C/min to 1550°C and held for two hours.

The porous ceramics were then infiltrated with molten Al-4wt% Mg alloy (5083 Al-alloy, Smithmetals, UK) with a pressureless process. The infiltration was carried out in a tubular furnace (Lenthon, UK). The sintered alumina scaffolds were placed on top of aluminium alloy pieces inside an alumina crucible. The tube was flowed with nitrogen for 1 hour to reduce the oxygen in the system. Several aluminium alloy pieces were usually placed right before the sample to be infiltrated, as external getter to reduce the concentration of oxygen inside the tube [30] (Fig.67). The furnace was heated with a nominal heating rate of 35°C/min to 400°C where the temperature was held for 30 minutes to allow the formation of porous MgO layer as reported by Srinivasa Rao [29] and to avoid the formation of γ -Al₂O₃ at the aluminium surface which is negative for infiltration. The temperature was again increased up to 950°C for 180 minutes to complete the infiltration. After the infiltration was completed, a water-cooling low-speed diamond blade (500µm thick) was used to cut rectangular beams for bending tests (20x2x3mm³) with the tensile faces parallel to the

ceramic layers. The tensile faces were mirror polished. Single-edge notched specimens (SEN(B)) were used to evaluate the fracture toughness K_{Ic} and crack resistance curve (R-curve). An initial notch was cut in the specimens with a low-speed blade that was subsequently sharpened with a razor blade using a 1 μ m diamond paste. Sharp cracks of almost the half ($a/W \sim 0.5$) of the thickness of each specimens were obtained for the R-curve measurements to favour a more stable crack propagation [40]. To evaluate the influence of sample geometry on the R-curve sample of bigger dimension were also tested (20x3x3mm³ and 20x4x3mm³, the latter geometry with two different a/W ratio 0.25 and 0.5). In accordance with the standard (ASTM-E1820-1), the notch size of SEN(B) specimen for K_{Ic} measurement were between 0.12 and 0.3 of W . The orientation of the notch was such that the crack could growth perpendicularly to the ceramic layers (crack-arrested orientation).

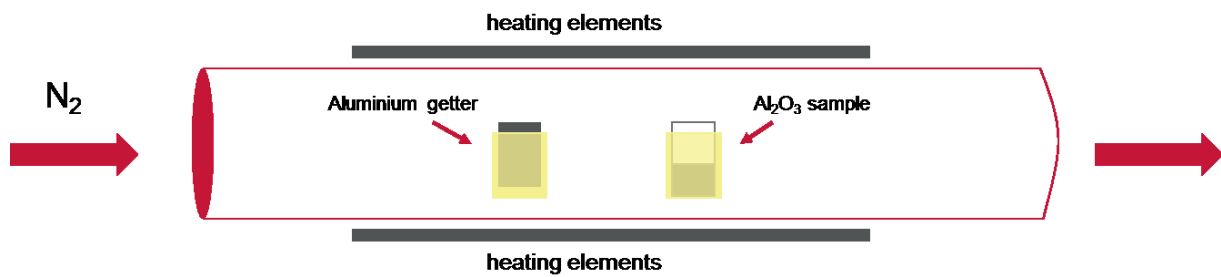


Fig. 67 Schematic representation of pressureless infiltration set-up.

6.2.2 Microstructural and mechanical characterization

The microstructure of the materials was analysed via scanning electron microscopy (SEM, Leo Gemini 1525). Crack path and damage evolution during R-curve tests were examined with optical microscopy (Zeiss, AxioCam), SEM (Leo Gemini) and X-ray tomography (Phoenix vTomeX/X-ray, Germany). The Archimedes method (Sartorius, YDK01, Goettingen, Germany) was used to evaluate the density and porosity of the freeze casted porous scaffolds. Phase composition analysis was performed by X-ray diffraction (XRD, PAN-analytical, Almelo, Netherlands). Scan data were collected with CuK α ($\lambda=1.54178$ Å) radiation at a step size of 0.1° and 150s for steps.

Four-point bend tests were performed to generate stress and strain curves and calculate the flexural strength. The experiments were carried out using Zwick-Roell Z010 with a load cell of 100kN capacity, and the associated software was TestXpert II. The tests were performed on un-notched composite bars using support span of 12mm. The displacement rate was set as 0.2mm/min in general accordance with ASTM [41] (C1161). The fracture toughness tests were performed on SEN(B) specimens on the same apparatus, using the same support span of 12mm. K_{Ic} values were determined by monotonically loading the bars until failure at constant displacement rate of 0.1mm/min. Three (3PB) and four-point (4PB) bending tests were performed to compare the test conditions on the plane-strain fracture toughness K_{Ic} . The work of fracture was evaluated from the area under the load-displacement curves. For the R-curve measurements, samples were tested in four point bending ($S \sim 18\text{mm}$) with an Instron 8500 machine at a testing rate of 0.01mm/min. The beams were loaded until crack propagation was observed in the load/displacement curve (change in the compliance of the material). The specimen was then unloaded and the crack was measured with an optical microscope (Zeiss, AxioCam). In some cases the crack path was also measured with scanning electron microscopy and X-ray tomography to compare different observation techniques. Different measurements of crack propagation were taken with the precaution of loading the sample always in the same position. The beam deflections were measured using a linear variable differential transformer (Solartron, LVDT).

Nonlinear elastic fracture mechanic analysis was used to evaluate fracture resistance of the samples as the crack propagated through the microstructure. The J-integral versus Δa crack extension were estimated. In the J-integral two contributions were taken into account, the elastic $J_{el} = K_{Ic}^2/E$ and the plastic $J_{pl} = 1.9A_{pl}/Bb$ where E is the Young's modulus, A_{pl} is the plastic area under the load-displacement curve, B the specimen width and b the un-cracked ligament length. From the evaluation of J it is possible to extract the values of K with a sample J - K equivalence for nominally mode I fracture ($K_J = (J \cdot E)^{1/2}$) [17]. The Young's moduli E for each tested composite were estimated as the midpoint between the upper and lower bounds determined using the "rule of mixtures" defined by Voigt and Reuss models [34,42]. These boundaries have been calculated considering E values for Al-4Mg of 73GPa [43] and for Al_2O_3 of 400GPa [40]. The experimental data were fitted with a model proposed by Bloyer et al. [13] to describe the bridging contribution to the overall near-tip stress

intensity. The model proposed that the contribution given by the crack bridging can be calculated with the following equation:

$$K_b = \int_0^L \sigma(x) h(a, x) dx \quad (6.1)$$

where $\sigma(x)$ is the traction distribution acting on the crack surface and $h(a, x)$ is a weight function employed to estimate the stress intensity reduction caused by the crack shielding and L is the bridging zone length. For the SEN(B) geometry the weight function can be written as:

$$h(a, x) = \sqrt{\frac{2}{\pi a}} \cdot \frac{1}{\sqrt{1 - \frac{x}{a}}} \cdot \left[1 + \sum_{(v, \mu)} \frac{A_{v, \mu} \cdot \left(\frac{a}{W}\right)^\mu}{\left(1 - \frac{a}{W}\right)^{\frac{3}{2}}} \cdot \left(1 - \frac{x}{a}\right)^{v+1} \right] \quad (6.2)$$

where a is the crack length and the coefficients $A_{v, \mu}$ are reported in the Table 5:

Table 5 Coefficients $A_{v, \mu}$ of polynomial fit for SEN(B) weight function, where v and μ are the rows and columns of the matrix.

v	$\mu=0$	1	2	3	4
0	0.4980	2.4463	0.0700	1.3187	-3.067
1	0.5416	-5.0806	24.3447	-32.7208	18.1214
2	-0.19277	2.55863	-12.6415	19.7630	-10.986

If the bridging contribution K_b is added to the intrinsic toughness K_{Ic} of the material, the total toughness K_f can be estimated as:

$$K_f = K_{Ic} + K_b \quad (6.3)$$

To estimate K_b is necessary to know the traction function $\sigma(x)$ that simplistically can be considered constant over the total bridging zone and equal to the constrained flow stress σ_c of the metal layers. The total contribution of the reinforcement is obtained multiplying the traction function with the volume fraction f of the reinforcement. Therefore the equation (6.1) it can be re-written as:

$$K_f = K_{Ic} + f \sigma_c \cdot \int_0^L h(a, x) dx \quad (6.4)$$

The value of the flow stress was chosen minimizing the residual obtained by the square of the difference between the experimental data and the model.

6.3 Results

6.3.1 Microstructure

Directional freeze casting and pressureless infiltration were used to produce ceramic/metal layered composites with micrometre size features. Controlling the cooling rate at the bottom of the cold finger it was possible to force the ice crystals to grow vertically assuming the shape of lamellae. During their growth the ice crystals expelled the ceramic particles that remained entrapped between them. After sublimation the lamellar pattern was reproduced in the ceramic green body (ice-templating). To better align the ice crystals during their growth and therefore the ceramic lamellae in the final microstructure, a patterned cold finger was used. The patterning consisted of insulated tape covering the cold finger in which parallel cuts were produced with a scalpel to ensure more controlled nucleation sites for the ice crystals. Sucrose was added to the suspension in order to induce the formation of micro-roughness on the lamellae walls and small bridges between them that play both a critical role on the shear at the ceramic-metal interface [39]. The microstructures of the all samples produced are summarized in Fig.68.

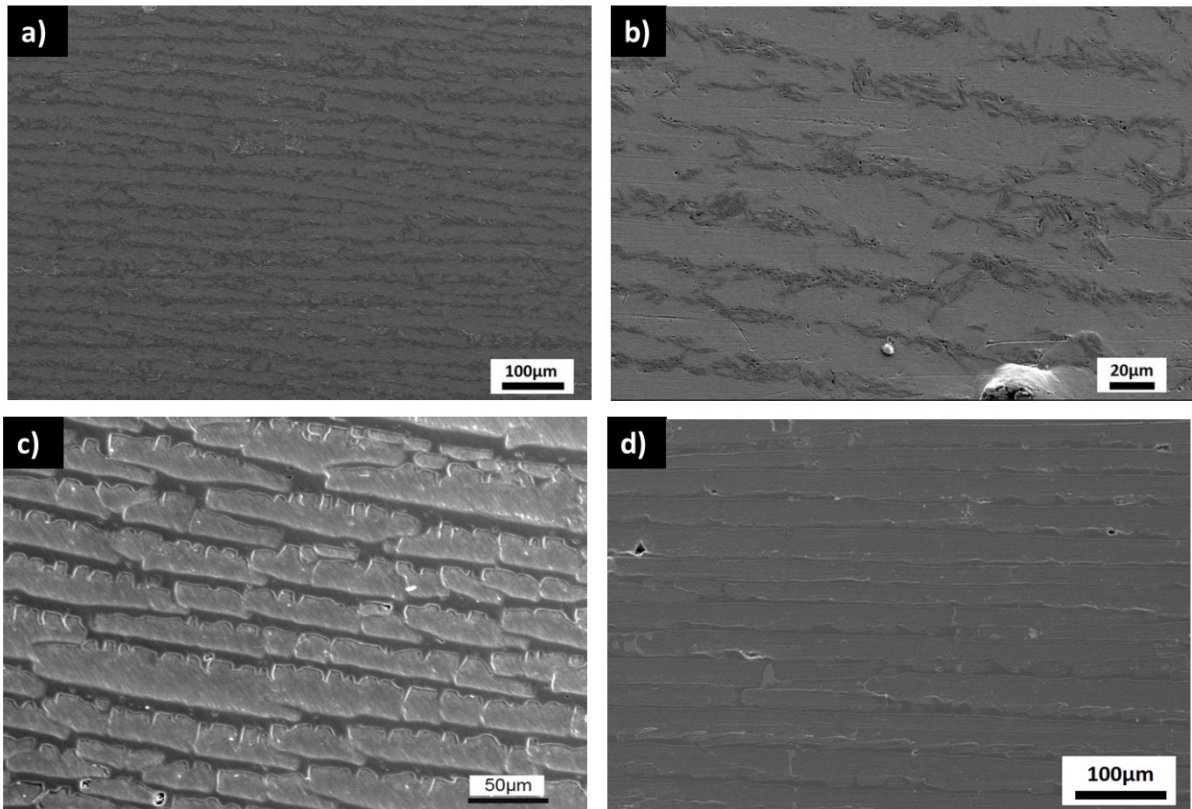


Fig. 68 Microstructures of produced composites. a)-b) alumina platelets based composites, c) 50wt% lamellar composites d) 30wt% lamellar composites.

One of the noteworthy traits of freeze casting is the possibility to manipulate the microstructural features changing some process parameters such as freezing rate, solid loading or particles size as it can be appreciated in Fig. 68. In this study three parameters have been changed to obtain scaffolds with different morphologies. When alumina nanoparticles were used two different solid loading were considered 30wt% and 50wt% (approximately 10 and 20vol% respectively) with two freezing rates 5 and 15°C/min. The porosity of the scaffolds after sintering and the lamellae thickness are reported in Table 6. The final porosity varied between ~65% to ~87% and the lamella thickness between ~3 to ~8μm.

Table 6 Microstructural features of freeze casted Al₂O₃/Al composites. The metal layer width in platelets-based scaffolds is not reported because the platelets are not perfectly aligned within each lamella and metal layers can be observed between platelets.

	Porosity (%)	Lamellae width (μm)	Metal layer width (μm)
Nano-30wt%-5°C/min	79.6 $\pm$ 0.3	4.1 $\pm$ 0.9	23.3 $\pm$ 6.0
Nano-30wt%-15°C/min	80.7 $\pm$ 0.2	3.3 $\pm$ 0.6	18.3 $\pm$ 4.1
Nano-50wt%-5°C/min	66.0 $\pm$ 1.5	8.2 $\pm$ 1.4	27.4 $\pm$ 3.7
Nano-50wt%-15°C/min	66.9 $\pm$ 1.4	6.4 $\pm$ 0.9	23.8 $\pm$ 2.9
Platelets-30wt%-5°C/min	86.6 $\pm$ 0.1	$\sim$ 6.3 $\pm$ 1.7	N.A

When platelets were used (bimodal distribution platelets+nanoparticles) the solid loading adopted was 30wt% and the freezing speed chosen was 5°C/min. Slower freezing speeds have been reported to better align particles with higher aspect ratio than spherical nanoparticles [19]. The final porosity in this case was slightly higher $\sim$ 86% due probably to the remaining porosity within the platelets inside each lamellae, that did not always sinter completely. For the same reason the lamella size is more difficult to define being each lamella formed by a nacre-like overlapping of platelets (Fig.69). The lamellae thickness in this case was estimated around $\sim$ 6 μm . Pressureless infiltration allowed a complete infiltration of all preforms even the most porous ones (platelets) with a compressive strength of 4.9 $\pm$ 17MPa; contrarily to previous study where the application of external pressure did not allow the infiltration of weaker preforms [16]. Evaluation of residual porosity from X-ray tomography volume reconstructions showed values lower than 0.2vol% meaning that almost complete infiltration was achieved.

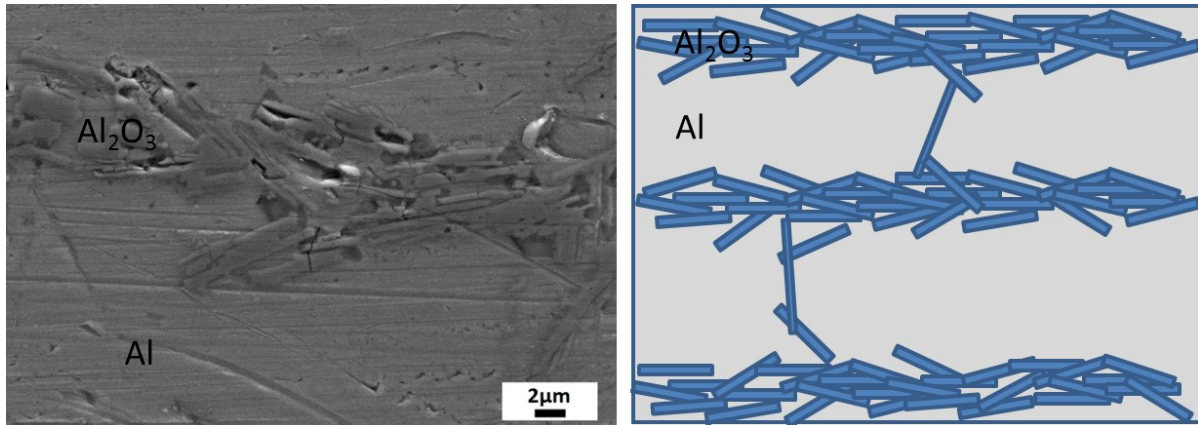


Fig. 69 Alumina platelets arranged within a lamella. The platelets are not perfectly aligned and it is possible to observe some residual porosity due to not complete sintering. It is also possible to observe that the metal in some parts has infiltrated between the platelets generating a nacre-like structure within the single lamella, where the alumina platelets are alternated with a thin metal layer.

The presence of AlN due to the nitrogen atmosphere and MgAl_2O_4 was identified by X-ray analysis (Fig.70). The extent of both compounds, as reported by Srinivasa Rao et al. [29], depending on the temperature reached, the amount of Mg used in the alloy and the dwell time considered.

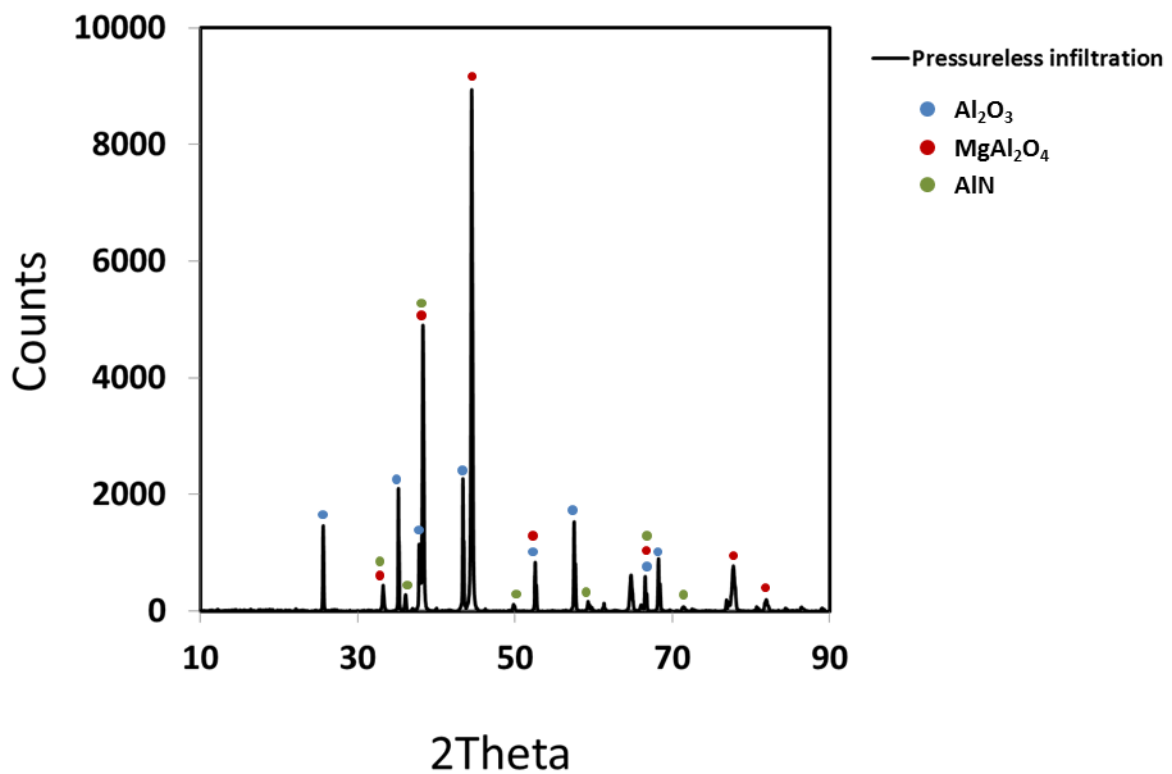


Fig. 70X-ray spectrum of pressureless infiltrated sample.

6.3.2 Strength and fracture toughness

Table 7 summarizes the ultimate strength and plane-strain fracture toughness K_{Ic} in the direction perpendicular to the ceramic layers for the tested materials and their work of fracture.

Table 7 Flexural strength, fracture toughness (3-4PB) and work of fracture of studied composites.

Initial slurry ceramic loading-freezing rate	Metal Content (%)	Ultimate strength (MPa)	Fracture toughness (3PB) K_{Ic}	Fracture toughness (4PB) K_{Ic}	Work of Fracture (kJ/m ²)
50wt%-5°C/min	~66%	426± 51	14.4± 1.5	11.7±1.2	3.29±0.37
50wt%-15°C /min	~67%	436±46	15.4±0.8	12.2±1.2	4.32±0.53
30wt%-5°C/min	~80%	486±59	14.6±0.8	12.2±1.1	5.15±1.76
30wt%-15°C/min	~81%	575±56	15.6±0.8	12.9±2.2	5.58±0.99
30wt%Platelets-°C/min	~86%	735±102	N.A.	12.6±2.5	7.74±1.1

As reported in Table 7 increasing the freezing rate has an effect on the final flexural strength of the composites which increases as the thickness of the lamellae decreases. This result can be related to a decrease of the flaws dimensions in the thinner lamellae walls and therefore to the probability to find critical defects that could start the crack propagation. Also, composites with higher metal content (ceramic loading of 20vol%) showed higher bending strength. All the considered composites displayed higher flexural strength than those of standard commercial aluminas [40] or the Al-4Mg alloy [44]. The composite produced starting from alumina platelets freeze casted scaffold revealed the highest flexural strength with a maximum measured value of 894MPa and an average value of 735MPa. Load vs displacement curves acquired for the different composites (in terms of ceramic/metal vol% and freezing conditions) during flexural strength tests showed (Fig.71) that samples with higher content of ceramic display a more brittle behaviour than the sample with 30wt% of initial solid loading. Moreover it is possible to notice that platelets-based composites undergo a higher amount of deformation before failure.

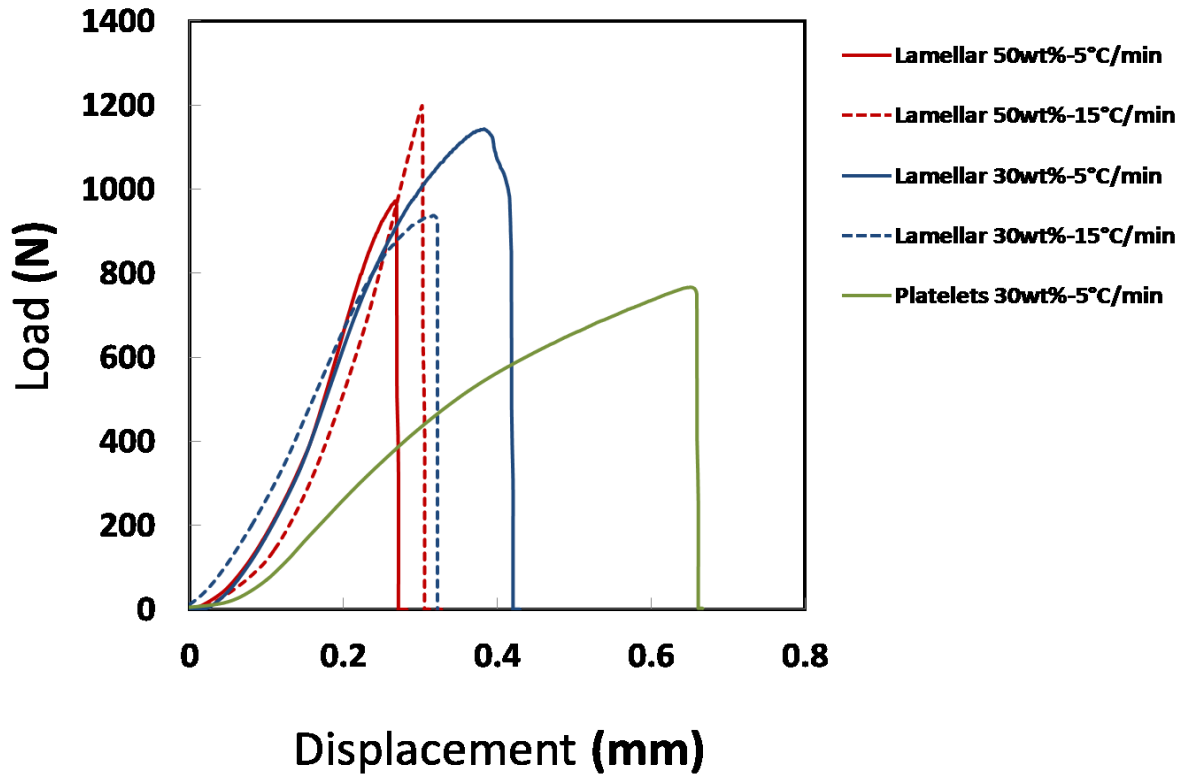


Fig. 71 Load vs displacement curves obtained during flexural strength tests for lamellar and platelets based composites at different solid loading and freezing speeds.

Fracture toughness for crack initiation was evaluated in three and four point bending. Values in 3PB resulted be slightly higher than in 4PB. As already reported in previous studies [16,17] refinement of the lamellae size at higher freezing speeds slightly increase the initial fracture resistance of the composite. Only 4PB was used to evaluate the fracture toughness of platelets based composites. Although only slight differences were observed in the values of K_{Ic} measured by 3PB and 4PB (Table 7), clearly the work of fracture had the tendency to increase as the metal content increased. The work of fracture has been evaluated as the area under the load/displacement curves obtained on notched samples (Fig.72). The values of K_{Ic} reported are in the same range of values of other laminated composites. As reported by Bloyer et al. [13] there is always some uncertainty on the evaluation of K_{Ic} depending upon whether the pre-crack is located in the metal or in the ceramic layer. It has been demonstrated that the stress field at the crack tip to allow the crack to re-nucleate in the following ceramic layer, has to reach a critical value in order to fracture the brittle phase at

some distance ahead [43]. The increase of the metal thickness imposes a larger far-field stress necessary to propagate the fracture in the brittle phase. However in this case both the metal and the ceramic layers were reduced as the freezing speed increased and because the metal volume increase was minimal, the refining of the whole structure seems to be responsible for the higher fracture toughness.

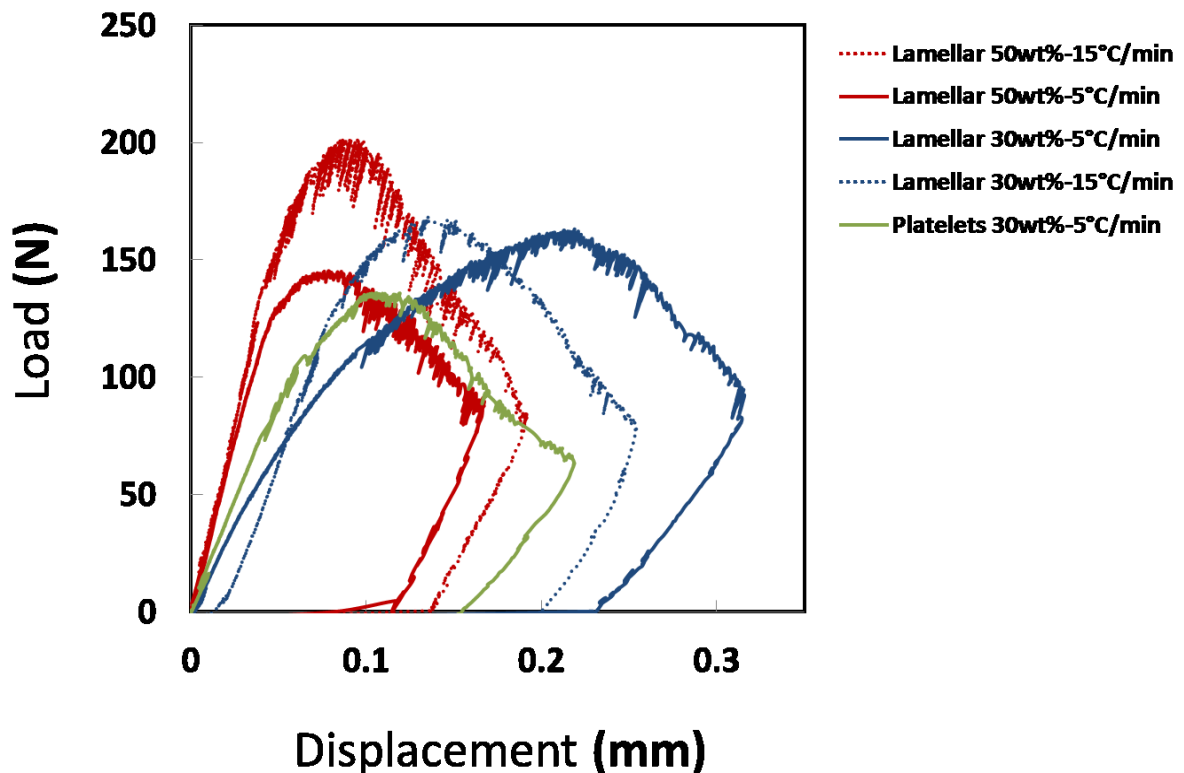


Fig. 72 Load vs displacement curves obtained on notched SEN(B) specimens tested at 0.01mm/min.

6.3.3 Resistance-curve behaviour

As already reported in many studies on laminated ceramic-metal and ceramic-ceramic composites [10,13,45–48], these materials exhibit a rising resistance-curve behaviour.

One of the main issues in this type of analysis is the accuracy in determine the crack length. Direct or indirect approaches can be used to estimate the crack length. One of the indirect methods often employed is the compliance methods [13,16]. Crack lengths can be indirectly

estimated from the compliance values using different equations related to the type of sample geometry employed. While indirect methods for measure the crack length are faster and less inclined to human error, they cannot be evenly applied for all types of materials and architectures. Therefore direct evaluation of the crack length is often the only solution to obtain a more precise and trustable result. Direct observation of the crack length has been chosen in this study.

Crack extension measurements have been done comparing three different direct observation methods: optical microscope, scanning electron microscope and X-ray tomography. For the X-ray tomography a maximum and average values have been considered. The average has been evaluated measuring the crack length at different position within the microstructure. Between these different direct evaluations, even if the crack length measurements at same points are slightly different (Fig.73), due to different resolutions capacity of the different techniques used, no significant variations were reported in the final R-curves.

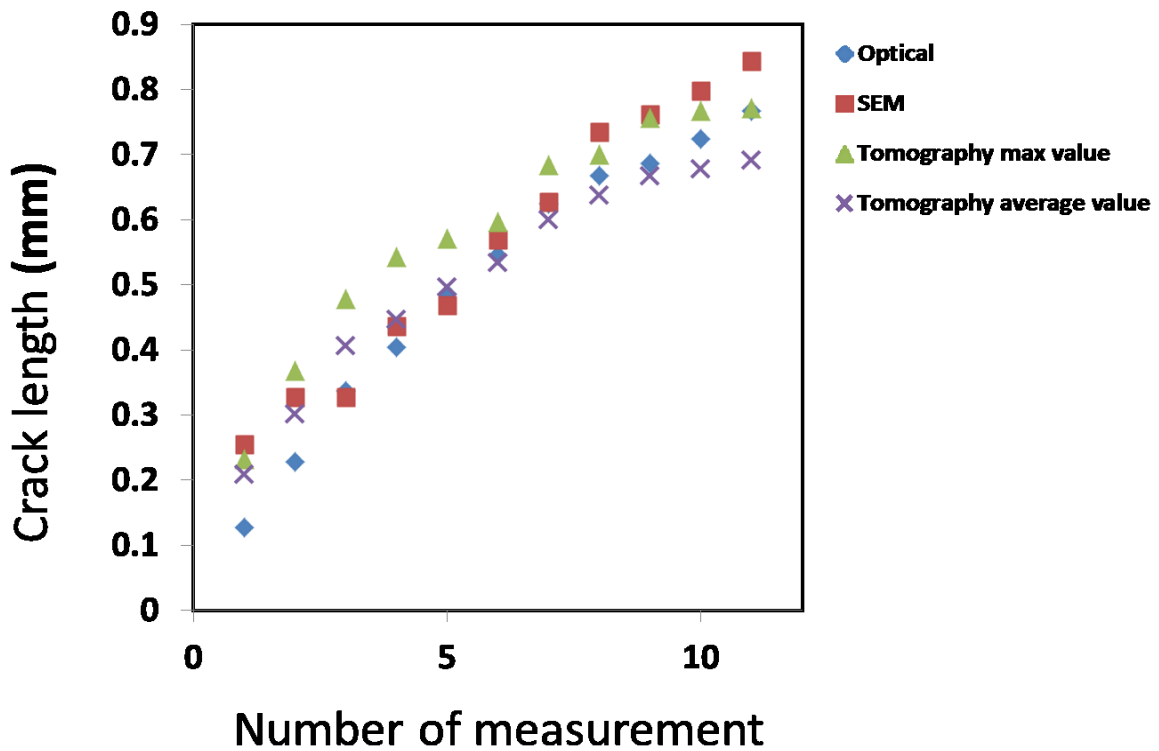


Fig. 73 Crack length measurements obtained directly with different observation techniques (SEM, optical microscope and tomography) and indirectly with the compliance method.

The materials became tougher as the crack propagates inside the microstructures due to the activations of several extrinsic and intrinsic toughening mechanisms. The crack shielded by the bridging of the metallic phase required additional energy to propagate. Energy is also dissipated by other mechanisms such as crack deflection, micro-cracking, plastic deformation etc. The result is a rising R-curve (Fig.74). The R-curve does not reach a steady-state plateau using the crack lengths obtained from the three different direct evaluation methods; the R-curve after an initial linear part it seems to increase exponentially.

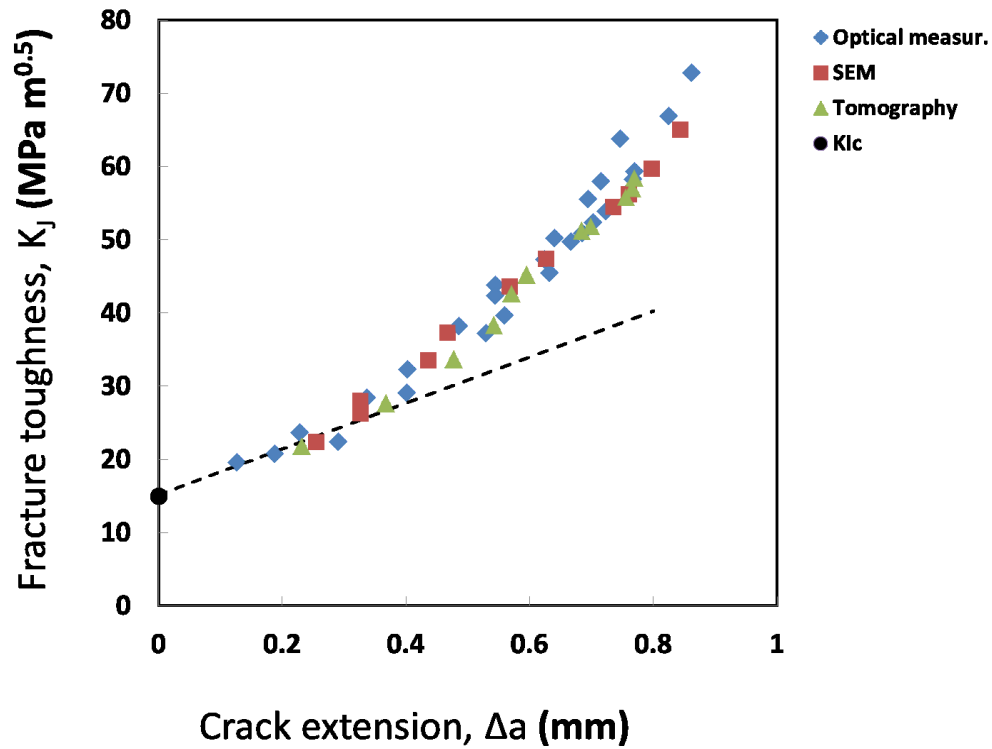


Fig. 74 R-curve of a lamellar composite (50wt%-15K/min) obtained calculating the crack length with three different direct observation techniques (SEM, optical microscope and X-ray tomography). A linear fitting is included that fit properly the points up to a crack length of 0.23mm along with the ASTM [49] limits that for this tested sample is valid up to 0.3mm.

Analysing the compliance of the sample as the crack propagates within the microstructure, it shows almost constant values up to ~ 0.6 after which it starts to increase.

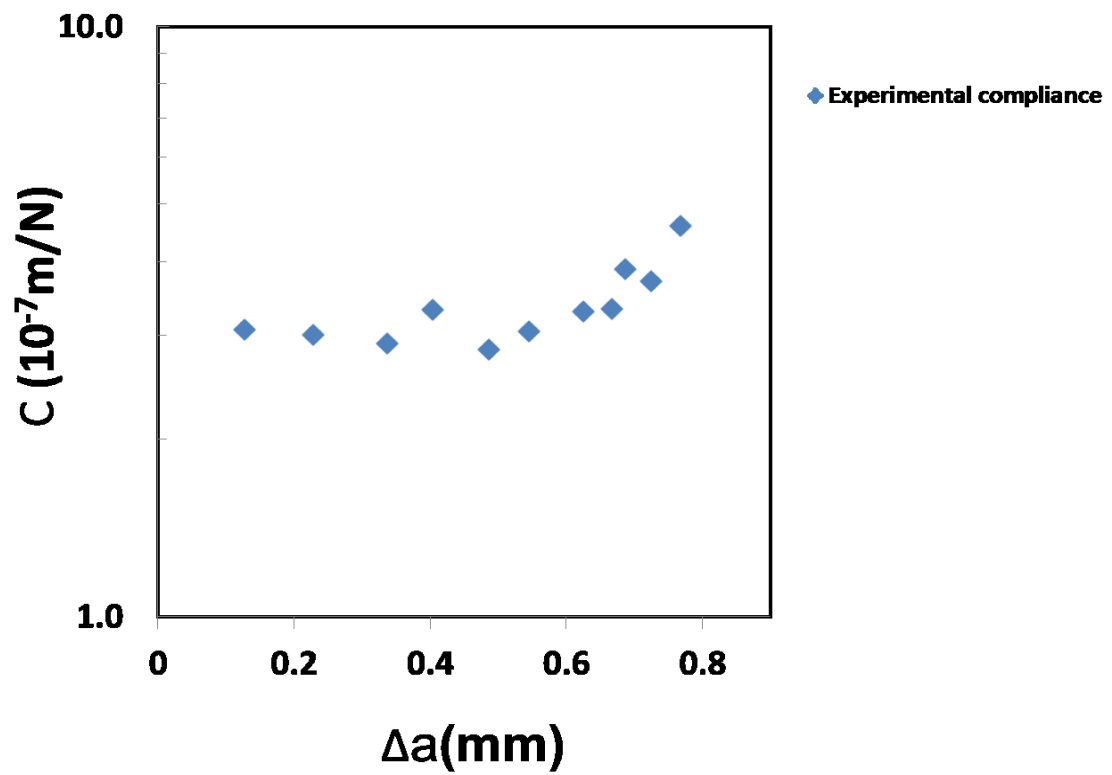


Fig. 75 Experimental compliance for a lamellar composite (50wt%-15K/min).

Different from the lamellar composites is the R-curve for the platelets-based composite. In this case the R-curve also seems to reach a plateau after 0.4mm of crack propagation as shown in Fig.76.

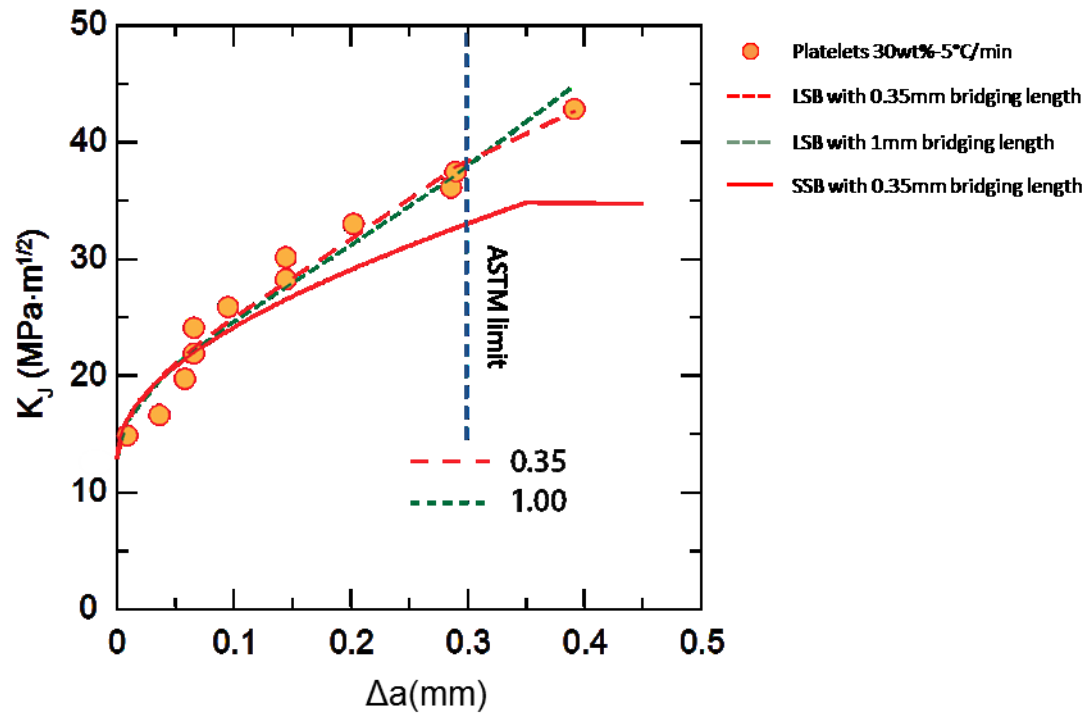


Fig. 76 R-curve for platelets-based composite. The R-curve differently than the normal lamellar composites reaches a plateau with a maximum K_J of $\sim 40 \text{ MPa} \cdot \text{m}^{0.5}$. The dashed or the plain lines are the predictions obtained if LSB (long scale bridging) or SSB (small scale bridging) condition prevail respectively. For the LSB model two different bridging lengths have been considered (0.35mm and 1mm). ASTM [49] limits is also included. In this case the difference between the fracture toughness values predicted by the ASTM limit and the SSB is smaller than in the case of lamellar composites (see Fig. 80).

Also in this case the experimental compliance for the platelets-based composites changes very slowly as the crack propagates and it is possible to notice that the values are bigger compared to the lamellar composites, result that is related with the higher content of metal in the former case (Fig.77).

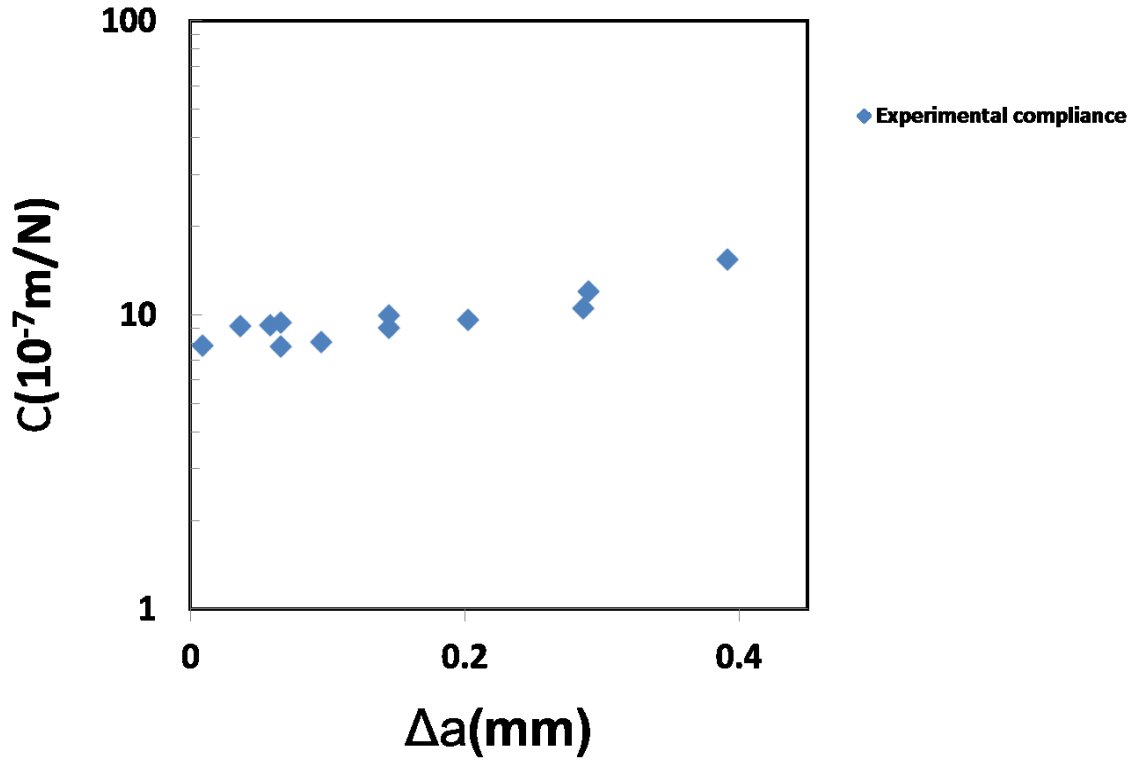


Fig. 77 Compliance vs crack length for platelet-base composite.

The differences noticed in the two R-curve behaviours have been well reported in metal/ceramic laminates [10,11,13]. As reported in previous studies the propensity of the R-curve for laminates materials to reach a steady state is mainly attributed to which bridging conditions prevails, small-scale (SSB) or large scale bridging (LSB). Small-scale bridging (SSB) condition prevails when the bridging length is much smaller than both the crack length and the in-plane sample dimensions. Contrarily when the bridging length is large the analysis becomes dependent from the crack length and the sample geometry. For metal/ceramic laminates LSB conditions usually prevails when testing laboratory samples. However according to the ASTM (E1820) [49] the R-curve is to be considered accurate when the SSB conditions are satisfied. The platelets based composites reach a (steady-state) fracture toughness K_{Jc} of approximately $40 \text{ MPa}\cdot\text{m}^{1/2}$ after 0.4mm of crack propagation while in the lamellar ones the final values after 0.8mm are around $\sim 70\text{-}75 \text{ MPa}\cdot\text{m}^{1/2}$. However according to the ASTM (E1820) [49] the validity of the test is limited up to a maximum crack extension

capacity given by $\Delta a_{max}=0.25b$ (where b is the un-cracked ligament). In this case the validity of the results are up to 0.25-0.3mm of crack extension that means a final value for the lamellar composites of $\sim 25\text{MPa}\cdot\text{m}^{1/2}$ and for the platelets one of $\sim 38\text{MPa}\cdot\text{m}^{1/2}$. Different load/displacement curves obtained during crack propagation for a lamellar composite and a platelet-based one are reported in Fig.78. In both cases it is possible to observe that the compliance does not change significantly as the crack propagates within the microstructure.

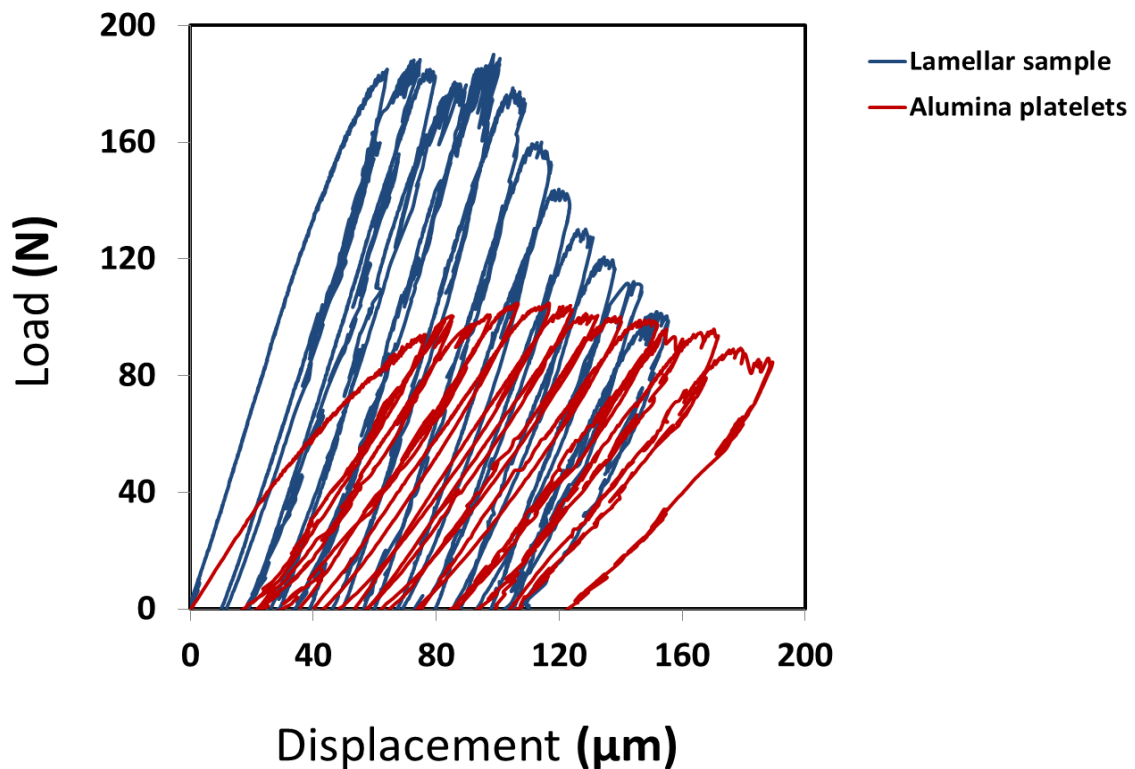


Fig. 78 Load vs displacement curves obtained for load and unload crack propagation within the alumina platelets based samples and the lamellar one.

To better understand the influence of the sample geometry and try to quantify the dimension of the process/damage zone, samples with bigger dimensions and therefore longer un-cracked ligaments were tested. As reported in Fig.79 for the bigger samples (4mm thick with an initial notch of 1mm) the curve rise linearly up to 1.25mm of crack propagation after which the linear fitting stop working properly. This limit corresponds to a final fracture toughness of around $60\text{MPa}\cdot\text{m}^{1/2}$. Applying the more conservator ASTM limit

[49] the validity of the test extends up to a crack propagation of 0.75mm that corresponds to a final K_{Jc} of $45\text{MPa}\cdot\text{m}^{1/2}$. Comparing the R-curves of samples with different geometries (Fig.80) it is possible to notice that before the curves diverge all of the curves share a first common linear increment. The linear part extends to longer crack lengths as the sample dimension increase postponing the exponential divergence. In any case is clear that even with the bigger sample the curve does not reach saturation and therefore exponentially increases up to values above $100\text{MPa}\cdot\text{m}^{1/2}$.

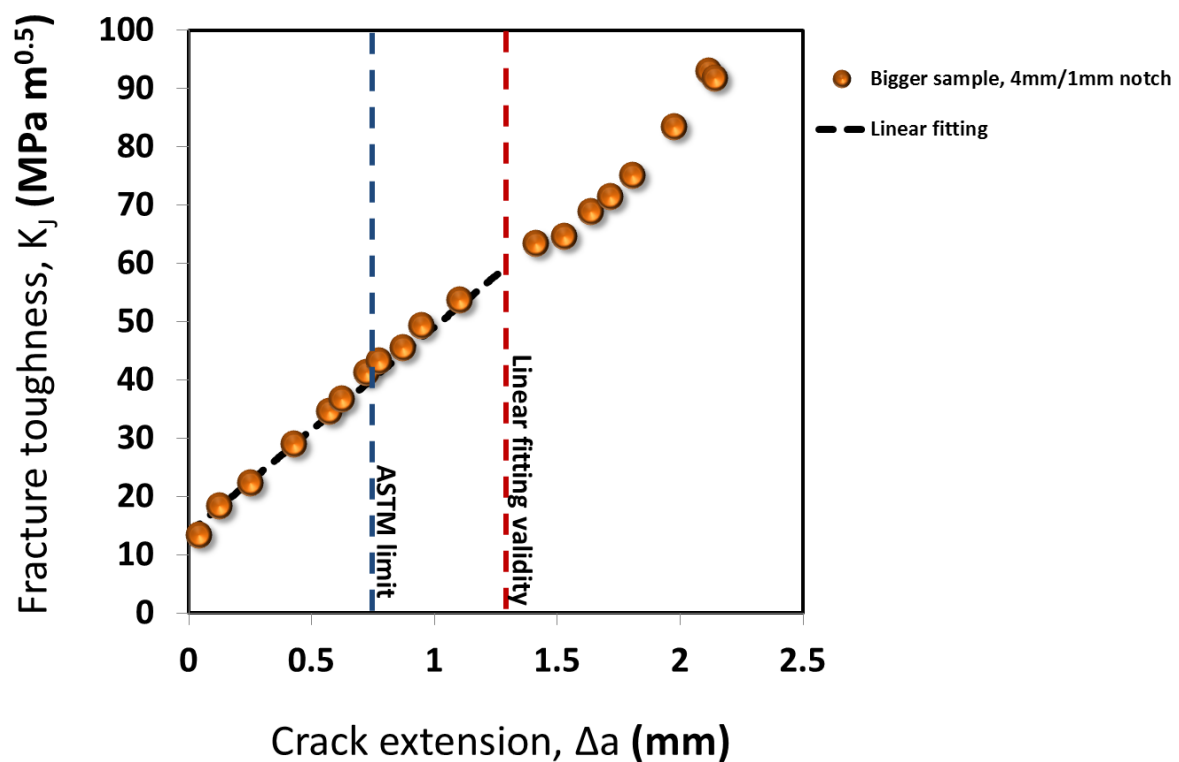


Fig. 79 R-curve obtained for a 4mm thick sample (50wt%-15K/min) with a ratio $a/W=0.25$. According to the ASTM the validity of the test for such geometry is to be considered up to 0.75mm of crack propagation, however the curve rise linearly up to 1.25mm. Both limits are reported by the blue and red dashed lines.

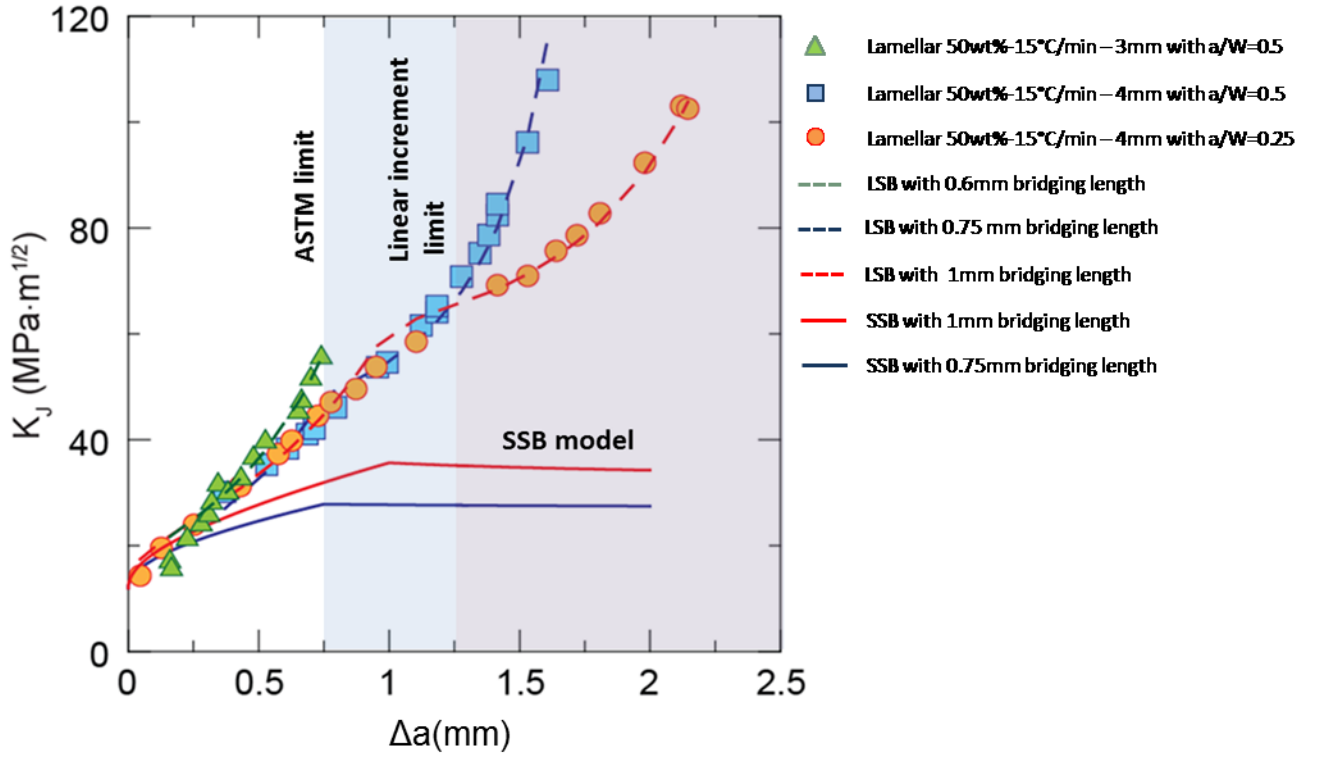


Fig. 80 R-curve obtained for same lamellar sample (50wt%-15K/min) with three different geometries. Green points are representative of the R-curve for a sample of 3mm thickness with a a/W ratio of 0.5, the blue points for a sample of 4mm with a a/W ratio of 0.5 and the orange points for a sample of 4mm with a a/W ratio of 0.25. Dashed lines are the R-curve predicted using the model for bridging conditions and using slightly different values for the constrained flow stress. The plain lines represent the predicted R-curves for SSB conditions.

Predictions of the R-curves for three different geometries of lamellar composites and for the platelets-based composite, reported as dash lines in Fig. 76-80, were obtained solving equation (6.4) over the length of the bridging zone. The values of the constrained flows (σ_c) for each condition were obtained iterating the solutions of equation (6.4) and choosing the values of σ_c that minimized the residuals R (the difference between the experimental and the predicted values). The values of the calculated flow stresses are reported in Table 8. These calculated values are clearly higher than the flow stress of the metal in unconstrained conditions ($\sim 300\text{MPa}$) [43].

Using a specimen width much larger than the bridging zone, equation (6.4) can be used to estimate the fracture toughness of saturation if the small scale bridging conditions (SSB) prevail. In this case the R-curves in both cases reach a saturation plateau. However the

maximum predicted values obtained with this approach are lower than those predicted within the ASTM limits.

Table 8 Calculated values of constrained flow stresses.

Sample	Calculated Constrained Flow stress σ_c (MPa)	Average Calculated Flow stress σ_c (MPa)
Lamellar 3mm a/W=0.5	805	853
Lamellar 4mm a/W=0.5	800	
Lamellar 4mm a/W=0.25	955	
Platelets 3mm a/w=0.5	1600	//

6.3.4 Crack growth observations

Stable crack growth during repetitive loading of the composites, it allowed observing the main toughening mechanisms acting within the microstructure. The observation was done after every loading cycles within the SEM and the x-ray tomography. Differences could be observed between the platelet based composites and the normal lamellar ones. While in the latter the main mechanisms were metal bridging behind the crack wake, plastic deformation of the metal bridges and the metal layer in front of the crack tip, and micro-cracking in front and laterally of the crack, in the platelets based composites the damage process seems different. It was more difficult to identify a clear crack path instead a major damage area was observed with many cracks starting radially from the notch root (Fig.81). These cracks together with a vast plastic deformation of the metal phase blunt the crack propagation. These differences in the fracture mechanisms can be related to the different R-curve shown by the two different structures.

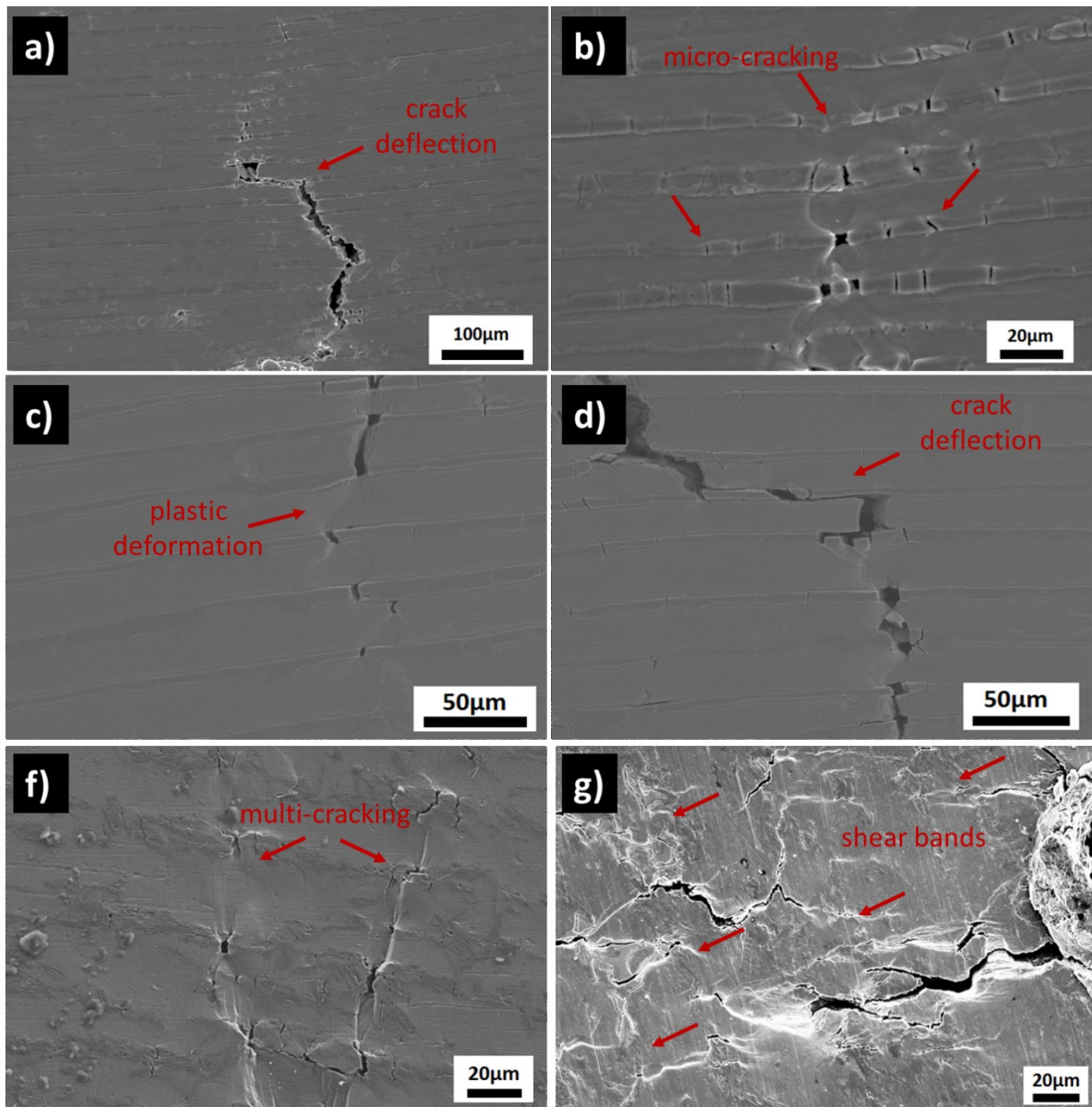


Fig. 81 Crack propagation within the studied microstructure. a-d) crack propagates in the lamellar composite; crack deflection, metal layer plastic deformation and microcracking can be observed; f-g) crack propagation and fracture mechanisms acting within platelets-based composite; multiple cracking can be observe at the notch root.

From the X-ray tomography reconstructions, crack deflection during the tests and wide distribution of the damage was observed. Moreover it was possible to observe that the crack area was not homogenously distributed along the width of the sample as can be observed by the 3D tomography reconstruction in Fig.82. In many occasion the crack length was major at the centre of the sample and minor on the later sides due to some border effects that can affect the real estimation of the crack length (Fig.82).

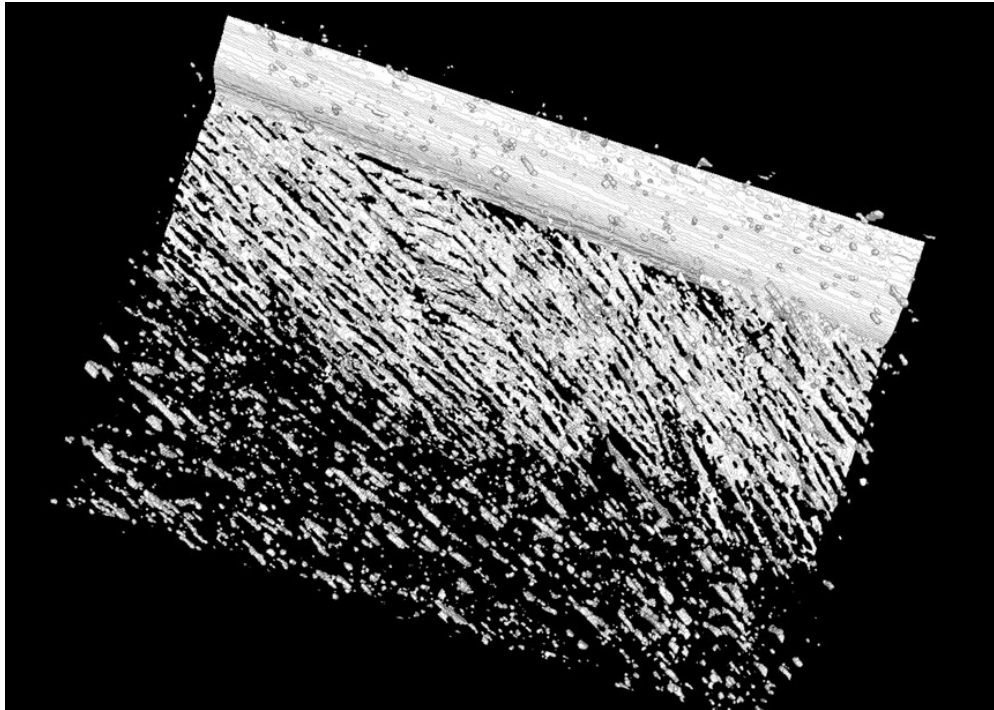
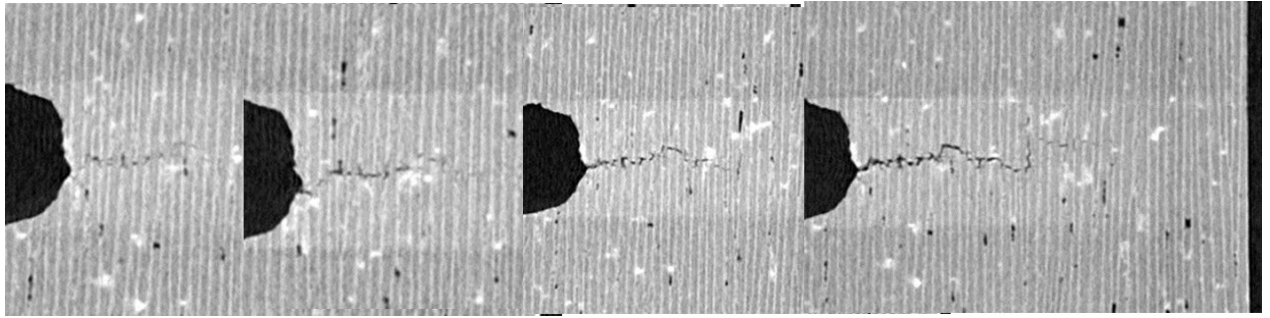


Fig. 82 X-ray tomography of crack propagation within 50wt%-5K lamellar composite. a) Sequence of crack growth at different load and unload test. The crack at different points deflects from the primary plane of propagation b) 3D reconstruction of damage area.

Observation of the fracture surface of the lamellar and platelets base composites showed no de-bonding at the metal/ceramic interface implying a strong adhesion (Fig.83). Extensive plastic stretching was revealed in the metal layers contributing significantly to the toughening of the composite. Other microstructural analysis revealed the presence of roughness at the interface between the ceramic and the metal layers that could influence the shear stress between them and contribute to the toughening of the structure.

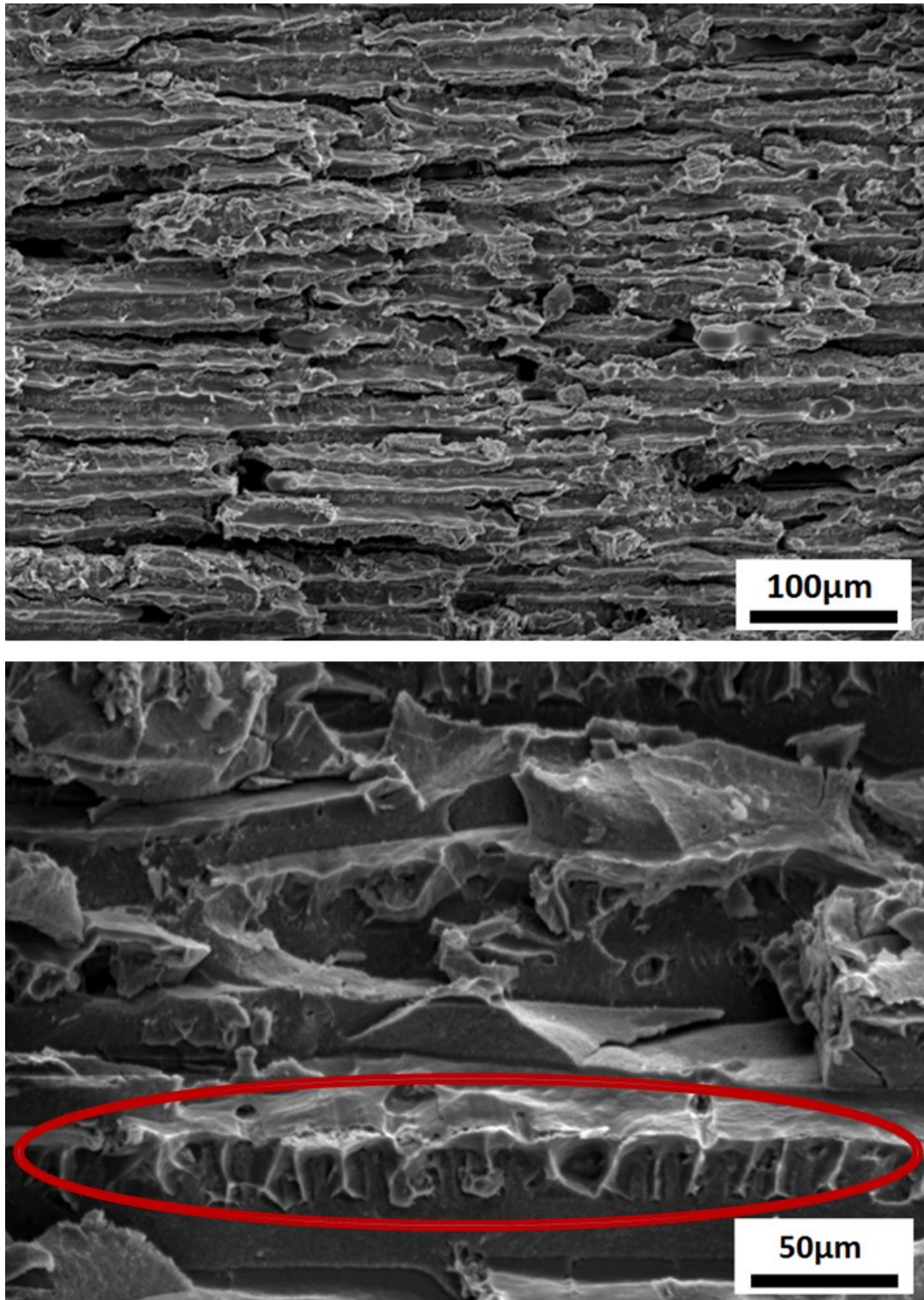


Fig. 83 Fracture surface of lamellar composite. b) Detail of good wetting of metal on ceramic surface. The metal wets small particulars creating interlocking between the metal and the ceramic layer.

6.4 Discussion

All the studied ceramic/metal layered composites are stronger than the single constituents, with the platelets based composites showing the highest strength. The refinement in the normal layered scaffolds of the microstructure (lamellae and pore size) slightly improved both the strength and the fracture toughness. In terms of strength this correlation can be related to a lower probability of find a large flaw within the lamellae and therefore higher mechanical response of the final material. The composites showed values of K_{Ic} evidently higher than pure alumina but lower than the aluminium alloy deployed that have values of fracture toughness K_{Ic} of $\sim 43 \text{MPa}\cdot\text{m}^{1/2}$ [43]. Moreover comparing the flexural strength of the produced composites with other $\text{Al}_2\text{O}_3/\text{Al}$ composites made from different types of aluminium alloys and alumina reinforcement, it is possible to notice that higher strength is achieved when high aspect ratio reinforcement such as fibres or platelets were employed (Fig. 84) [50–52]. The lamellar organization of the ceramic phase also allows to achieve similar or higher level of strength respectively for composites obtained from preforms with higher or lower amount of ceramic [53–55]. It is interesting to observe that composites obtained with similar pressureless process (Lanxide) show lower flexural strength than our composites even at higher ceramic content. It might possible that residual porosity affected their mechanical performance [56]. In terms of fracture toughness and initial K_{Ic} the choice of using a lamellar organization with the particular aluminium alloy employed seems to give a high resistance to fracture value compared with other studied combinations (Fig.85).

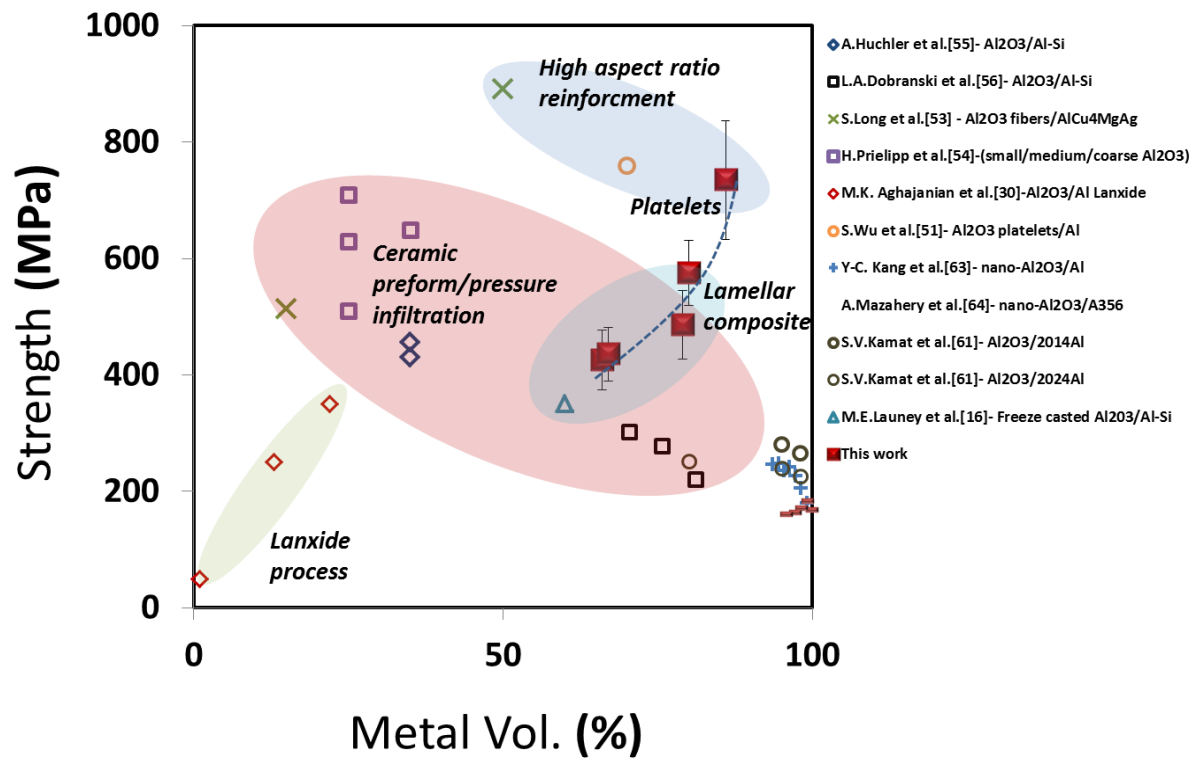


Fig. 85 Comparison of maximum strength vs metal volume percentage for different alumina/aluminium composites. Some of the referenced studied reported the ultimate strength of the composite under tensile test. Data taken from [16,30,50,52–55,60,62,63].

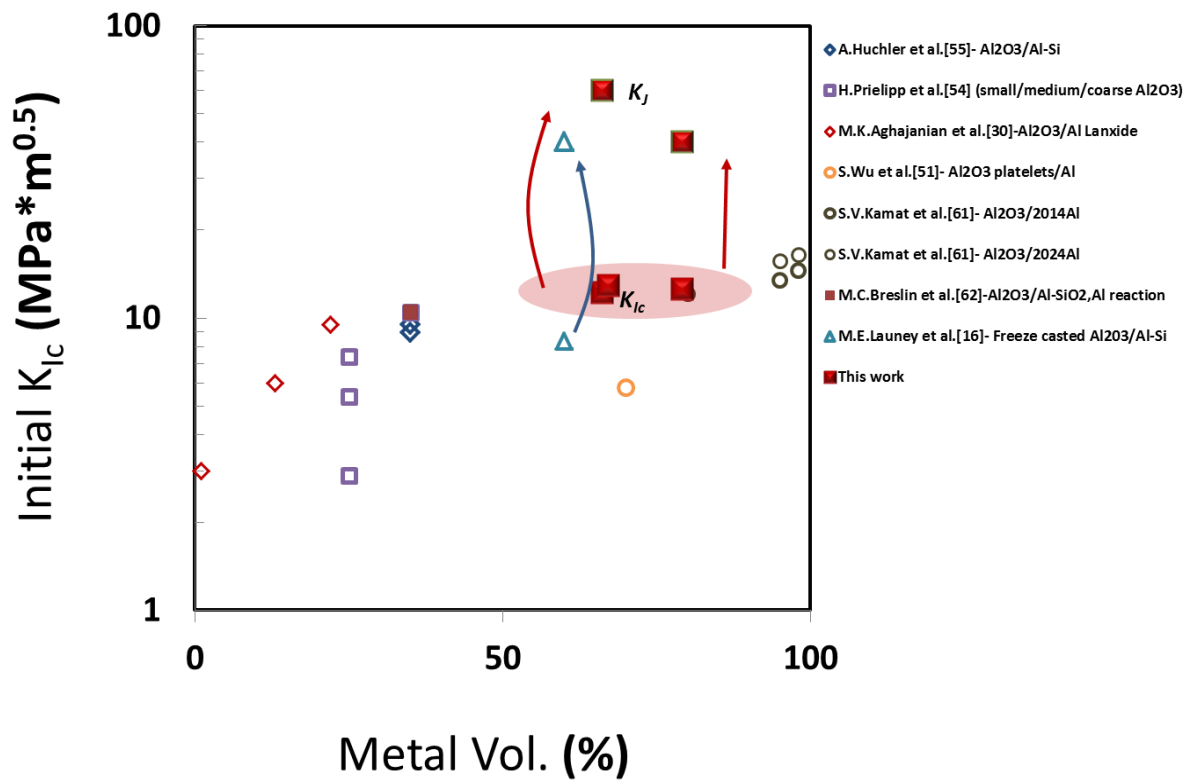


Fig. 84 Comparison of fracture toughness vs metal volume percentage for different alumina/aluminium system. K_{Ic} of the tested composites is also reported. For comparison also the K_{Ic} from the work of Launey et al. is reported. Data taken from [16,30,50,53,54,60,61].

Moreover the control on the structural architecture at several length scales achieved by freeze casting generates in these microstructures the activation of several toughening mechanisms that makes them tougher as a pre-existing crack propagates. This crack propagation process is therefore characterized by a resistance curve as those show in Fig.74, in which the stress intensity factor increases with crack extension. The evaluation of crack initiation parameters K_{Ic} is not sufficient to represent entirely the actual fracture resistance of these materials, not taking in consideration several length-scales toughening processes that occur within the microstructure.

The direct observation of crack propagation allowed us to identify in the extrinsic mechanisms the primary toughening mechanisms acting in these metal/ceramic composites. Extrinsic toughening mechanisms are mechanisms that act behind the crack tip in the crack wake [6] that hinder the crack growth by shielding the crack-driving force actually experienced at the crack tip [16]. One of the most active was ductile-ligament bridging, where the presence of unbroken metal bridges behind the crack tip that plastically deform, imposed closure traction to the crack advance. Failure in the composites involves the transmission of the crack from a brittle layer to another, across the ductile metal that imposes a shielding effect on the crack. Extra stress has to be applied to overcome this resistance imposed by the metal layers. When the crack arrested at the interface, before renucleating in the next ceramic layer, the metal layers exhibited extensive shear band formation before failure by ductile rupture (Fig.81c). This intense shear banding often resulted in the renucleation of the crack deviated on one side of the next layer compared to the previous one. The shielding effect is therefore enhanced because such offset cracking when the metal layer shear off at different angle increases the work of rupture of the ductile bridge.

Within all the composites analysed multiple cracking, another important toughening mechanism, was observed in the brittle ceramic layers. Multiple cracking is often an additional toughening mechanisms as it promotes greater distribution of damage and energy absorption [36]. The occurrence of this fracture mechanism and the transition from single to multiple fracture, depends on the flow properties of the metal, the scale of the microstructure and the properties of the metal/ceramic interface [36,47]. In these layered composites, the parameter that mostly controls this transition is the ratio of the metal layer

thickness t_m to the ceramic layer thickness t_c . There is a critical ratio above which multiple cracking always occurs. This critical value, in turn, is related to the ratio between the metal constrained yield stress σ_m and the ceramic fracture stress σ_c and tends to increase as σ_m/σ_c decrease. However the model predicts, whatever are the physical properties of the metal and the ceramic, that multiple cracking prevails if the thickness of the metal is 2.5 times larger than the ceramic layer [16,36]. In this study, composites always show $t_m/t_c > 2.5$ ($t_m/t_c \approx 5.5$ and 3.5 for 30wt% and 50wt% lamellar composites respectively) implying that multiple cracking should always be observed.

Lamellar scaffolds with 50 and 30wt% showed similar fracture toughness and toughening mechanisms. In both types of structure crack deflection can be observed in different points (Fig.81a-d and sequence in Fig.82). It is possible that the formation of multiple cracking within a single lamella could decrease its resistance giving to the crack a preferential way to propagate and deflect from the original plane of propagation (Fig.81d). It is well known that crack deflection is another very effective toughening mechanism that requires energy to be spent when the crack propagates. The fracture process in the platelets based composites is different even for similar metal content. At low stress intensity values shear bands seemed to be generated around the crack notch (Fig.81f). Shear sliding was recorded at higher K that promotes significant crack-tip blunting. A vast area of damage is produced around the notch root and many cracks and micro-cracks were formed.

Differently from previous studies on freeze casted hybrid composites [16,17] where steady-state R-curves were often observed, in this study, apart from the platelets-base composites, all studied lamellar composites showed a rising R-curve behaviour characteristic of large scale bridging that have been observed in many laminate materials [10,13,46–48,57,58]. This result could point to the fact that using the compliance method does not perfectly describe the mechanical response and the real fracture toughness vs crack length behaviour for these types of microstructures. The experimental compliance is almost constant for certain crack propagation before a slight increase. This behaviour could reveal that there is a contemporary activation of different mechanisms, microcracking and plastic deformation on one side that tend to increase the compliance, and bridging on the other side, that has the opposite effect. Clearly bridging is manifested within the microstructure but alone is not sufficient to fully describe the mechanical response of the materials. This consideration is

strengthened by the fact that the applied bridging model is not exhaustive to fully describe the fracture resistance of these materials not taking into consideration the simultaneous activation of the others mechanisms and therefore it gives an underestimation of the real fracture resistance of the composites.

Another possibility to evaluate the toughness of these types of structures is to consider the limits of validity established by specific ASTM [49]. Nevertheless it is possible to observe from Fig.80 that the K of saturation proposed both by the models and the ASTM limits [49] are significantly different. Again this result can be correlated to the fact that the used model, taking into account only bridging phenomena, does not entirely describe the system and all the toughening mechanisms actually occurring. Finally also regarding the ASTM limits, it has been observed in this study (as reported in Fig. 80) that the resistance curves are also clearly sensitive to the size of the test specimens: as the width of the specimen increases the linear portion of the curve tends to extend at higher crack extension and the apparent fracture resistance increase. R-curves always approach infinity when the crack length becomes equal to the specimen width and when the LSB effects become significant therefore this behaviour must be taken into account [58]. Previous studies revealed that metal thickness and metal yield strength influence the shape of the R-curve [45]. With thin metal layers ($t_m < 1 \mu\text{m}$) steady-state R-curves are observed; instead thicker metal layers generate usually a continuously rising curve caused by large scale bridging (LSB). The reason why the R-curve of the platelets based composites tends to level off at certain values of K_I , could be related to the fact that each single lamella is in fact a nacre-like disposition of platelets interlayered by thin metal layers and possibly the fracture process is mainly influenced by the plastic deformation of the metal phase.

Finally comparing these systems with other laminates ceramic/metal structures, it is possible to observe that the refinement of the microstructure obtained through freeze casting allows achieving higher values of K_{Ic} and therefore higher resistance to fracture of the composites (Fig.86).

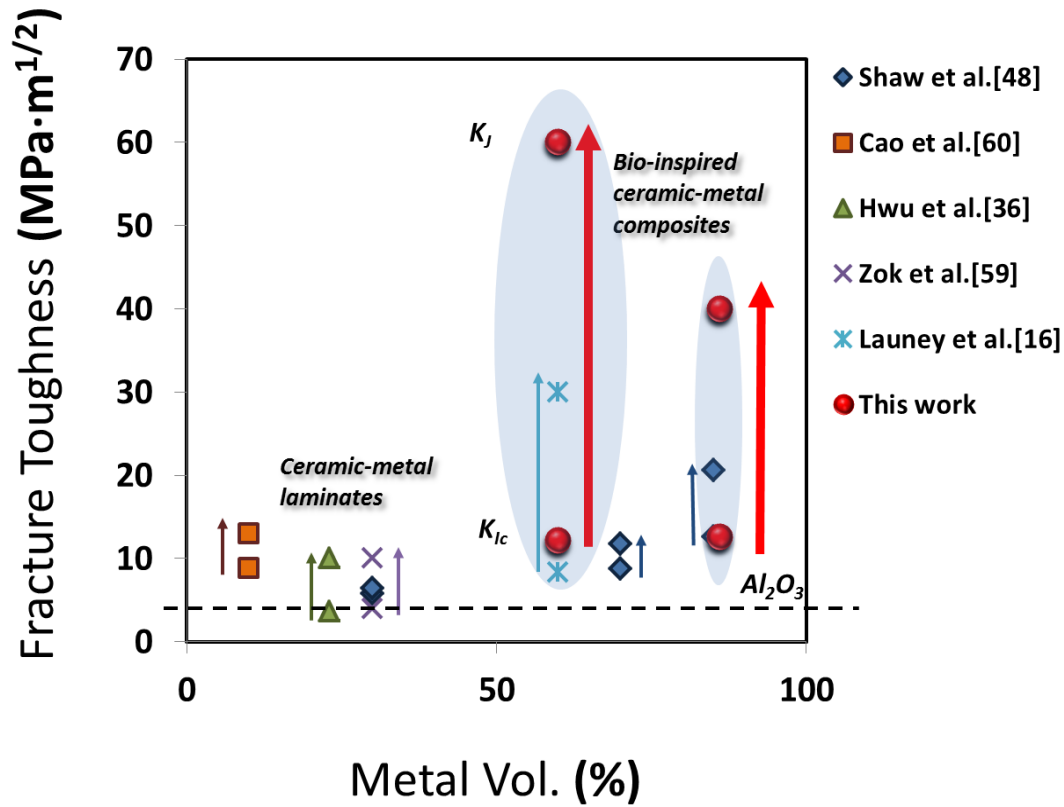


Fig. 86 Comparison of fracture toughness vs metal volume content for different types of $\text{Al}_2\text{O}_3/\text{Al}$ laminates systems. Data taken from [10,16,47,58,59].

6.5 Conclusion

In this study ceramic/metal composites with excellent combination of strength and fracture resistance have been developed taking inspiration from natural materials. The use of a pressureless infiltration process allowed the infiltration of highly porous ceramic scaffolds with different particles morphology producing materials that show advanced combination of mechanical properties and lightweight. Platelets-based composites exhibited the best combination of strength and toughness, with final values of $\sim 800\text{MPa}$ and $\sim 40\text{MPa}\cdot\text{m}^{1/2}$ respectively. Bio-inspiration is a competitive way to produce laminated ceramic/metal composites. Crack growth analysis has been intensely investigated to better understand the toughening mechanisms that take place within these microstructures and resistance curves were evaluated. In particular we investigated different ways of estimating the R-curve comparing different direct crack length measurements. Meanwhile the indirect method may

overestimate the actual crack length and therefore give an overestimation of the fracture resistance, the direct observation of the crack length is the most reliable method. However even with a direct observation of the crack length, when the R-curve tends to diverge as often happened in laminate materials, it is important to interpret properly the results without misjudging the real behaviour.

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7 SiC/Polymer composites

7.1 Introduction

Many modern technologies require the use of materials that can combine several mechanical and functional properties in a way that is not usually found in traditional bulk metals, ceramics or polymers. The continuous research of new structural materials that can associate low density with high strength and stiffness, good wear, impact and corrosion resistances defines the technological progress of sectors such as aeronautic, transportation, sport and healthcare. The possibility of combining different features in one material extending its possible fields of use has been achieved through the design of composites. Carefully combining two or more materials it is possible thus to optimize and implement specific properties but sometimes at the expense of others. Synthetic composite materials found mature application in many areas from sport equipment (tennis rackets, golf-club, ski, snowboard etc.) to aerospace or bone and dental prosthesis. Many different types of composites have been developed in the last decades and they can be mainly divided in particle-reinforced composites, fibre-reinforced composites and structural composites such as laminates or sandwich structures. Particulate composites have been widely studied, where the introduction of strong and rigid particles leads to transfer part of the applied load from the matrix to the particulate itself. The percentage of the reinforcement, its homogeneous distribution within the matrix and the adhesion between the two phases play critical roles in the optimization of the final performance. The particulate can be metallic, polymeric or ceramic. Hard-metals for example are composed of hard ceramic carbide particles such as tungsten carbide (WC) or titanium carbide (TiC) [1] dispersed in a metallic phase (nickel or cobalt) [2]. These materials are usually used in the production of cutting tools for hard steels. The carbide particles are extremely hard and they provide cutting properties, however they are brittle, brittleness that is overcome by dispersing them in a ductile metallic phase. Elastomers and plastics are frequently reinforced with particulates of different types. Many modern rubbers for example are reinforced with carbon black. Carbon black is composed of small spherical carbon particles that are produced during the combustion of natural gas or oil. The addition of these particles to the vulcanized rubber increases its tensile strength, shear strength, toughness and abrasion resistance [3,4]. Their

implementation results advantageous when the powders are extremely small (20-50nm) and homogeneously dispersed in the matrix.

Amongst the most employed composites in advanced technologies are fibre-reinforced composites that have been shown to ensure high strength and/or stiffness with low densities. These composites can be divided into short or long fibre composites. One of the main parameters that influences the mechanical response of fibre-reinforced composites is the length of the fibres and therefore the amount of load that can be transmitted from the matrix to them. During a push-out test if the fibre-reinforced composite is loaded under tension, a shear stress τ_c appears between the matrix and the fibre. If the shear stress along the length of the fibre is considered uniform, because the capacity to transmit load is nullified at the extremities of the fibres, to achieve an effective strengthening and stiffening of the structure is necessary that the fibres reach a critical length l_c . This critical length depends on the diameter d of the fiber itself, on its strength σ_f and on the strength of the interface between the matrix and the fiber τ_c [5]:

$$l_c = \frac{\sigma_f d}{2\tau_c} \quad (7.1)$$

Fibres are considered continuous when $l_f \gg l_c$ (usually $l_f > 15l_c$) otherwise they are considered discontinuous or short fibres. In the case of short fibres where the length is significantly lower than l_c , the matrix tends to deform around the fiber and in this way there is no significant load transmission and reinforcement effect. In this case the composite can be considered as a particulate composite. The efficiency of the reinforcement using short fibres is therefore lower than longer fibres however, these composites have acquired significant importance among commercial applications. Glass chopped fiber based composites are widely used in many applications as well as short carbon or aramid ones. Their use is related to high volume of production in continuous manufacturing processes (compression molding, injection molding and extrusion) and with the possibility of fabricating complex geometries. Differently for composites reinforced with continuous fibres, where their tensile strength can be predicted by the rule of mixtures, in the case of short fibres the mechanisms for bearing load is more complicated because each individual fiber is involved in the transmission of the load between the matrix and the fiber itself. For

short fibres aligned in a specific direction the longitudinal tensile strength σ_c can be evaluated as [5]:

$$\sigma_c = \frac{l_f \tau_c}{d} V_f + \sigma_m (1 - V_f) \quad (7.2)$$

where d and l_f are respectively the diameter and the length of the fibre, τ_c is the smaller between the matrix and the fibre shear resistance and σ_m is the strength of the matrix. Although the strengthening achieved employing short fibres can be lower than continuous fibres (especially when $l_f < l_c$), the introduction and dispersion of stiff and strong reinforcement can be still beneficial for the toughness of the composites. The presence of a short fibre for instance can initiate a series of inelastic processes occurring at or near the interface Fig.87a, along with crack bridging phenomena that can enhance the fracture resistance of the matrix.

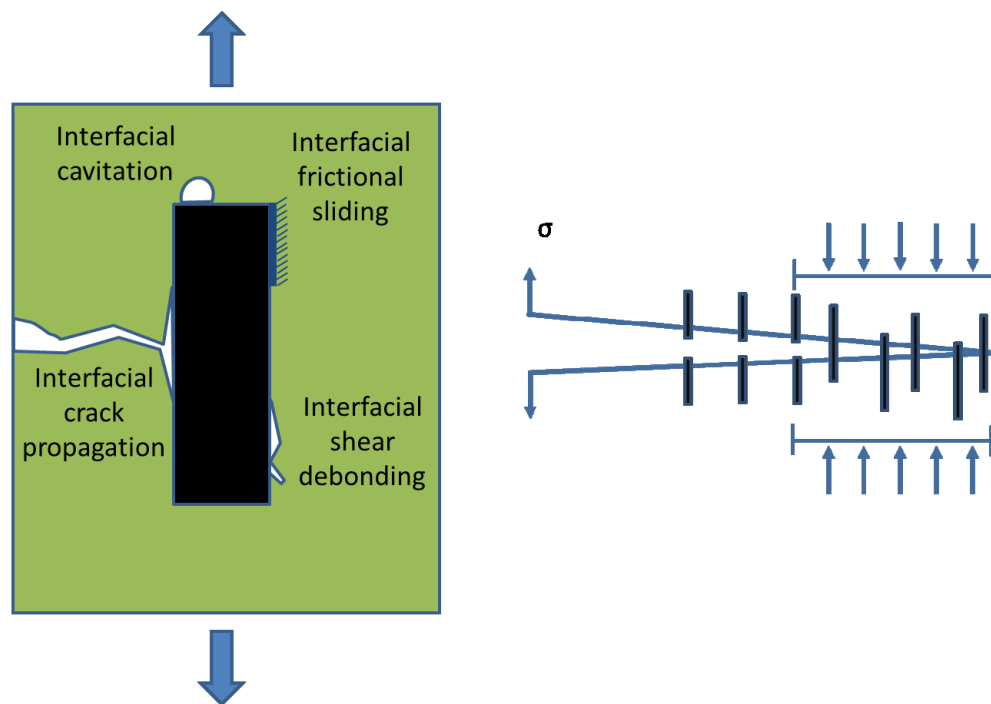


Fig. 87 a) Inelastic processes initiated when a crack approach a reinforcing fibre. The activation of all these mechanisms absorbs energy and therefore could increase the fracture resistance of the composites; b) crack bridging generated by a brittle reinforcement can generate a closure stress in the wake of the crack tip and increase the toughness of the composites. Adapted from [6].

One of the main advantages of using short fibres is their extremely high strength, especially for fragile fibres. The probability of finding a defect of critical dimension able to generate fracture decreases with reducing material volume and this is beneficial for fibre-reinforced composites. Many different types of short fibres are available, from organic (Aramid, Kevlar etc.) to inorganic (SiC, SiO₂, Al₂O₃ etc.) [7] and many different composites have been produced, such as polymeric (PMC), metallic (MMC) and ceramic (CMC) matrix composites. More recently, with the growth of nanotechnologies new types of nano-fillers have been developed and employed to produce innovative composite materials with superior mechanical properties. Therefore many new studies have been published on the production of stronger and tougher composites reinforced with carbon nano-tubes (CN Ts) [8–10], graphene [11–13], nanoclay and nanosilica [14].

Another category of composite materials widely studied are the laminates. Alternating layers of different materials, usually introducing ductile phases as reinforcement, it has been possible to produce materials with high strength and fracture resistance in preferential direction. Clear examples of this design strategy are the works from Hwu et al. [15], Zok et al [16], Bloyer et al. [17], Shaw et al. [18]. Alternating layers of different ceramics such as Al₂O₃, SiC, ZrO₂ and metals, such as Al, Ni, Cu etc., they were able to produce laminate materials with high toughness and respectable strength. More details on structural features and mechanical properties of laminate structures have been already presented in the previous Chapter 6.

Many natural materials are also composites where hard minerals and soft bio-polymers are hierarchically organized over many length scales from nano to macro levels. These particularly complex architecture solutions have inspired many design principles used in modern man-made composites. Wood for example is composed by tough and flexible cellulose fibres hold together in a stiff lignin matrix; bones are composites of ductile collagen fibrils interlayered by hard hydroxyapatite minerals; nacre interlays hard carbonate platelets with soft nanometric polymeric layers. The extraordinary mechanical properties achieved in natural materials that can combine in the same structure high strength and stiffness with damage tolerance meanwhile remaining lightweight, have therefore increased in the last decades the interest of replicate such composites using synthetic advance ceramics and polymers. Many examples of new approaches, using conventional or more

innovative processing techniques, have been reported with the intention of bio-mimicking natural materials in synthetic materials [19]. Nacre-like structures have been developed by bottom-up approaches such as layer by layer deposition processes [20–22], self-assembly [23,24] etc., but these techniques are often limited to the production of thin films and are difficult to scale-up to produce bulk materials. More conventional techniques such as tape-casting [25] or hot pressing [26] are not suitable to reproduce the hierarchical organization found in natural materials. Alternatively freeze casting has attracted recently the attention of many studies due to the possibility to reproduce similarly the structural organization of natural nacre, and to date this processing technique has produced numerous bulk hybrid materials with very unique properties [27–30].

In this study we used freeze casting to produce silicon carbide (SiC) based composites with polymeric compliant phases acting as ductile reinforcement and we investigate the effect of the hierarchical/lamellar organization of the reinforcements on the mechanical properties of the composites. We used as porous ceramic preforms the silicon carbide freeze casted scaffold described in Chapter 4. These scaffolds were infiltrated with PMMA generating composites with ceramic content ranging from 45 to 25vol% and lamellae size ranging from 9 to 30 μ m. The composites act as a laminate structure with interlayered SiC and PMMA sheets. Preliminary results are also presented on epoxy-based composites produced by epoxy infiltration of ultralight SiC fibre networks (described in Chapter 5) with a final ceramic reinforcement ranging from 2 to 8 vol%. In this case the epoxy resin being more than the 90vol% is the matrix phase reinforced with SiC short fibres orderly organized and aligned in lamellar structures with wavelengths between 15 and 50 μ m. As reported in some theoretical models based on a microstructure approach [31] and experimental results [32], the mechanical and physical properties of reinforced composites depend more directly on the continuous volume fraction of the reinforcement than the overall volume fraction. Therefore composites with a network-like reinforcement present higher mechanical properties than a random reinforcement distribution. The mechanical behaviour of these composites is described in terms of flexural strength, fracture toughness and resistance to failure (R-curve).

7.2 Materials and Methods

7.2.1 Microstructures

Porous silicon carbide preforms were prepared by freeze casting following the procedure described in chapter 4 and chapter 5 respectively for SiC lamellar structures and SiC network-like fibre preforms. SiC lamellar structures with two different ceramic loading of 9.4 and 20.3vol% and freeze casted at 15°C/min were infiltrated with PMMA to investigate the influence of the microstructure on the mechanical properties of the composites. A free radical polymerization of methylmethacrylate (MMA, SAFC) initiated by 2,2'-azobisisobutyronitrile (AIBN, Sigma Aldrich, 0,5wt% in MMA) was conducted at 70°C for 12hr. An annealing step was performed at 150°C for 2h in nitrogen atmosphere to complete the polymerization reaction. The oven was cooled at $\sim 1^{\circ}\text{Cmin}^{-1}$ to room temperature to minimize thermally induced residual stresses [33].

SiC network-like fibres preforms with ceramic loading of 1.5, 3 and 7vol% were infiltrated with epoxy resin. The resin used was composed of diglycidyl ether of bis-phenol A (DGEBA) epoxy base (Araldite LY556, Huntsman) combined with a hardening agent methylhexahydrophthalic acid anhydride (Albidur HE 600, Evonik Industries AG). The used system of epoxy and hardener has low viscosity that allowed the impregnation of complex ceramic preforms. To determine the proper mixing ratio between the two components the following formula was used:

$$M_{hardener} = \frac{100 * AHEW}{EEW} \quad (7.3)$$

AHEW is the hardener **A**mine **H**ydrogen **E**quivalent **W**eight, in this case 170g/eq and EEW is the **E**poxy **E**quivalent **W**eight, in this case comprised between 183 and 192g/eq. Given these values, the mixing ratio to use was 100:91, LY556 to HE600 by weight. Before infiltrating the preforms, the resin was heated at 60°C to decrease its viscosity and facilitate the infiltration process that was performed under vacuum overnight followed by a curing cycle of 2h at 90°C and by a post-cure of 1h at 160°C [34]. Using the same procedure, pure epoxy samples were prepared to study the effect of the reinforcement on the properties of the un-reinforced epoxy.

7.2.2 Characterization

The Microstructure of the materials was analysed via scanning electron microscopy (SEM, Leo Gemini 1525) and X-ray tomography (*Phoenix vTomeX/X-ray, Germany*). After the infiltration was completed, a water-cooling low-speed diamond blade was used to cut rectangular beams for bending tests ($20 \times 2 \times 3 \text{ mm}^3$) with the tensile faces parallel to the ceramic layers. The tensile faces were mirror polished. Single-edge notched specimens (SEN(B)) were used to evaluate the fracture toughness K_{Ic} and crack resistance curve (R-curve). An initial notch was cut in the specimens with a low-speed blade that was subsequently sharpened with a razor blade using a $1 \mu\text{m}$ diamond paste. Sharp cracks of almost the half ($a/W \sim 0.5$) of the thickness of each specimens were obtained for the R curve measurements to favour a more stable crack propagation [35]. All faces were mirror polished to better observe the crack propagation during R-curve measurements. In accordance with the standard (ASTM-E1820) [36], the notch size of SEN(B) specimen for K_{Ic} measurement were between 0.12 and 0.3 of W . The orientation of the notch was such that the crack could grow perpendicularly to the ceramic layers (crack-arrested orientation). Four-point bend tests were performed to generate stress and strain curves and calculate the flexural strength. The experiments were carried out using Zwick-Roell Z010 with a load cell of 100kN capacity, and the associated software was TestXpert II. The tests were performed on un-notched composite bars using a support span of 12mm. The displacement rate was set as 0.2mm/min in general accordance with ASTM (E1820) [36]. The fracture toughness tests were performed on SEN(B) specimens on the same apparatus, using the same support span of 12mm. K_{Ic} values were determined by monotonically loading the bars until failure at constant displacement rate of 0.1mm/min. Three point bending (3PB) were performed for the SiC/PMMA lamellar composites and four point bending (4PB) for the SiC network-like fibre/epoxy ones. For the R curve measurements, samples were tested in four point bending ($S \sim 18 \text{ mm}$) with an Instron 8500 machine at a testing rate of 0.01mm/min. The beams were loaded until crack propagation was observed in the load/displacement curve (change in the compliance of the material). The specimen was then unloaded and the crack was measured with an optical microscope (Zeiss, AxioCam). Different measurements of crack propagation were taken with the precaution of loading the sample always in the same position. The deflections were measured by a linear variable differential transformer (LVDT).

Nonlinear elastic fracture mechanisms analysis was used to evaluate fracture resistance of the samples as the crack propagated through the microstructure. The J-integral versus Δa crack extension were estimated. In the J-integral two contribution were taken into account, the elastic $J_{el}=K_{Ic}^2/E$ and the plastic $J_{pl}=1.9A_{pl}/Bb$ where A_{pl} is the plastic area under the load-displacement curve, B the specimen width and b the un-cracked ligament. From the evaluation of J it is possible to extract the values of K with a sample J - K equivalence for nominally mode I fracture ($K_J=(J \cdot E)^{1/2}$). More details about this test have been reported in Chapter 6.

7.3 Results

7.3.1 Microstructure and mechanical behaviour of SiC/PMMA lamellar composites

Freeze casting and in-situ polymerization were used to produce SiC/PMMA composites with a lamellar architecture. The porous scaffolds used to produce these composites were obtained varying the initial ceramic loading of the freeze casted suspension and keeping constant the freezing rate. High freezing speeds of 15°C/min were selected to shape the porous SiC scaffolds. The freezing rate were chosen based on previous studies where higher freezing speed led to tougher and stronger composites [33,37]. Different ceramic loading, ~9 and ~20vol%, influenced the final ceramic fraction and morphology of the freeze casted scaffolds. Fig.88 show the two examples of scaffolds produced in this study. Freeze casting suspension with an initial solid loading of 9vol% lead to porous scaffolds with ceramic content of 25vol% and lamellae and pore size of $3.17 \pm 0.8 \mu\text{m}$ and $13.0 \pm 3.9 \mu\text{m}$ respectively (Fig.88c-d)). Increasing the solid loading the ceramic content increased up to 45vol% and the lamellae and pore size were $9.3 \pm 1.5 \mu\text{m}$ and $12.7 \pm 3.2 \mu\text{m}$ respectively (Fig.88a-b)). Suspensions with lower solid loading yielded to scaffolds with a more dendritic morphologies characterized by tiny bridges running perpendicular to the lamellae direction, typical of freeze casted architectures. Good alignment and completed infiltration were achieved for all compositions.

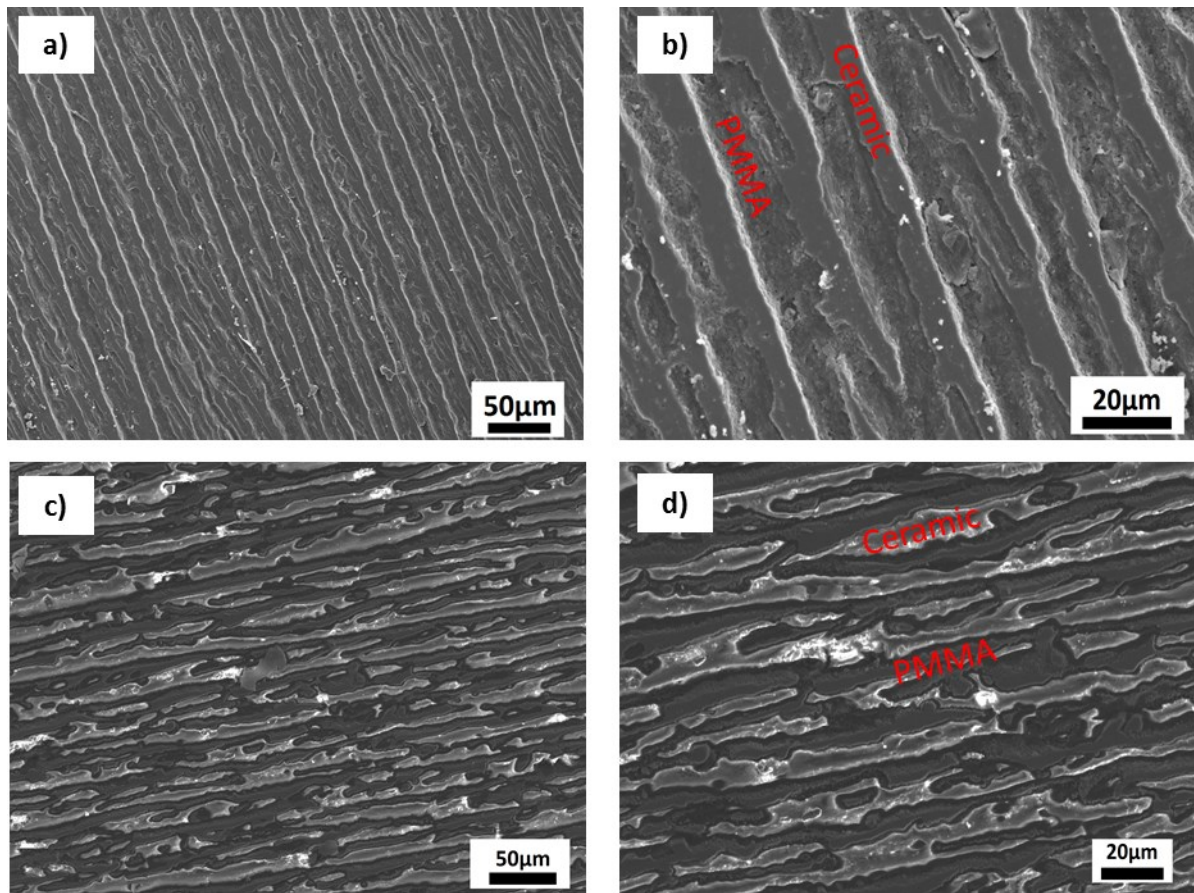


Fig. 88 Freeze casted SiC scaffolds infiltrated with PMMA. a- b) 45vol% scaffold frozen at 15°C/min where the darker phase is the ceramic phase meanwhile the brighter one is the PMMA. c) - d) 25vol% scaffold frozen at 15°C/min where the brighter phase is the ceramic.

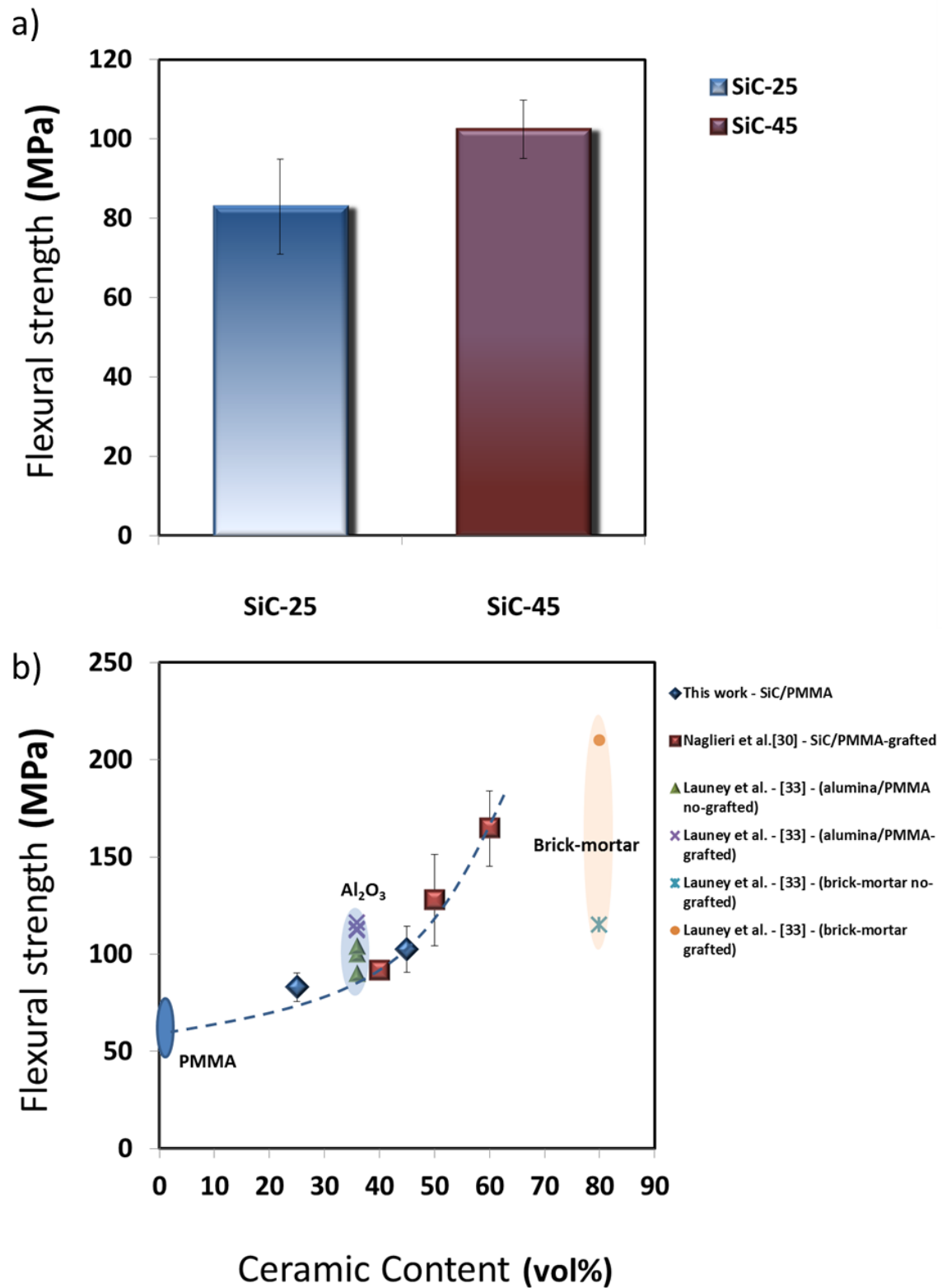


Fig. 89 a) Flexural strength SiC+PMMA composites with two different ceramic loading 25 and 45vol% b) Comparison with previous work on bio-inspired SiC and Al₂O₃/ PMMA composites In the work of Launey et al. [33] strong adhesion between the PMMA and the alumina layer is generated grafting the two phases with a coupling agent (silanization process).

Four point bending test were performed to evaluate the flexural strength of the two systems. SiC/PMMA with a ceramic fraction of 45vol% show a maximum value of flexural strength of 118.3MPa with an average value of 102.4 ± 11.9 MPa. Obviously, reducing the ceramic amount the flexural strength decreased to a maximum value of 91.7MPa and an average value of 82.9 ± 7.4 MPa. Comparing these values with the values obtained by Naglieri et al. [30] with similar structures, the trend clearly shows the expected increase in flexural strength as the ceramic volume fraction increase (Fig.89).

Three point bending test were used to evaluate the fracture toughness. Initial stress intensity factors K_{Ic} of 3.3 ± 0.35 MPa $\cdot$ m $^{1/2}$ and 2.8 ± 0.21 MPa $\cdot$ m $^{1/2}$ were found for lamellar composites with ceramic content of 45vol% and 25vol% respectively. For the composite with higher ceramic content J_R -curve measurements were performed to evaluate its R-curve and to better identify the toughening mechanisms occurring within its microstructure (Fig.90).

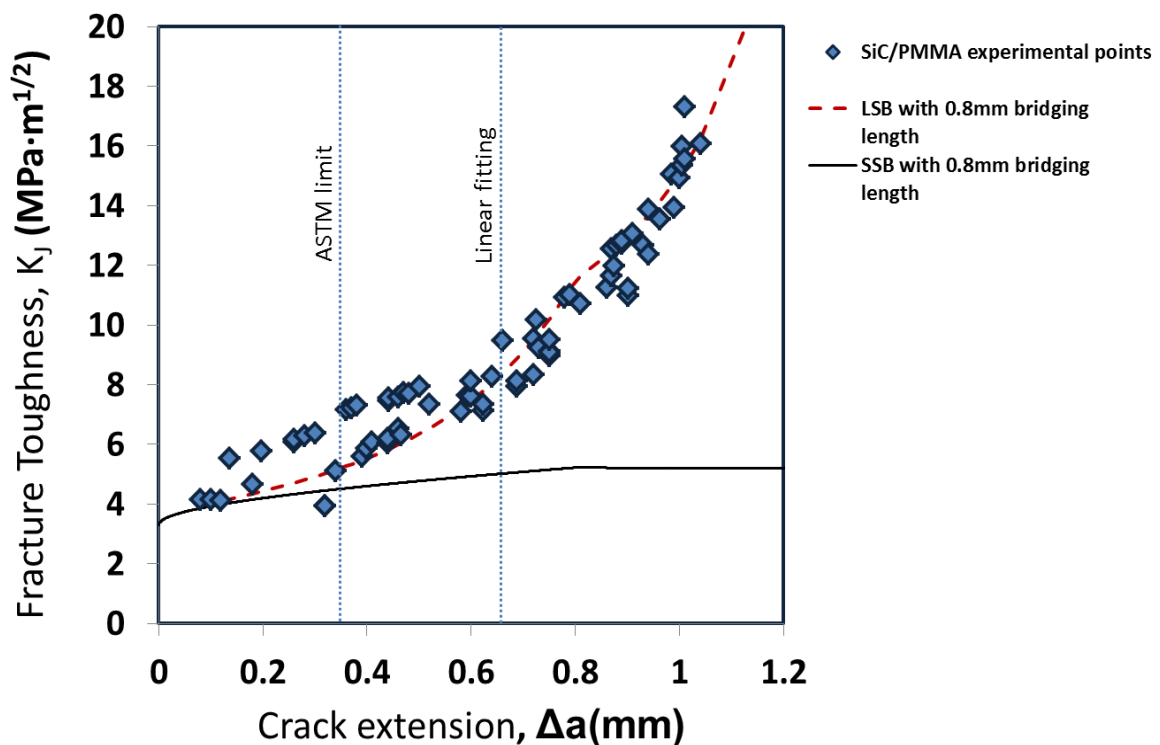


Fig. 90 R-curve behaviour of SiC-PMMA composites. A rising R-curve has been measured for SiC/PMMA composite with 45vol% ceramic loading. It is possible to notice that it tends to rise linearly before diverging exponentially.

Stable crack propagation was achieved during the test as it is possible to observe from the force-displacement curve (Fig.91). As the crack propagate within the microstructure we measured an increasing fracture resistance with J values going from 0.19 to 0.3 kJ/m² at $\Delta a \sim 0.4$ mm that corresponded to stress intensity factor ranging from ~ 6 to 8 MPa·m^{1/2}. Considering values exceeding the crack extension limit of 0.4mm that were “invalid” for the ASTM E-1820 [36], we could identify two different regions in the R-curve: a linear rising and a final part where the curve diverges.

The crack resistance reached values of ~ 10 MPa·m^{1/2} at the end of the linear part and is much higher up to ~ 20 MPa·m^{1/2} at the end of the diverging zone. Crack-path interaction with the microstructure was evaluated with a post-test observation of the tested sample as reported in Fig.92. The crack propagated steadily perpendicularly to the maximum tensile stress. The bridging of the PMMA layer behind the crack tip was the main toughening mechanism observed. The polymer layers did not break as the main crack was transmitted from a ceramic layer to the following one but they deformed and stretched hindering the crack growth.

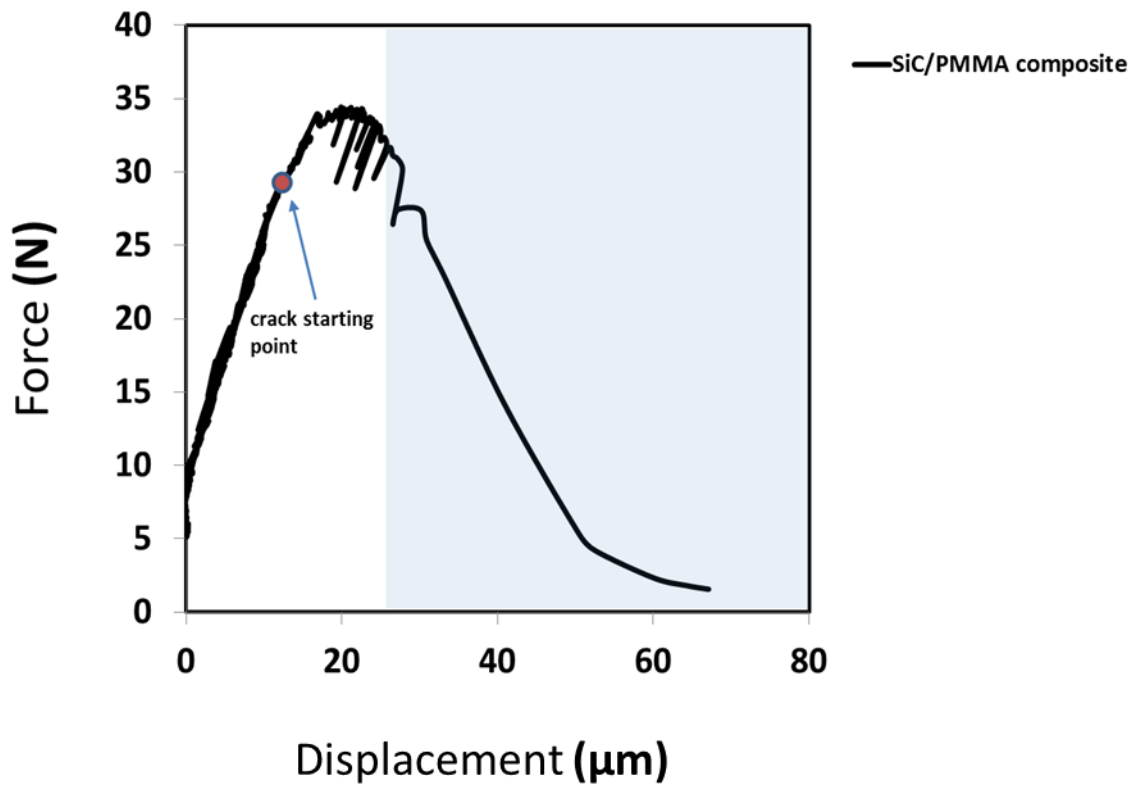


Fig. 91 Force/displacement curve for SiC/PMMA composite with 45vol% ceramic content. The red dot underline when the crack propagation starts. The fracture process is clearly observed from the change in the compliance of the material. The stress rise up to reach a plateau during which the load is constant and after the load decreases without a catastrophic failure.

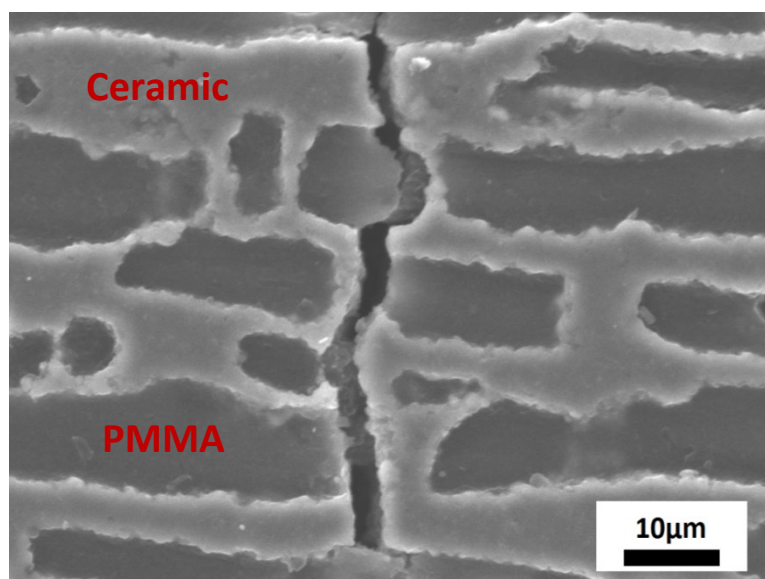
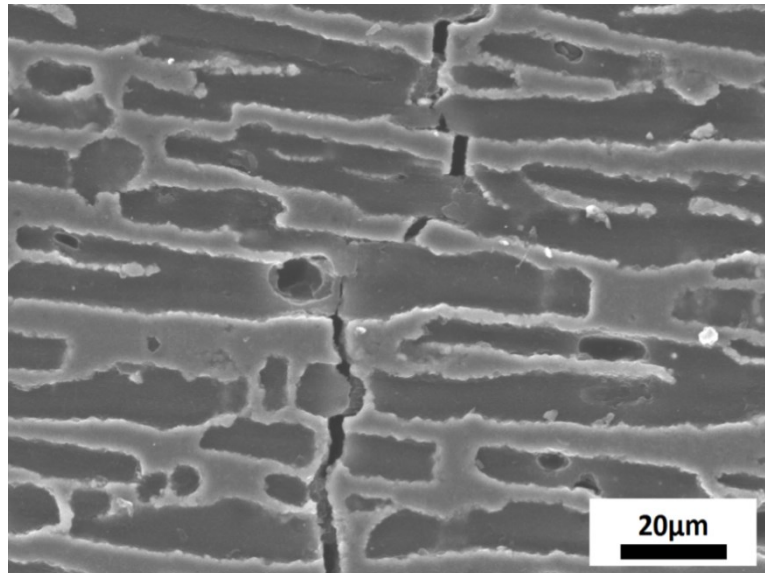
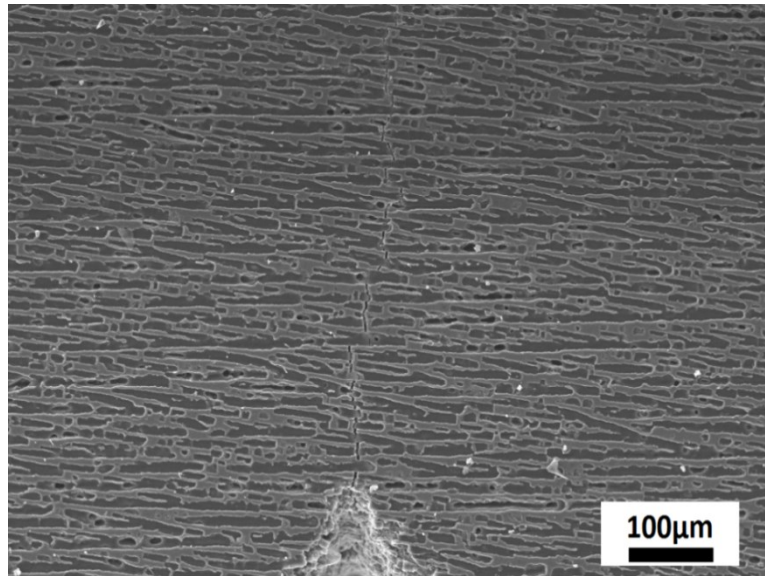


Fig. 92 Crack propagation within the SiC/PMMA microstructure. From the three images it is possible to notice as the polymer layers bridge the crack meanwhile the crack propagates within the ceramic layers.

The crack moreover at some point (Fig.92) re-nucleated slightly deviated from the main plane of propagation in a sort of “pull out” of the lamellae with the significant shear deformation of the previous polymeric layers. Fig. 93 shows a typical fracture surface of the tested samples. Inter-granular fracture within the silicon carbide ceramic layers was observed meanwhile the PMMA layers showed extensive plastic deformation with microvoids and dimples. Good bonding between the ceramic and the polymer layers was observed with no significant appearances of interfacial debonding.

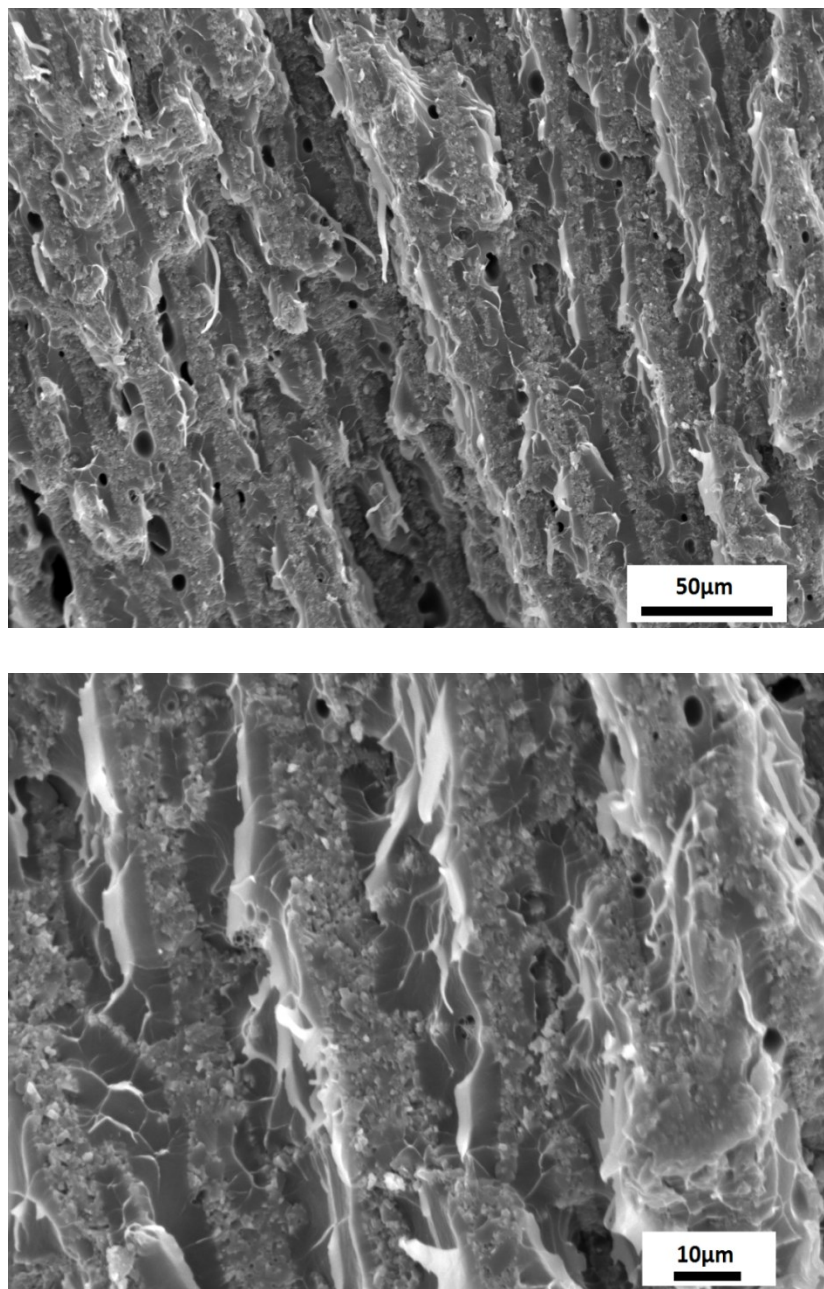


Fig. 93 Fracture surface SiC/PMMA composites. The fracture surface is extremely rough due to the crack deflection during the fracture. Moreover it is possible to notice characteristic features of plastic deformation within the polymeric layers along with cavitation. All these mechanisms took part to the toughening of the composite.

7.3.2 Microstructure and mechanical behaviour of SiC ultralight network-like fibre composites

Many studies have proved that the addition of rigid fillers such as carbon nanotubes, graphene, fullerene etc. increases the fracture resistance of brittle epoxy resin [9,10,13]. A good dispersion of the fillers within the polymeric matrix is a crucial factor that could limit the effectiveness of the reinforcement. In this study fibres-based composites were produced combining freeze casting of short SiC fibres and epoxy infiltration. Using the freeze casting to produce the fibre preform allowed having a layered distribution of filler within the whole structure. Different ceramic fibres loading (2, 4 and 8vol%) were used and in all cases complete infiltration was achieved as no residual porosity can be observed after infiltration (Fig.94). Even at lower ceramic loading the preforms retain the lamellar arrangement of the fibres imposed by freeze casting.

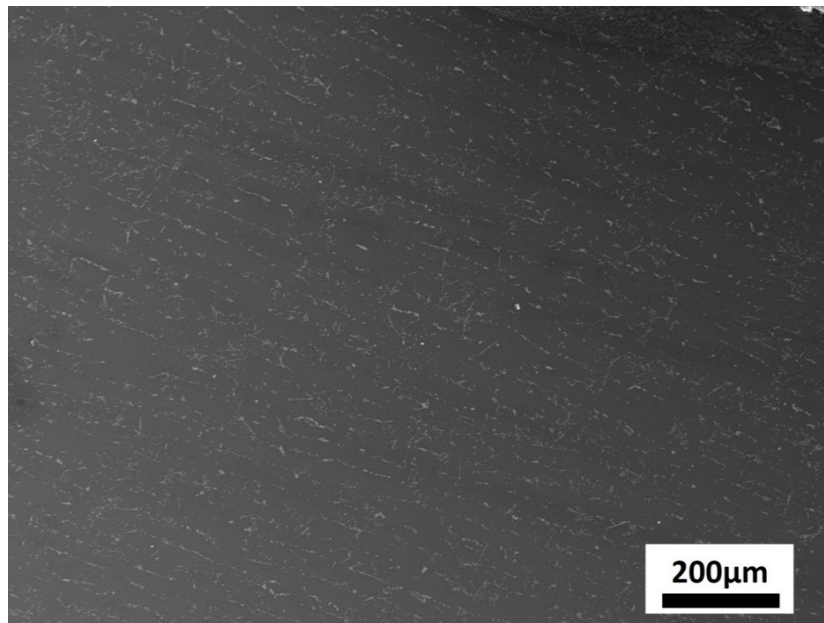


Fig. 94 SiC fibres/Epoxy composite microstructure with 4vol% fibres loading. It is possible to notice that the fibre alignment obtained by freeze casting is preserved in the final composite.

Bending tests showed that increasing the fibre content was detrimental for the bending resistance of the composite (Fig.95). The highest flexural strength of the composite was achieved with solid loading ranging from 2 to 4vol% with maximum values similar than those

for pure epoxy (~200MPa). Increasing the fibre content up to 8vol% the flexural strength drastically decreases to ~110MPa. This suggests that the optimum weight fraction for epoxy infiltrated SiC fibres scaffolds is around 4vol%. Higher fibre contents can produce defects that act as crack initiation point decreasing the composite flexural strength.

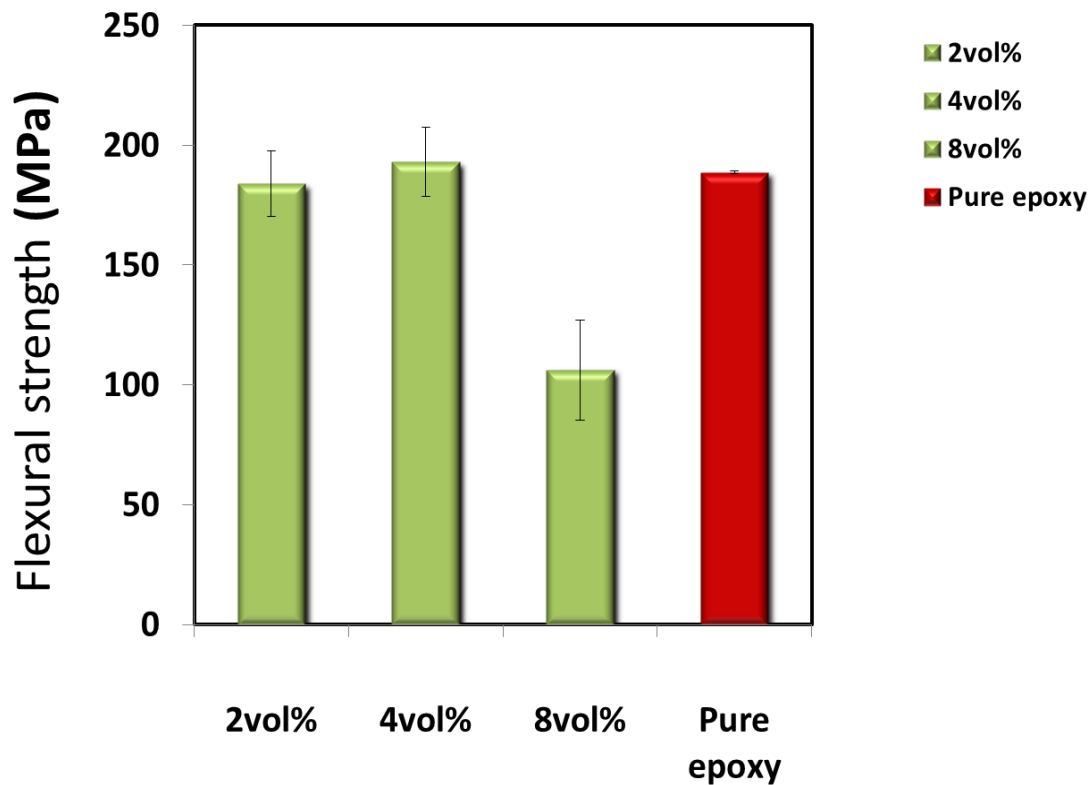


Fig. 95 Flexural strength of SiC fibres/Epoxy composites with different vol% of reinforcement compared with pure epoxy samples.

Four point bending tests were performed on SEN(B) samples to evaluate the fracture resistance of the fibre based composites. As already showed for the flexural strength trend, the highest values were achieved with lower solid loading (Fig.96). In this case the highest fracture toughness of $2.6\text{MPa}\cdot\text{m}^{1/2}$ was achieved with a solid loading of 2 vol%.

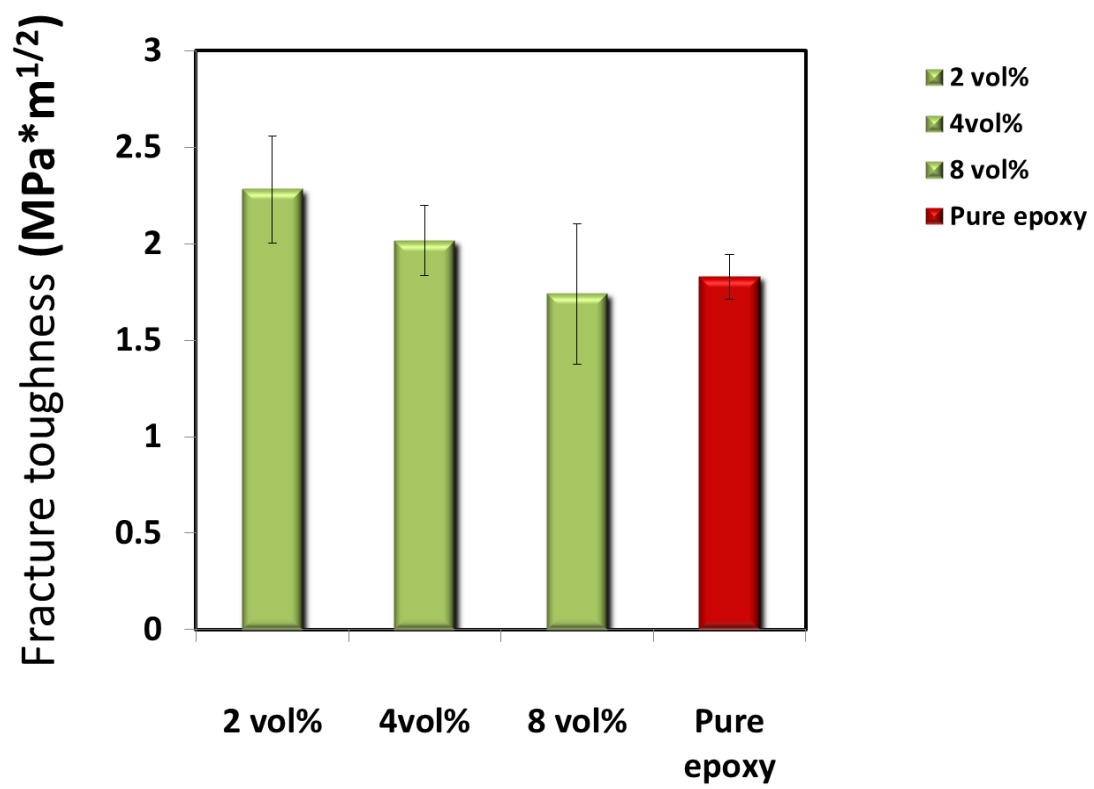


Fig. 96 K_{Ic} of SiC fibres/epoxy composites vs pure epoxy.

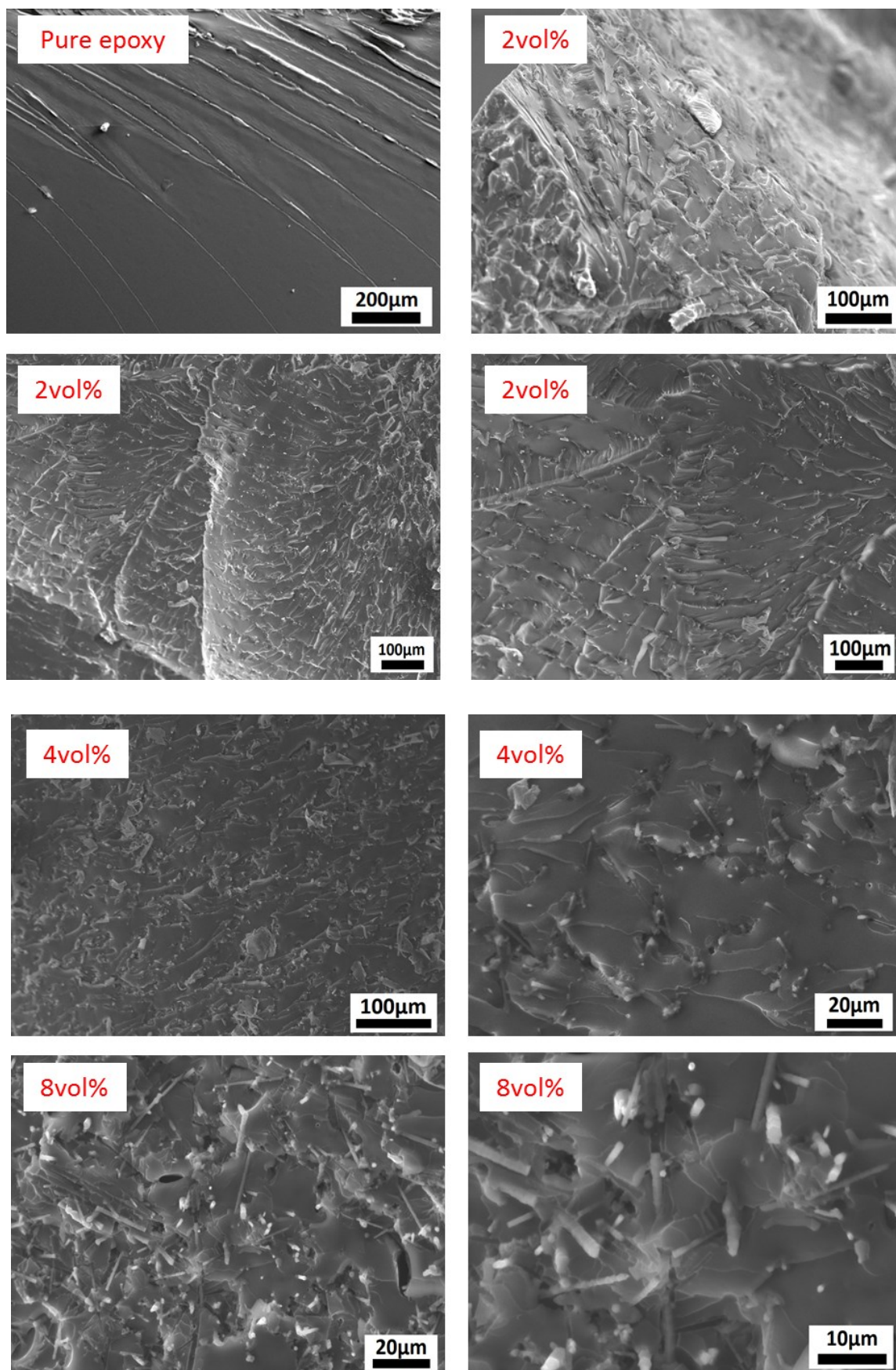


Fig. 97 Fracture surfaces of composites with different vol% of reinforcement compared with fracture surface of pure epoxy.

The introduction of fibres in the epoxy induces different fracture mechanisms as it is possible to observe on the fracture surfaces shown in Fig.97. The fracture surfaces are in fact rougher than the smooth surface of pure epoxy and some pull-out of the fibres can be observed. The crack does not propagate straight as in pure epoxy but it seems deflect at different points and its path is influenced by the aligned disposition of the fibres as the micro-roughness of the fracture surface reveals. This micro crack deflection can explain the increased fracture toughness of the composites. As the fibre content increases agglomeration of fibres can be observed that can be detrimental for the mechanical properties. However the fracture toughness of the composite was higher than pure epoxy, R-curve behaviour was not observed in this type of composites as the crack propagates, after significant deformation, in an unstable manner within the microstructure up to failure (Fig.98).

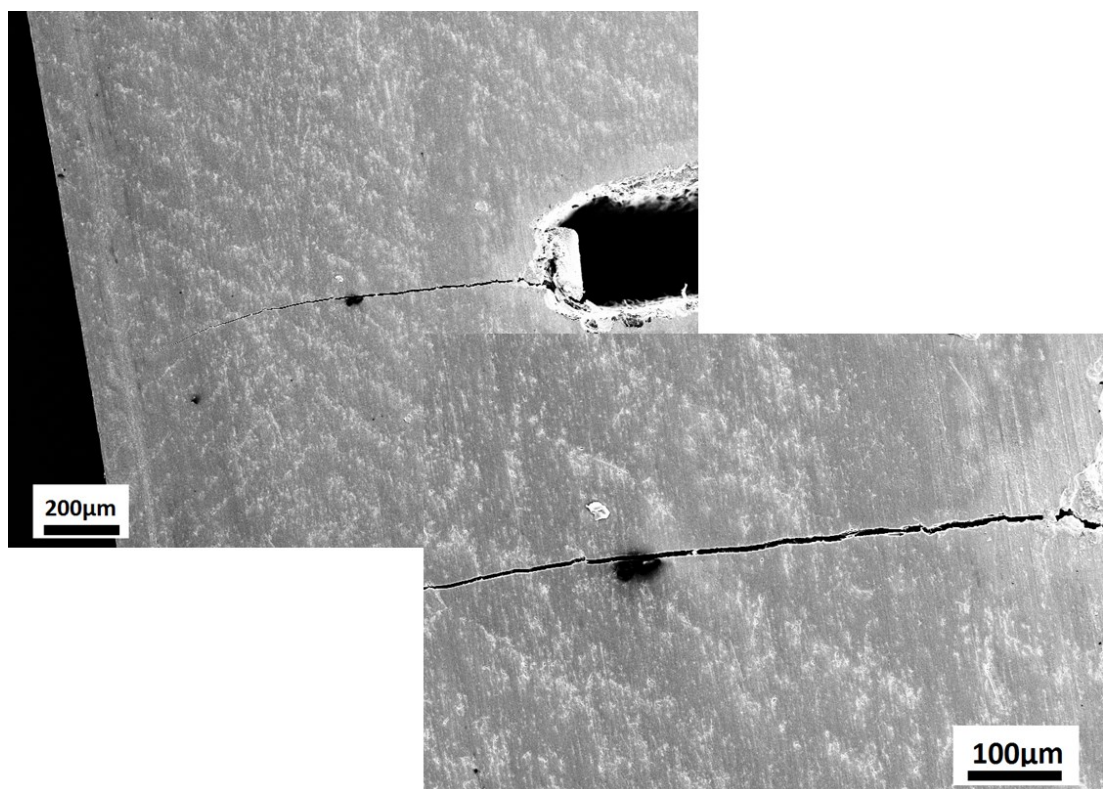


Fig. 98 Crack propagates in unstable manner within the fibre/epoxy composite.

7.4 Discussion

7.4.1 SiC/PMMA lamellar composites

Nature-inspired composites with unusual combinations of mechanical properties can be produced exploiting the architecture control provided by freeze casting and the use of ductile compliant phases. As reported in the previous chapters the final microstructures can be modified by controlling the initial solid loading of the suspension and the freezing conditions adopted during the freeze casting. In this study the freezing rate has been kept constant at 15°C/min and the effect of the solid loading on the microstructure and the mechanical properties of the final composites has been investigated. The solid loading of the initial slurries influences the ceramic fraction of the final composites and the lamellae/pores size and morphology. Increasing the solid loading of the initial suspension generates ceramic scaffolds with higher ceramic fraction. For instance the two composites analysed in this study were produced from suspensions containing a solid content of 9 and 20vol%. Using similar freezing conditions the latter showed a larger ceramic fraction up to 45vol% vs the 25vol% of the former. As reported by Naglieri et al. [38] the freezing rate influences also the ice morphology that goes from a lamellar morphology at low freezing speeds to a more dendritic one as the cooling speed increases. In our case using high freezing speed for the two solid loading, both final composites showed a dendritic configuration with high number of bridges connecting the ceramic walls.

The flexural strength of the composites is directly related to the ceramic fraction; therefore the scaffolds with higher ceramic content showed higher flexural resistance. Comparing our results with those of Naglieri et al. [30] (Fig.89b) it is possible to observe that the scaffolds produced in this study, with 45vol% of ceramic, show flexural strength in trend with those reported in literature, meanwhile the scaffolds obtained with lower ceramic loading (25vol%) almost reach the upper bond value of the PMMA flexural strength and similar values obtained for Al₂O₃/PMMA non-grafted composites produced by Launey et al. [33]. Regarding the fracture toughness the scaffolds with lower ceramic fraction and therefore higher polymer content showed lower values of fracture toughness compared with the higher ceramic content composites, but higher K_{Ic} than pure PMMA ($\sim 1.2 \text{ MPa}\cdot\text{m}^{1/2}$ [33]).

However even if the polymeric fraction is much larger than the composites with higher ceramic content, around 20vol% more, the decrease in terms of K_{Ic} it is only minimal. This suggests that the lamellar architecture and the ceramic bridges represent keys factors that can enhance the resistance to fracture of these composites. The effect of the ceramic bridging and the micrometre roughness on the ceramic walls are already known to be efficient toughening mechanisms in both natural and synthetic materials [33,37,39]. The composite with 45vol% showed a stable crack propagation that allowed measuring an R-curve behaviour, which suggests the occurrence of extrinsic toughening mechanisms. Among them we observed crack deflection, un-cracked polymeric ligament in the crack wake, plastic deformation of the polymeric layers, pull-out of the ceramic layers; all these mechanisms dissipate energy and generate a resistance curve with the fracture toughness increasing as the crack propagates within the microstructure. As already seen in previous layered composites, where the ceramic layers are alternated by polymeric or metallic layers, this composite showed a rising R-curve typical of large scale bridging phenomena. Taking in consideration the limits expressed by the ASTM [36] the K_{Ic} rises up to $\sim 6\text{-}8\text{MPa}\cdot\text{m}^{1/2}$, however exceeded these limits the curve linearly rise up to $\sim 10\text{MPa}\cdot\text{m}^{1/2}$ and after diverges. The divergent part of the curve is when large scale bridging becomes predominant and the test turns out to be geometry dependent. These values are in perfect agreement with SiC/PMMA freeze casted composites found in literature [30]. These values are much higher if compared with traditional SiC materials. Its monolithic form for instance reaches low values of $2\text{MPa}\cdot\text{m}^{1/2}$ (Hexoloy SA) [40] with no evidence of R-curve that instead can be generated using some sintering additives that create an intergranular glassy phase as in ABC-SiC. In this last case the K_{Ic} can reaches up to $9\text{MPa}\cdot\text{m}^{1/2}$ [30,40]. The produced SiC/PMMA composites display higher fracture toughness but for the high polymeric content much lower strength.

7.4.2 SiC ultralight network-like fibre composites

The presence of rigid SiC short fibres generates different fracture and toughening mechanisms in the resin matrix. Some of these mechanisms involve shear yielding, crack deflection, pull-out and crack pinning. Contrary to the neat epoxy, where the mirror-like fracture surface revealed a brittle mode-I fracture, in the composites the crack moves out of its initial propagation plane each time it interacts with the reinforcement, as it is possible to

observe in the set of picture in Fig.97. Consequently the force needed to propagate the crack is larger than in the pure resin. Fig.97 shows the fracture surface of composites with different content of reinforcement. It is possible to observe that the lamellae alignment of the fibres given by freeze casting is kept in the final microstructure and that the crack propagation is further influenced by this arrangement. Many shear bands are created between each fibres layer as result of the interaction between the crack and the reinforcement. Moreover as the fibres content increase the fracture surface become rougher and the alignment of the fibres less precise as the preform becomes more isotropic than at lower fibre content (see Chapt.5). This less organized disposition of the fibre generates some fibre agglomeration that can be detrimental for the fracture toughness at high volume content of reinforcement and it can explain the lower values of K_{Ic} . It has been also reported in the literature that the fracture toughness of nano-composites starts to decrease beyond certain weight fraction of reinforcing filler, because voids, micro-cracks etc. are generated within the microstructure [13]. Fig.97 also shows the evidence of some SiC fibres that have been pulled out even though the amount of pull-out is not high due to the short length of the fibres. A good interfacial adhesion between fibres and epoxy can also been observed. The absolute values obtained both for strength and fracture toughness for these types of polymer-based composite are fairly high if compared with other nano-reinforced epoxy composites [14]. However it is possible to notice that the fracture toughness of the pure epoxy employed in this study is much higher than the values usually reported in literature ($\sim 0.5/0.6 \text{ MPa}\cdot\text{m}^{1/2}$) [14,41,42]. This result can be related to the high ratio resin/hardner used to produce the based epoxy, or to a relatively blunt initial notch. However, normalizing the fracture toughness of the produced composite with the fracture toughness of the employed epoxy, it is possible to compare the effect of the reinforcement with previous studies where carbon nanotube, graphene and nanoclay have been used as reinforcement. Our freeze cast fibre reinforced epoxy composite show similar values with CNT and graphene as reported in Fig.99. It is also possible to notice that using different types of filler such as nano-clay they can reach similar values only with much higher solid loading. Increasing the amount of reinforcement although the inclusion of short SiC fibres within the epoxy matrix increased its fracture toughness, the composites did not show R-curve behaviour not having stable crack propagation.

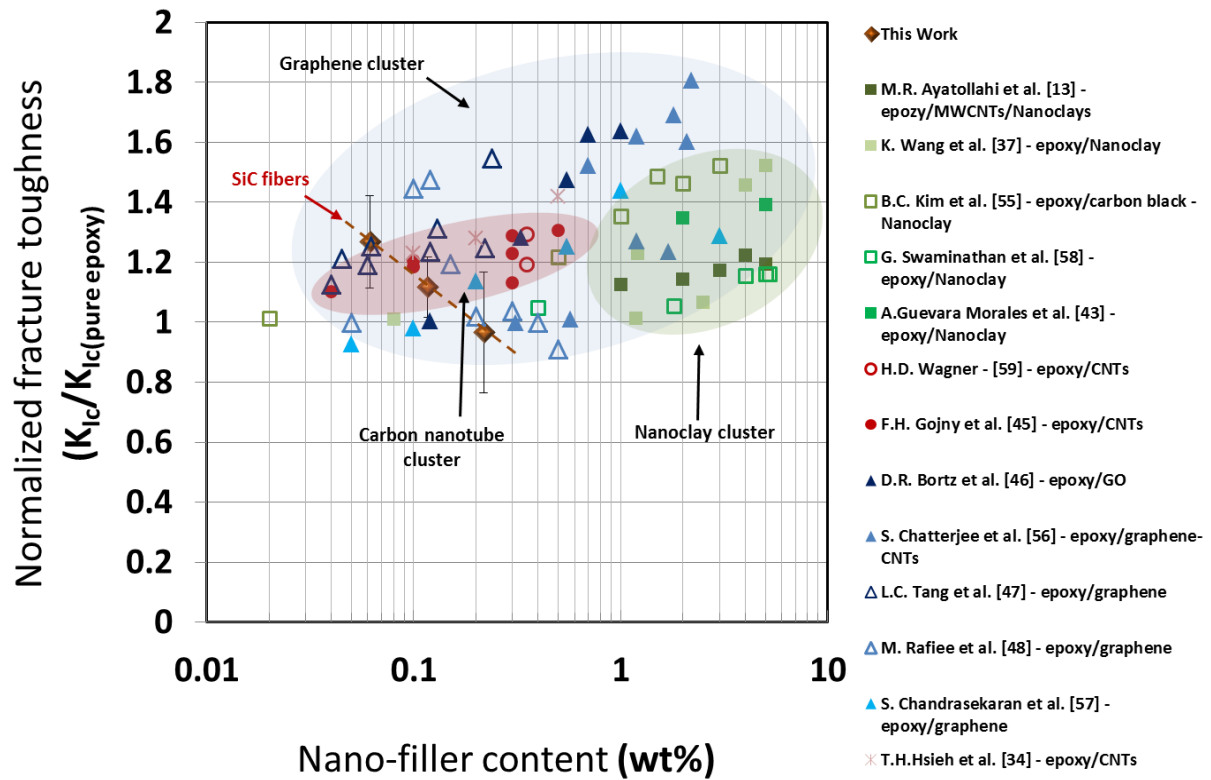


Fig. 99 Normalized fracture toughness vs nano-filler content for graphene, CNT and nanoclay cluster compared with our SiC fibres in reinforced epoxy composites. Literature data are obtained from the following references [37,43,45–48,55–59].

In terms of final strength of the composites, the use of SiC micro-fibres allow to obtain similar amount of reinforcement than obtained with CNT or graphene at comparable filler content. The use of other ceramic cluster such as alumina or clay generate same reinforcement efficiency at higher filler content and exceeded a certain wt% is detrimental for the final strength of the composites.

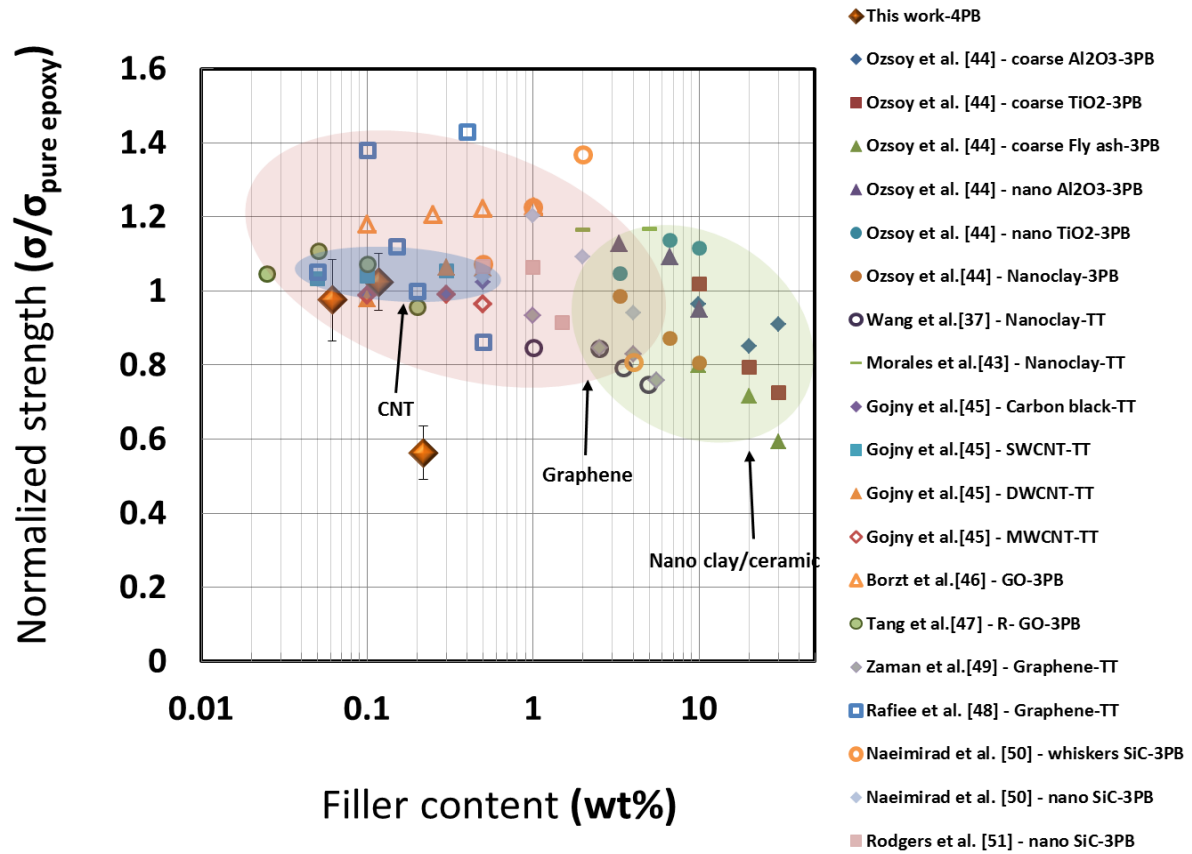


Fig. 100 Normalized strength versus the filler content for different reinforced epoxy-based composites compared with SiC fibre reinforced one (red diamond points). Different testing conditions were employed in these studies, 3PB, 4PB and tensile test(TT). Literature data are obtained from the following references [37,43–51].

As it can be observed in Fig.99-100, the reinforcement achieved with short SiC fibres is similar to the effect produced with CNT and graphene. This result is obtained even though the calculated strength of the employed SiC fibres (2GPa, 3PB test Chapter 5) is lower than the theoretical strength of CNT (>45GPa, values over 100GPa can be found in literature [52]) or graphene (130GPa). These are however theoretical values or values measured testing defects-free structures that are difficult to achieve in large-scale production. The introduction of defects and voids in the ordered carbon architectures lower drastically their properties and therefore the overall strengthening capacity, as reported recently in the work of Shekhawat et al. [53]. The use of not perfect CNT or graphene can explain the modest reinforcement achieved with their implementation. Another factor that can be unfavourable for the reinforcement effect produced by these types of fillers is that they are usually extremely small. In our case the employed SiC fibres have lengths that are similar to

the critical length necessary to have full load transfer from the matrix to the reinforcement. Considering that the critical length can be evaluated from the following equation [6] (derived imposing that the matrix and the fiber fail at the same strain):

$$l_c = \frac{\sigma_f d}{\sigma_m} \quad (7.4)$$

where σ_f and d are respectively the strength and the diameter of the fibres (~2GPa and 1.5 μ m) and σ_m the strength of the matrix (200MPa) the critical length is around 15-20 μ m. Moreover it is possible to observe analysing the strengths and toughness of the SiC/PMMA composites produced that moving towards higher solid loading and therefore to a more isotropic distribution of the fibres within the composites, both mechanical properties tend to decrease. The organization of the fibre in ordered layers might have therefore a significant effect on the mechanical properties [54]. Contrarily when increasing the solid loading a decrease in the layer disposition can be observed along with a higher number of agglomerates that can be detrimental for the mechanical properties.

7.5 Conclusion

Using freeze casting we have produced SiC based polymer composites with innovative combination of mechanical properties. In the case of the SiC/PMMA lamellar composites we demonstrated that with a precise control of the architecture over different length scale playing with different processing parameters such as freezing speed and solid loading, it is possible to generate layered structure that are at the same time strong and damage tolerant. The R-curve analysis revealed that several intrinsic and extrinsic toughening mechanisms act within these kind of microstructure, from crack bridging to the plastic deformation of the polymeric layers.

Regarding the SiC short fibres/epoxy composites we have demonstrated the possibility of toughen the neat resin using SiC short fibres and we showed a clear dependence of mechanical properties with the filler concentration. The mechanical response increase up to a certain threshold after that the effect of the filler is negative. However freeze casting

allows a layered distribution of fibres within the whole structure. At higher fiber concentration local agglomeration may occur that reduces the effect of the reinforcement. Therefore lower fiber concentration of 2 vol% showed the highest reinforcement result.

7.6 References

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8 Conclusions and future research

Millions of years of evolution have made Nature an extraordinary source of inspiration for the development of new classes of man-made materials with superior traits. Copying the designs that Nature has developed to survive severe conditions can be the key to extending the current limits of materials engineering. Therefore in the last decades bio-inspiration has become an important branch of materials engineering. Even though we are still far from perfectly replicating the microstructural organization found in natural composites, in the last years many studies have revealed that bio-inspiration can be a possible answer to the production of a new range of multipurpose materials. The present research work was undertaken with the intent of producing Al_2O_3 and SiC bio-inspired based composites using freeze casting. Freeze casting or ice-templating can produce ceramic preforms with hierarchical features spanning different length scales. These hierarchical ceramic preforms have been subsequently infiltrated with polymeric or metallic second phases in order to fabricate ceramic-based composites. The mechanical responses of both the ceramic preforms and the composites have been investigated. The composites' toughening mechanisms have been carefully analysed. This work has highlighted how, using bio-inspiration in structural advanced ceramics such as SiC and Al_2O_3 , it is possible to produce multifunctional materials with superior mechanical properties that can be adapted to different applications. This chapter summarises the main findings and suggests areas of future research.

8.1 Porous silicon carbide (SiC) scaffolds

Strong SiC macroporous structures with porosity ranging from ~50% to ~75% have been fabricated through freeze casting (ice templating). The technique allows the fabrication of porous scaffolds with layered architectures and unique mechanical responses. The ideal rheological behaviour for freeze casting has been achieved by employing TMAH as a dispersant (Fig.35). The role of different parameters such as solid loading and freezing speed on the scaffold microstructure has been determined (Fig.36). A significant improvement of the sinterability of the ceramic particles within the lamella walls has been achieved

employing liquid phase sintering along with a careful control of the sintering atmosphere using a doped sintering bed (4wt% of Al_2O_3 added in the SiC powder bed). The freeze cast SiC scaffolds exhibit crushing and flexural strengths that are similar or slightly higher than those of macroporous SiC produced with other techniques (Fig.55). A bimodal particle size distribution (obtained through the addition of ~ 40 nm nanoparticles) resulted in a significant improvement in the compression strength of the materials but it also influences the lamellae organization (Fig.38). Further investigation is needed to assess the role of particle size distribution on mechanical response and lamellar alignment.

8.2 Ultra-light and strong SiC net-like structures

Ultralight and strong SiC scaffolds have been produced by combining ice-templating and short SiC fibres. Optimal dispersion of the fibres has been achieved utilizing a chitosan-based suspension (Fig.60). Using the sintering approach developed in chapter 4 it has been possible to fabricate extremely light (porosity up to 98%) network-like structures. The mechanical and thermal properties of the material have been investigated using in-situ compression tests in the SEM to better understand the failure process. The materials exhibit strengths and elastic moduli in the range of other metamaterials usually produced through more complex processes and with a limited material choice. This approach could be employed with other materials such as alumina fibres. Simple models have been used to predict the strength of the porous network, but the experimental results are always lower than the predictions. This result has been explained with the lower strength of the junctions between fibres. The design of a test to measure the strength of the individual junctions it would be interesting to prove the previous hypothesis.

8.3 Alumina-Aluminium lamellar composites

Layered metal/ceramic composites have been produced by combining freeze casting of Al_2O_3 particles with pressureless infiltration of an aluminium 5380 alloy. Alumina particles with different morphologies have been employed: spherical nanoparticles and platelets. In both cases, complete infiltration of the scaffolds has been achieved. Mechanical testing revealed that, when compared with traditional processes such as hot pressing, the

microscopic layered architecture imposed by freeze casting improves the mechanical response of the laminate. One of the goals of this study has been to analyse the mechanical response of these bio-inspired composites combining different characterization techniques (SEM, X-ray tomography). However, more work is still needed to understand which structural features from natural materials should be replicated and which are less important, because, as reported by Barthelat “it is not always necessary to work at nano-scale to obtain good mechanical properties” [1]. Moreover more work is needed to properly describe these materials taking into account all the fracture mechanisms acting at different length scales. Their mechanical performance is not always fully understood and often traditional ASTM standards are not applicable. ASTM standards developed for ceramics, metals or traditional composites in fact might not be fully able to describe these systems. Beside the complete study presented in this chapter, some preliminary work has been conducted to produce lamellar ceramic/metal composites for high temperature applications, and others to more carefully reproduce the nacre architecture with the combination of alumina platelets and slip casting. The methods and preliminary results achieved are summarized in the following paragraphs.

8.3.1 High temperature ceramic/metal composites

Bio-inspired lamellar ceramic-based composites reinforced with nickel alloys could be interesting for high temperature applications. These materials can be fabricated through the infiltration of freeze cast scaffolds. However it is well documented that nickel has a poor wettability on ceramic substrates [2] therefore the use of alloying elements is necessary to decrease the contact angle at high temperature [3]. Many other factors influence the wettability of a metal on a ceramic substrate, such as temperature, dwell time during the infiltration process and the use of active elements such as Ti, Cr and Si that could lead to complex reactions with the ceramic parts. Some of these strategies have been tried to improve the wettability of molten nickel on freeze cast Al_2O_3 and SiC ceramic scaffolds as described in previous chapters.

Spark plasma sintering (SPS) was used to perform the infiltration of the freeze cast ceramic preforms through a squeeze casting-like process taking advantage of the fast heating rates to avoid undesirable reactions. Previous studies used SPS to produce ceramic-metal ($\text{B}_4\text{C}/\text{Al}$)

composites through a powder metallurgy route, mixing the starting powders and trying to avoid reactions such as the formation of aluminium carbides which are detrimental for the mechanical properties[4]. A specific die design, shown in Fig.101, was developed to allow a safe infiltration process. The die was composed of two parts, an interior die where the ceramic scaffold and the metal were placed and an exterior part that worked as a barrier to avoid, in case of failure of the interior die, possible damage to the SPS chamber. The exterior barrier had a hole aligned with the horizontal pyrometer to control the working temperature.

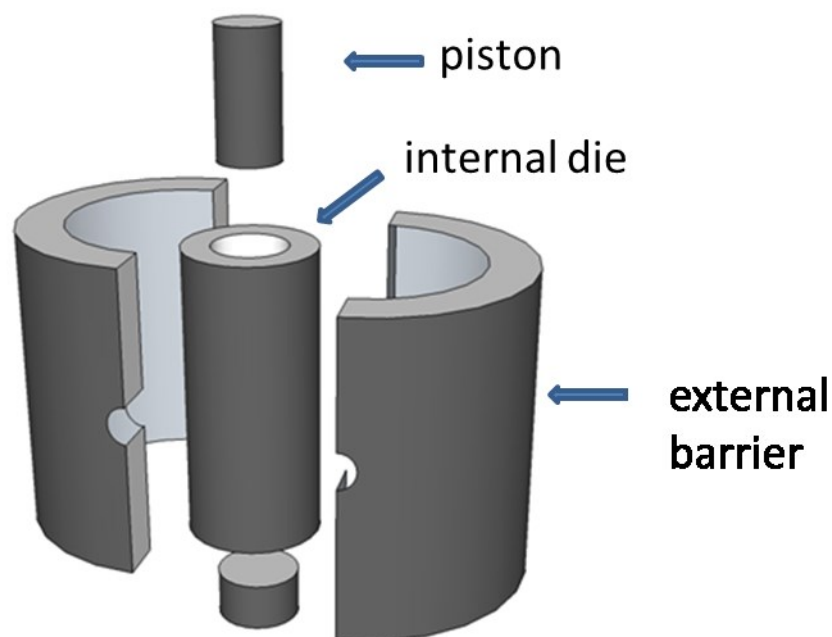


Fig. 101 Schematic representation of the die used to perform the pressure assisted infiltration of nickel alloys within freeze casted ceramic scaffolds.

A temperature range between 1400 and 1500°C was employed for all the formulations with a heating rate of 100°C/min and an initial contact pressure of 5kN. The infiltration process was controlled following the vertical movement of the vertical piston of the SPS. The pressure applied by the piston was increased when no infiltration (no movement) was noticed.

The first infiltration attempt was with an Al_2O_3 scaffold and a Ni35Ti20Al10Cr alloy. As reported in many studies the addition of Ti, Cr and Al helped to reduce the contact angle of Ni on Al_2O_3 [2,5–7]. The resulting microstructure is presented in Fig.102.

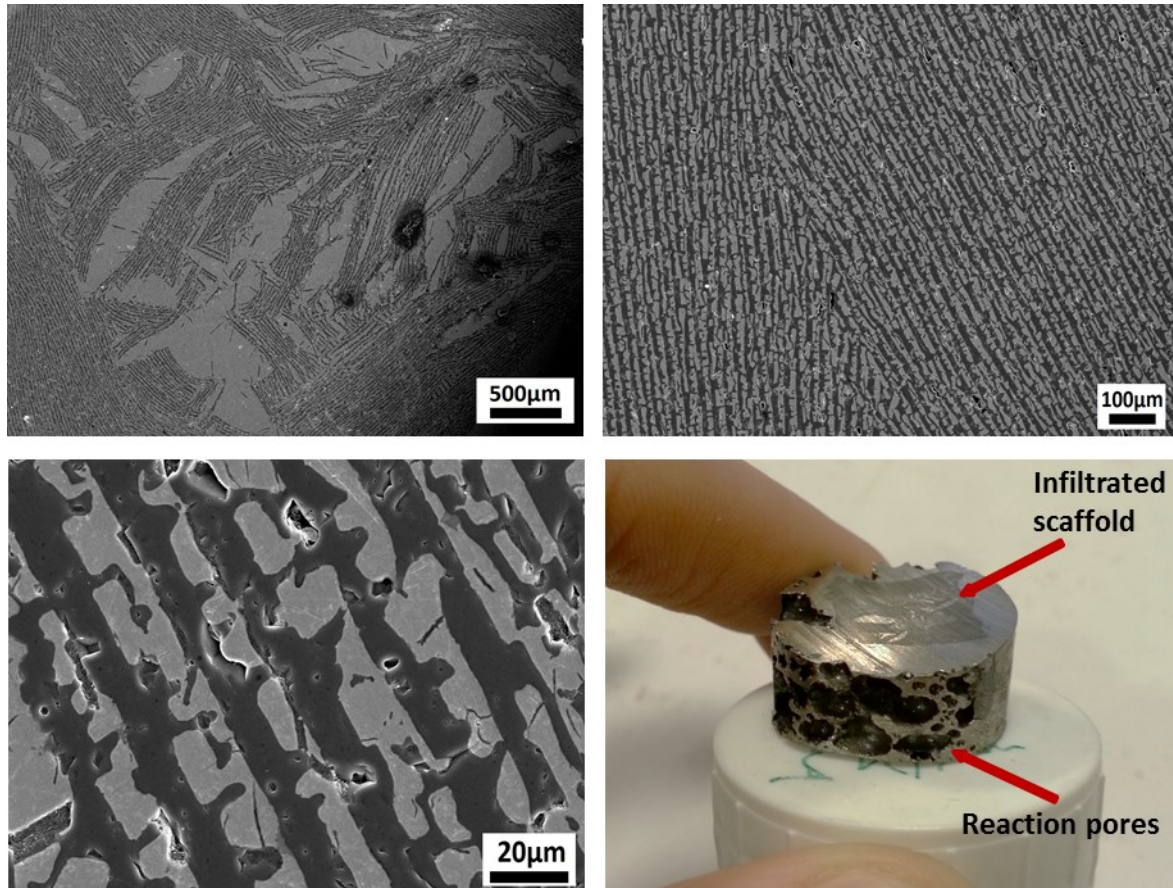


Fig. 102 Freeze casted alumina infiltrated by Ni35Ti20Al10Cr with a pressure assisted process.

The infiltration is partially successful. The scaffold in different points presents a distortion of the lamellar arrangement probably due to the high applied pressure. However, it is also possible to notice that the metal alloy perfectly infiltrated the alumina scaffold in some parts, preserving the lamellar arrangement. Reaction points can be observed on the side of the scaffold and on the lateral side of the metal/scaffold block, where pores can be observed. The reaction, with possible release of gas, could occur between the different alloying elements and the graphite die employed in the SPS. Carbon rich areas have been detected by EDX at different points of the scaffold meaning that the carbon of the SPS set-up diffuses into the sample. The process could be improved by producing the nickel alloy before the infiltration step, reducing the possibility of reactions.

The second and third attempts were performed on a SiC freeze cast scaffolds. As reported in the literature, the alloying of nickel with Cr [8,9] and Si [10] could increase the wettability of nickel on SiC preforms. In Fig.103 the microstructure of a SiC scaffold infiltrated with a Ni50Cr alloy is reported.

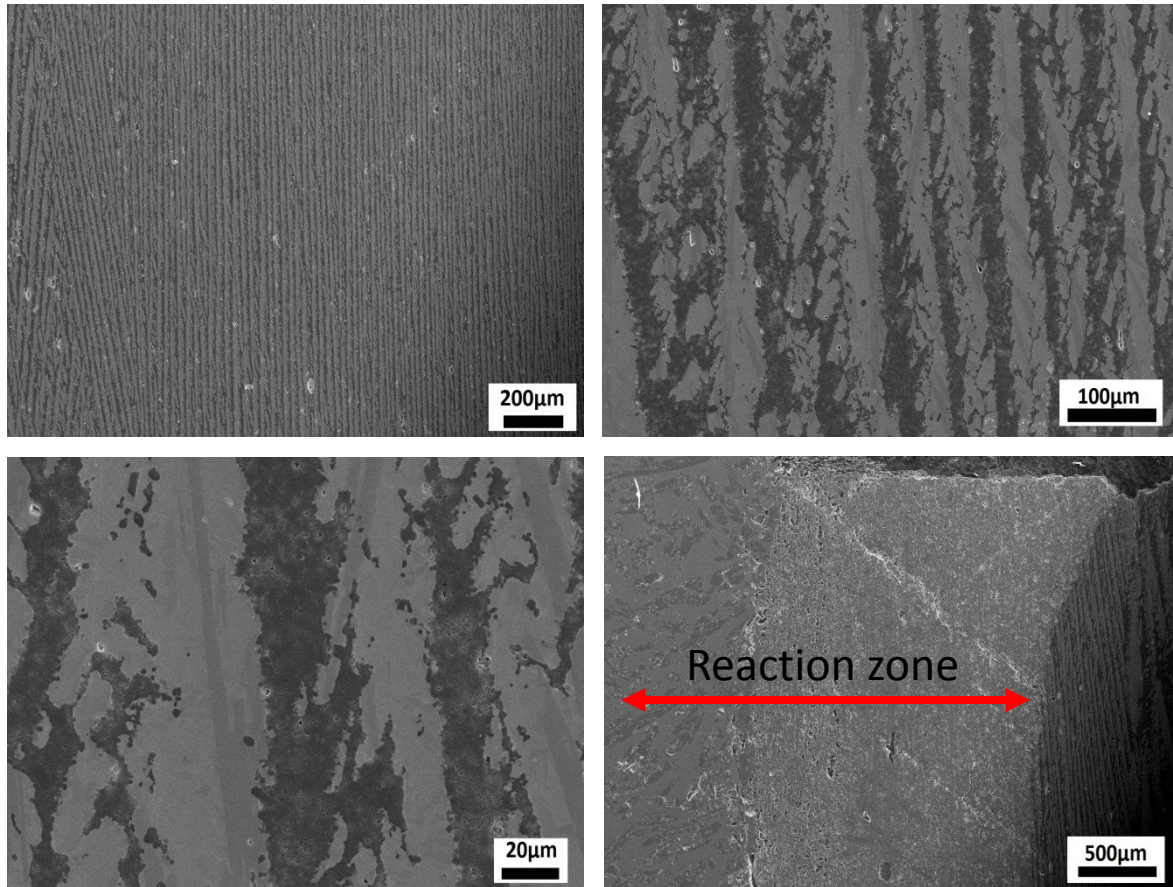


Fig. 103 SiC freeze cast scaffold infiltrated with a Ni50Cr alloy during a pressure assisted infiltration process within SPS.

The alloy seems to wet the ceramic scaffold reasonably well. The lamellar architecture is not compromised, but large reaction zones are still noticeable on the side of the scaffold. Moreover, it seems that even the SiC within the single lamella partially reacts. In the case of the SiC scaffold the presence of glassy phases formed during sintering from the addition of Al_2O_3 and Y_2O_3 must be considered in order to account for the possible reactions.

Fig. 104 shows the microstructure of a SiC scaffold infiltrated with a Ni20Si alloy. This infiltration process was the most successful, with the integrity of the scaffold almost completely conserved. Reaction zones are still present at the bottom and on the top of the scaffold where the scaffold came in contact with the graphite of the SPS die.

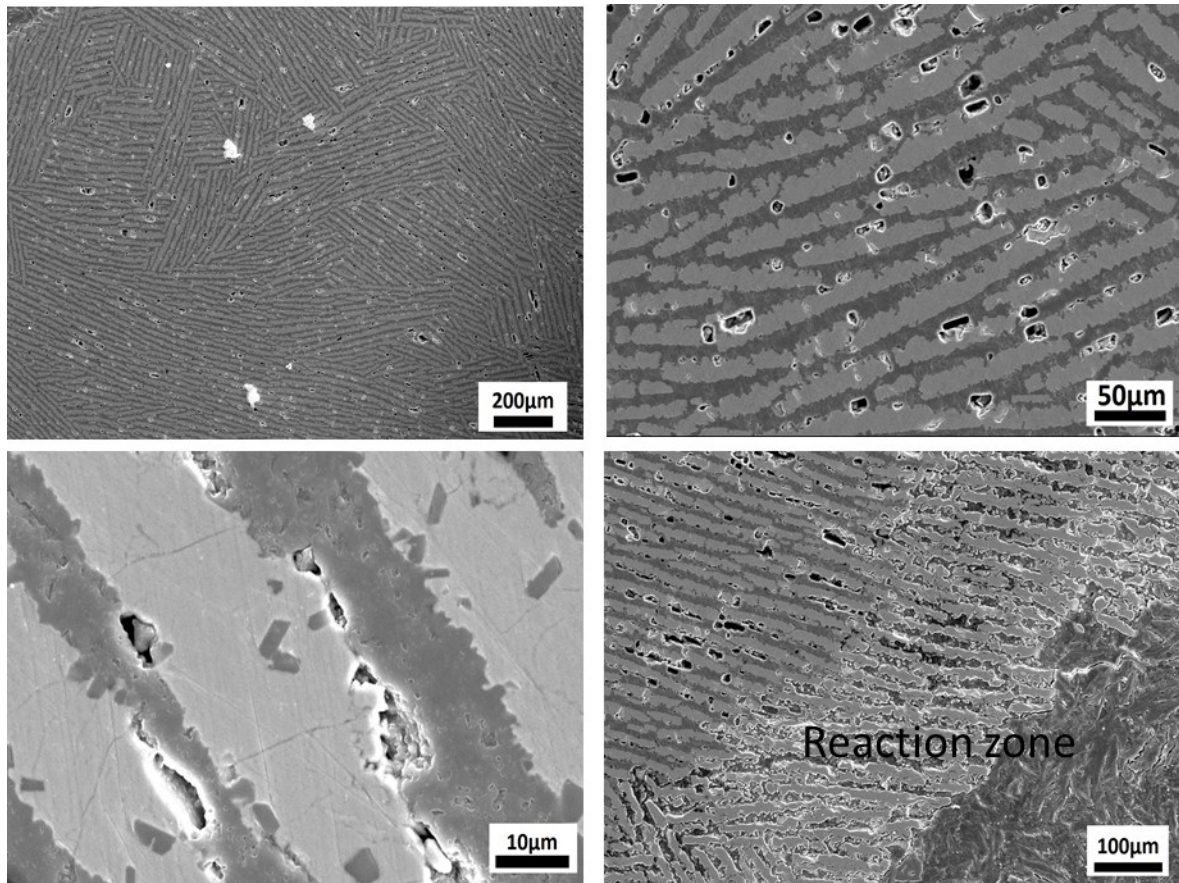


Fig. 104 SiC freeze cast scaffold infiltrated with a Ni20Si alloy during a pressure assisted infiltration process within the SPS.

These preliminary results showed the feasibility of the process. Careful control of the temperature, dwelling time, applied pressure and alloy formulation will have to be considered to consider the infiltration successful. Therefore further research is needed to optimize the process and to eventually assess the mechanical properties of these composites including at high temperatures.

8.3.2 Nacre-like structures from slip casting of alumina platelets

As reported already in many different studies [11–15], alumina platelets can be organized through different processing methods to closely replicate Nacre's design. They have been employed and aligned with different techniques to form the brick-arrangement typical of Nacre. The introduction of a second soft phase within this arrangement can be used to produce structural materials with interesting mechanical responses. As already shown by Behr et al. [15] a simple sedimentation process can lead to a good alignment of the

platelets; due to their shape they tend to sediment horizontally. However, with a simple sedimentation process they were able to achieve a ceramic loading of 28vol% that increased to 67vol% if isostatically pressed. Le Ferrand et al. [12] magnetically aligned the alumina platelets dispersed in a ceramic slurry, modifying their surface with nano-particles of Fe_2O_3 . Subsequently they were able to reproduce a nacre-like architecture in structures with high ceramic content through slip casting.

This preliminary study showed that a simple slip casting process of a properly tuned slurry, without applying any magnetic alignment, can be used to form a nacre-like structure using alumina platelets. The slurry had a ceramic loading of 28vol% of 70/30 of alumina platelets (Alusion by Antaria limited, Australia) and alumina nanoparticles (300nm, BaikaloX B-series SMA6 (Baikowski, France)). Alumina nanoparticles were added to favour sintering between the platelets and create structural “bridges” as observed in Nacre. Dolapix type CA (Zschimmer and Schwarz GmbH and Co., Germany) was used as dispersant and polyvinyl alcohol (PVA) 22000 (VWR, Belgium) as binder. The slurry was prepared by milling the alumina nanoparticles overnight to break down any possible aggregates. The alumina platelets were added after the removal of the milling media to avoid their fracture. The slurries were sonicated for at least 30 min and mixed for 24hr. After de-gassing, the slurries were gently poured in a gypsum mould. The slurry was allowed to settle for one day and the ceramic piece with the entire cast were dried at 100°C for at least two days. After drying, the piece is sintered at 1550°C for two hours. Fig.105 shows the architecture achieved after sintering. The platelet alignment spans over several millimetres and the final scaffold had a ceramic content up to 60vol%. The porosity can be reduced to 30% without any alteration to the microstructure with a subsequent unidirectional compression at a pressure of 300MPa. In future the scaffold can be infiltrated with different second phases such as, different polymers or metals, to closely reproduce the nacre structure. Mechanical properties of these composites will need to be assessed to capture the toughening mechanisms and evaluate the similarities and differences with Nacre.

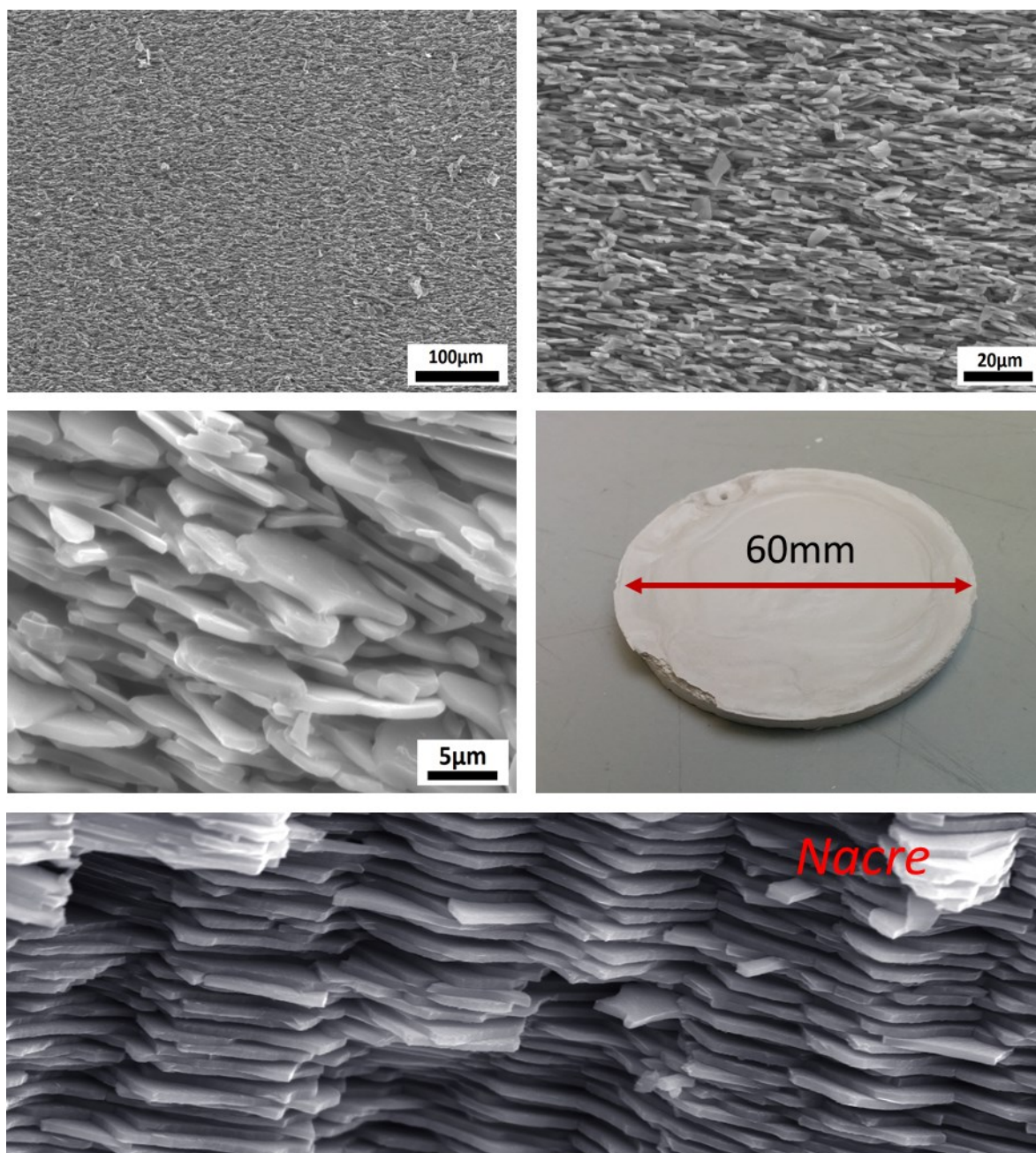


Fig. 105 Slip casting of alumina platelets allows a nacre-like organization to be obtained with an initial ceramic loading up to 60vol%.

8.4 SiC/polymer composites

The porous freeze cast SiC scaffolds reported in Chapters 4 and 5 have been infiltrated with two different polymers, PMMA for the macroporous SiC and epoxy resin for the ultralight network-like scaffold. The goal is to produce fracture resistant ceramic-based composites. R-curve behaviour of the lamellar SiC/PMMA composites have been investigated showing

similar values to those reported by Naglieri et al. [16] in similar systems, meanwhile the composites obtained by infiltrating the ultralight fibre scaffolds have led to promising results in terms of strength and fracture toughness. Regarding these specific materials, larger samples should be tested to follow the conventional standards employed for polymer-based composites.

8.5 References

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