

## **Tough salami-inspired C<sub>f</sub>/ZrB<sub>2</sub> UHTCMCs produced by electrophoretic deposition**

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### **Abstract**

One of the biggest challenges of the materials science is the mutual exclusion of strength and toughness. This issue was minimized by mimicking the natural structural materials. To date, few efforts were done regarding materials that should be used in harsh environments. In this work we present novel continuous carbon fiber reinforced ultra-high-temperature ceramic matrix composites (UHTCMCs) for aerospace featuring optimized fiber/matrix interfaces and fibers distribution. The microstructures - produced by electrophoretic deposition of ZrB<sub>2</sub> on unidirectional carbon fibers followed by ZrB<sub>2</sub> infiltration and hot pressing - show a maximum flexural strength and fracture toughness of 330 MPa and 14 MPa m<sup>1/2</sup>, respectively. Fracture surfaces are investigated to understand the mechanisms that affect strength and toughness. The EPD technique allows the achievement of a peculiar salami-inspired architecture alternating strong and weak interfaces.

Keywords: Ceramic-matrix composites (CMCs); ZrB<sub>2</sub>; Carbon fiber; EPD; Damage tolerance;

## 1 Introduction

Developing both strong and tough materials is a challenge of the materials science since these properties are mutually exclusive, and are simultaneously required for almost all engineering structural materials [1]. Due to this mutual exclusion, stronger and harder materials cannot be used for safety-critical applications where catastrophic failure is unacceptable. At the state of art, the best compromises between the side properties were achieved with metallic glasses, natural and biological materials, and structural and biomimetic ceramics [1]. The above advanced materials have highly complex architectures (*e.g.* hierarchical architectures are shown by biological materials and biomimetic ceramics) where the mechanisms that enhance different properties simultaneously can originate from multiple length scales [2]. Each individual contribute results in composite properties that far exceed those of their constituents and their homogeneous mixtures [2,3]. For example, the micro-architectures of nacre – which can be considered as staggered layers of brittle bricks held together by weak and stretchy mortar – play a key role in providing toughness by various damaging processes including crack deflection, crack bridging, and debonding ahead of the crack tip [4]. The strategies in dealing with strength versus toughness conflict lead to the bioinspired ceramics with 200 MPa of strength and 30 MPa m<sup>1/2</sup> fracture toughness,  $K_{IC}$  [5]. The strategies are more complex in the case of the developing of materials to be used in harsh environments since the fewest number of suitable materials and the impossibility to mimic the brick-and-mortar structure of nacre. Ultra-high temperature ceramics (UHTCs) are a class of ceramic refractory materials interesting for their high melting point (>3200 °C), chemical stability and resistance to erosion and ablation. For this reason, carbides and borides, such as ZrB<sub>2</sub>, TiB<sub>2</sub>, HfB<sub>2</sub>, ZrC, HfC, TaC, are potential candidates components that work in extreme environment condition; thermal protection systems, leading edges in hypersonic flights and nozzles for rockets [6-8]. Among the others, ZrB<sub>2</sub> has the lowest density, high strength-to-weight ratio and good oxidation resistance if combined with carbides such as B<sub>4</sub>C, SiC or metal silicides such as MoSi<sub>2</sub> [8,9]. On the other hand, like the others

UHTCs, it is susceptible to brittle fracture ( $K_{IC} < 5 \text{ MPa m}^{1/2}$ ) and displays low thermal shock resistance. It is well known that monolithic ceramics are not toughened by promoting plasticity, but they can be toughened up to  $10 \text{ MPa m}^{1/2}$  by the frictional interlocking of grains (grain bridging) during intergranular fracture [10]. Since UHTCs cannot exploit *in situ* phase transformations, glassy films, and have not any ferroic order to allow the domains switch at the coercive stress at crack tip, the main strategy to (i) enhance the intergranular fracture [11] rather than the transgranular crack propagation, and (ii) increase the tortuous crack path was the development of large elongated or plate-like grains [12]. In the last years, renewed research efforts improved the damage-tolerance of  $\text{ZrB}_2$  by moving from ceramics to Ceramic Matrix Composites (CMCs). The first CMCs enabled a toughness increase by adding short SiC fibers [13,14], and started a novel class of materials called Ultra-High Temperature Ceramic Matrix Composites (UHTCMCs) [15]. UHTCMCs based on carbon fibers dispersed into  $\text{ZrB}_2$  matrix, can increase the failure tolerant behavior through damage processes ahead of the crack tip, such as crack deflection mechanisms, and behind of the crack tip, such as fiber bridging and fiber pull-out. These mechanisms consume energy during the fracture process, provided that the fiber/matrix interface is well designed and the chemical reactions at the fiber/matrix interface do not degrade the reinforcement properties [1,14,16,17]. By optimizing the production process to achieve an homogeneous dispersion of the UHTC matrix into the fiber preform, a good densification level and a good fiber/matrix adhesion avoiding fiber degradation, the toughness was increased up to  $10 \text{ MPa m}^{1/2}$  while keeping a flexural strength of 85 - 95 MPa [15,18]. The high amount, 65 – 70 %, of well dispersed fibers, the low crack resistance of the fiber/matrix interfaces, and the weak matrix allowed the easy fiber pull-out, delamination, fiber bridging, and hence led to a non-brittle fracture [18]. In these weak matrix composites (WMCs) the matrix is subjected to multiple cracking whilst the fibers provide strength and crack tolerance, in this way after the matrix is completely fractured by multiple microcracking, the total fracture occurs with the failure of the fibers [18]. A further development for UHTCMCs in terms of toughness can be borrowed from strategy behind the solution-polymerized acrylonitrile-

butadiene-styrene (ABS): the salami-like particles [19,20]. The dispersed salami-like particles consist in polybutadiene particles (PB) grafted (-g-) by acrylonitrile-styrene copolymer (SAN). The PB rubber particles, in the PB-g-SAN binary phase system, are characterized by a strong residual stress that facilitates the crazing and shearing, reducing the stresses on the crack wake. Thus, the concept of the salami-like particles is that of increasing the extrinsic crack-tip-shielding mechanisms that act behind the crack tip to inhibit its propagation. In the UHTCMCs, the corresponding microstructural features playing a similar role can be the load-bearing fibers, having a non-uniform distribution, and being concentrated in bundles where the fiber density increases at the outer periphery. Such graded structure, similar to the fiber distribution in a bamboo structure, should also enhance the specific flexural rigidity [2]. Hence, the aimed scenario is the promoting of extensive microcracking ahead of the crack tip, primarily between the bundles (in other words, along the weak matrix), which leaves uncracked-bundle bridges (the cross section should be appear like a slice of salami). The uncracked-bundle bridges (as the crazing and shearing phenomena activated by the salami-like particles [19,20]) will act as intact regions spanning the crack wake to inhibit its progress by further microcracking inside the bundles and crack deflection along the transverse orientation to the main fracture surface. At the end of the fracture processes, the salami-inspired UHTCMCs should fail under bundle pull-out mode.

In this work, Electrophoretic Deposition (EPD) technique was implemented into the conventional process for CMCs [18] in order to obtain a salami-inspired structure of UHTCMCs based on continuous carbon fibers. Even if EPD provides extraordinary control of nano- or microstructure of single- or multi-ceramics coatings and their adhesion/robustness [21], to the best of our knowledge, no one has deposited UHTC coatings on carbon fibers by EPD. The novel UHTCMC microstructure was developed and mechanically characterized in view of the above aimed scenario.

## **2 Material and methods**

### **2.1 EPD process**

EPD trials were performed in plane-parallel cell geometry and cathodic modality, keeping the electrodes 9 mm apart and applying constant DC potentials. Carbon fibers, C<sub>f</sub> (Granoc XN80-6K) were treated in a tubular furnace (Nabertherm, Germany) in order to remove the size agent, and machined as unidirectional fabrics. These C<sub>f</sub> plates were dipped in an ethanol-based colloidal suspension at 2 wt% of commercial ZrB<sub>2</sub> powder (H.C. Starck, grade B, Germany), and coated by applying an electric field of 11.1 V/cm for 100 s.

### **2.2 Slurry preparation, infiltration, and thermal treatment**

The ZrB<sub>2</sub> powder was mixed with 5 vol% of B<sub>4</sub>C (H.C. Starck, Grade HS, Germany), and dispersed in aqueous solution with a polyacrylate (PEI, Sigma-Aldrich- 50% (m/v) in H<sub>2</sub>O) by ball-milling in a polyethylene bottle with SiC balls for 3 hours. The UHTCMCs were fabricated by impregnating the coated unidirectional fabrics with the slurry, and subsequently stacking 8 layers in a unidirectional configuration. Vacuum-bagging in a furnace at 90 °C for 1 hour, was used to consolidate the green composite. Sintering was conducted in a hot uniaxial pressing at 40 MPa in low vacuum using an induction-heated graphite die of 30 x 30 mm. Cycles were carried out at 1900 °C for 10 minutes.

### **2.3 Microstructure and mechanical characterization**

The bulk densities were measured by Archimedes' method. The microstructures were analyzed with Field-Emission Scanning Electron Microscopy (FESEM, mod. SigmaCarl Zeiss NTS GmbH Oberkochen, Germany) coupled with Energy-Dispersive X-ray Spectroscopy (EDXS, mod. INCA energy 300; Oxford instruments, High Wycombe, UK). 4-pt flexural strength ( $\sigma$ ), and flexural modulus of elasticity ( $E$ ) at room temperature were measured on 25 x 2.5 x 2 mm<sup>3</sup> (length x width x thickness, respectively) bars, using a crosshead speed of 1 mm/min on Zwick-

Roell Z050 testing machine. Fracture toughness ( $K_{IC}$ ) was evaluated by fracturing chevron notched beams (CNB) in 4-pt bending configuration. The specimens were loaded with a crosshead speed of 0.05 mm/min. The test bars (25 mm  $\times$  2 mm  $\times$  2.5 mm, length  $\times$  width  $\times$  thickness) were notched with a 0.1 mm-thick diamond saw, and fractured using a fully-articulated steel four-point fixture with a lower span of 20 mm and an upper span of 10 mm using a screw-driven load frame (Instron, 6025).

### 3. Result and discussion

#### 3.1 EPD microstructure

The EPD technique resulted in a green  $ZrB_2$  layer that covered the entire length of the unidirectional carbon fabrics (Fig.1 (a)). The coating was crack-free and consisted of particles smaller than 4  $\mu\text{m}$  (inset in Fig.1 (a)). Through the polished cross section shown in Fig.1 (b), it can be seen that the EPD produced an external thick  $ZrB_2$  layer of 15-20  $\mu\text{m}$  where the particles were well packed to each other and well stuck to the  $C_f$  surface (inset in Fig.1(b)). The inner fibers ( $\sim$ 40  $\mu\text{m}$  far from the external layer) generally showed a discontinuous coating. Due to the high “sticking parameter” [22], particles took part in the formation of the deposit until forming a coating of about 3  $\mu\text{m}$ . This thickness was measured on the isolated external fibers, such as those highlighted by the arrows in Fig.1 (b). Those can be considered as isolated fibers dipped into the bulk suspension. Hence if the span between two close fibers is smaller than 6  $\mu\text{m}$  it will be closed during the EPD process by the particles that arrive from the bulk of the suspension. When all the spans (ideally) perpendicular to applied electric field are filled, and the adjacent joined fibers form a continuous wall, the particles from the bulk of suspension cannot penetrate further into the fabric and further increase the external coating which grows up to 15-20  $\mu\text{m}$ . In Fig.1 (b) it can be seen that the core of the fabric is isolated from the bulk suspension after the fifth layer of  $C_f$  (statistically there is a span smaller than 6  $\mu\text{m}$  between the first five layers) and the inner fibers are coated by few particles. Such stuck particles should be the starting 2 vol% of dispersed particles into the liquid media that infiltrates the unidirectional

fabric before the EPD process. The external layer can be addressed as the gut of those that will be the salami: the dispersed bundles of  $C_f$  into the UHTC matrix. This external layer should give rise to a good adhesion between the  $C_f$  bundles and the  $ZrB_2$  matrix as the covalently bonded grafted PB-g-SAN salami-like particles [19]. Another important feature of the coated fabric is the resulted density gradient of parallel  $C_f$  between the external and the core of the fabric. It is worth to notice that fiber density is higher at the outer periphery.

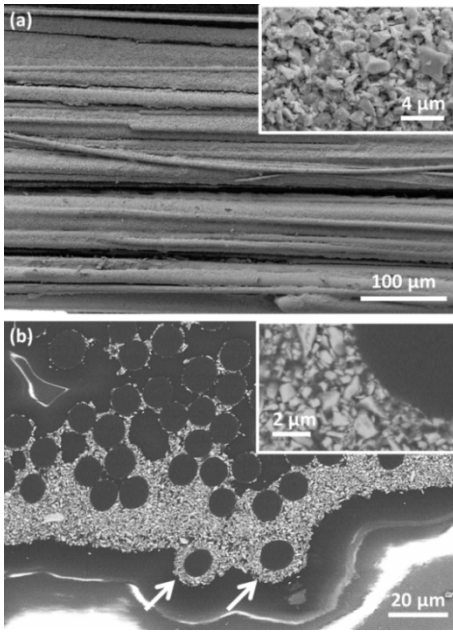


Fig.1 SEM images of dried electrophoretic deposited  $ZrB_2$  layer on the unidirectional fabric: (a) external surface, and (b) polished cross section.

### 3.2 Sintered microstructure

After sintering, a fully dense microstructure was achieved (Fig.2) with a relative density of 4.1  $g/cm^3$ . Only few triple and quadruple points between  $C_f$  were not filled during the slurry infiltration and remained after sintering, leaving 2.1 vol% of pores. The dark area within the  $ZrB_2$  matrix (the gray area in Fig.2 (b)) are  $B_4C$  grains which are characterized by lower density, 2.5  $g/cm^3$ , compared to the  $ZrB_2$  (6.1  $g/cm^3$ ). The presence of  $B_4C$  particles in the  $ZrB_2$ -based slurry used to impregnate the fibers after EPD allowed us to distinguish EPD  $ZrB_2$  from  $ZrB_2$ - $B_4C$  matrix (see Fig. 2 b). In the sintered material, we can recognize the individual bundles

circumvented by about 15  $\mu\text{m}$  of EPD  $\text{B}_4\text{C}$ -free  $\text{ZrB}_2$ , immersed in the  $\text{ZrB}_2$ - $\text{B}_4\text{C}$  matrix. Hence, the EPD favored the formation of a discrete distribution of fiber bundles inside the matrix. Furthermore it can be noticed that the  $\text{C}_f$  density is higher in the bundle periphery than in its center and, in the former, the fiber/matrix interfaces show jagged profiles (Fig.2 (c)). Since there are no evidences of interdiffusion or chemical reaction between matrix and  $\text{C}_f$ , the jagged profile should be due to the mechanical stresses that appear during the sintering process. We hypothesize that during the densification the shrinkage of  $\text{ZrB}_2$  grains induces compressive stress into the  $\text{C}_f$  that is equilibrated by the tensile stress produced into the  $\text{ZrB}_2$  grains around. These stresses act into concentric lines around the fiber circumference and parallel to the fiber axis, and can be released under the effect of radial shear stresses. The latter make the  $\text{C}_f$  planes slide, allowing carbon flow outward and  $\text{ZrB}_2$  grains penetration inward. The resulting interlocking thickness (Fig.2 (b)) between  $\text{ZrB}_2$  grains and  $\text{C}_f$  is more pronounced in the external carbon fibers layer, where the driving force for the  $\text{ZrB}_2$  shrinkage is larger. This strong interface should guarantee the desired good adhesion between the  $\text{C}_f$  bundles and the  $\text{ZrB}_2$  matrix.



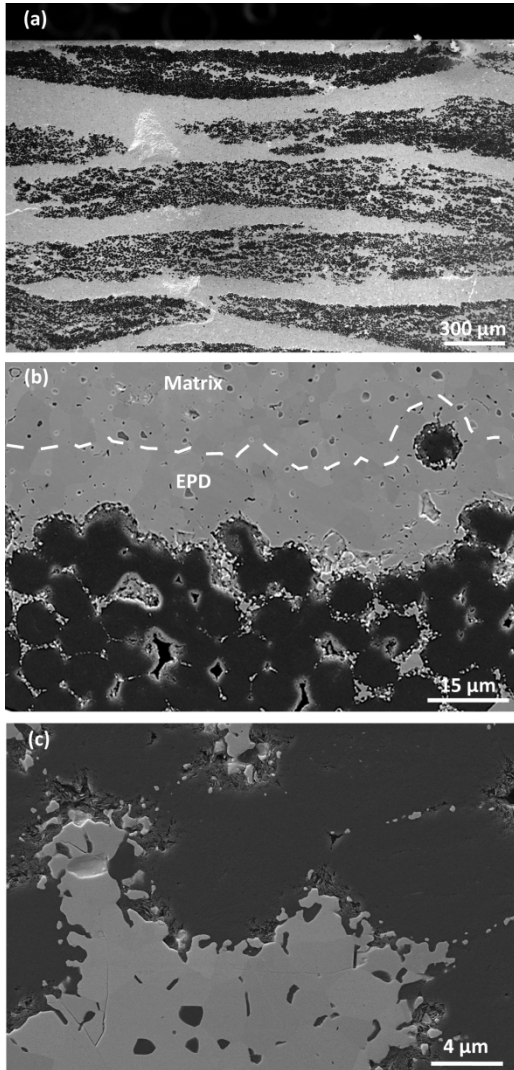


Fig.2 SEM micrograph of cross section of UHTCMC based on carbon fiber and  $ZrB_2/B_4C$  matrix.

### 3.3 Mechanical properties

The typical load-displacement curves are shown in Fig.3 together with the Work of Fracture (WoF) values (the area underlying the load-displacement curve divided by the doubled of the projected real surface). The average flexural strength of  $284 \pm 40$  MPa can be ascribed to the jagged matrix/fabrics interfaces, and to higher  $C_f$  density at the outer bundles periphery. The former allows a good mechanical coupling between the matrix and the bundles, the latter allows a good stress distribution since the  $C_f$  are more concentrated where the stress is larger. These

phenomena can be considered similar to what occurs in the bamboo plants where the not uniform distribution of the load-bearing fibers enables a more effective and homogeneous stress distribution [2]. It is worth to notice that the maximum flexural strength is still lower than the theoretical value of the side phases. This issue is common for the UHTCMCs and may be due to different reasons such as: tensile residual stress in the matrix due to CTE mismatch with the  $C_f$  [23,24], and no perfect alignment of the fibers. The small load drops on the load–displacement curves before the maximum flexural stress can be addressed to delaminations [25,26]. Thus, the shear or local effects which lead to delamination may be the onset cause that will leads to failure. It is likely that delamination starts inside the carbon fabric where the  $C_f/ZrB_2$  and  $C_f/C_f$  interfaces are characterized by lower interlaminar shear strength.

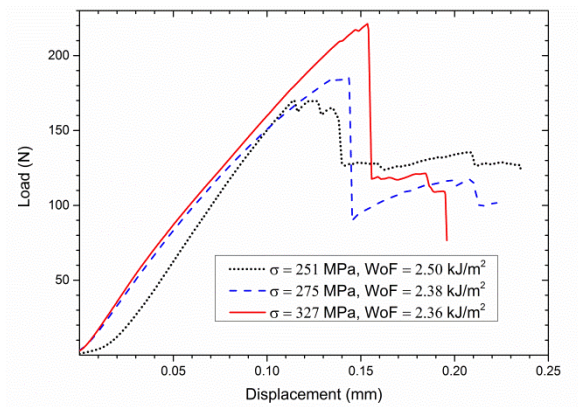


Fig.3 Load-displacement curves of 4 pt. for three different bars. The flexural strength ( $\sigma$ ) and adsorbed energy (WoF) for each bar is reported.

In order to gain insight into the damage mechanisms occurring during flexural loading, SEM micrographs were taken after failure (Fig.4). Interfacial damage and matrix cohesive damage phenomena can be both observed. The cracks deflect inside the bundles and close to the strong matrix/ $C_f$  interface. The highly cohesive strength between fibers and matrix prevents the cracks from propagating linearly along their initial directions. The cracks turn to the adjacent layer boundary into the bundles and continue to develop. The resulting crack path is highly tortuous and formed by multiple cracks spread between the layers. This fracture development produces

only partial delamination for each layer. This damage mode can sustain further loading, since the  $C_f$  inside the bundle stumps remain constrained, and should absorb more energy with consequent improvement in strength and toughness. In a similar way, the grafted PB domains cause an increase of the required fracture energy by facilitating crazing and shearing at the crack tip, and forming fibrils that act on the crack wake [19]. Hence, we think that this salami-inspired architecture on one hand allows a good stress distribution due to the  $C_f$  density gradient from inner to outer periphery of bundles. On the other side, the combination of strong (jagged) outer and (weak) inner interfaces prevents both the brittle failure of composites due to strong phases bonding and the easy interfacial debonding under low loading, in case of too weak interfaces. The fracture energy of  $2.41 \pm 0.08 \text{ kJ/m}^2$  is higher than that shown by similar materials (about  $0.1 \text{ kJ/m}^2$  [27]). The WoF decreases down to  $1.4 \text{ kJ/m}^2$  if it is calculated from the load-displacement curves of CNB (Fig.5), due to the stress concentration at the notch. Nevertheless, this value is still one order of magnitude larger than those shown by similar materials.

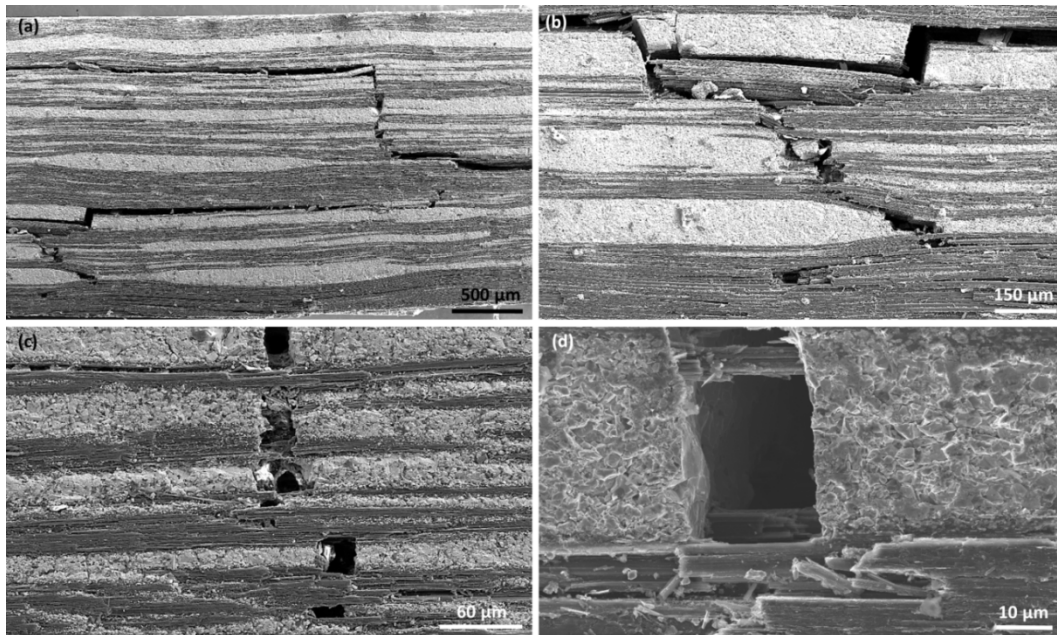


Fig.4 SEM images of failed composites under flexural loading.

The increase in fracture energy matches the increase of toughness to about  $11 \pm 2.5 \text{ MPa m}^{1/2}$  (Fig.5). In fact, as a general rule, cracks do not easily propagate in a material characterized by a

high WoF. As seen above, the strong jagged interface between matrix and  $C_f$  acts as hindrance for the crack propagation. The crack may be stopped at that interface and activates further toughening mechanisms such as microcracking inside the bundles - where the  $C_f/C_f$  and  $C_f/ZrB_2$  are characterized by a lower interfacial strength - and the consecutive crack deflection and propagation along the perpendicular direction. Crack deflection at the weaker interfaces is similar to what occurs in the bioinspired nacre-like composites where a weakness point is needed to fully activate the toughening mechanisms and induces the crack propagation parallel to long axis of platelet ( $C_f$  in our case) [1]. In our opinion, such an intricate microstructure gives rise to further toughening mechanisms during fracture including friction and interlocking of entire bundles of  $C_f$ , and the pull-out of single  $C_f$  from the same bundles.

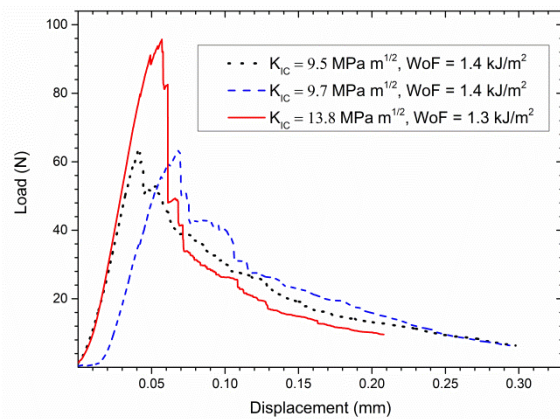


Fig.5 Load-displacement curves of 4 pt. fracture for three different chevron notched beams (CNB). The fracture toughness ( $K_{IC}$ ) and adsorbed energy (WoF) for each CNB is reported.

From the fracture surface of CNB specimens that exhibit the lowest and highest fracture toughness ( $9.5 \text{ MPa m}^{1/2}$  (Fig.6 (a)-(c)), and  $13.8 \text{ MPa m}^{1/2}$  (Fig.6 (d)-(f)), respectively), it is possible to make some qualitative considerations about the different toughening mechanisms. In both samples the matrix between the fabrics shows a brittle behaviour and the cleavage fracture is quite flat. The crack likely propagates through the matrix with a transgranular mode. In contrast, the volumetric shuffling of the material inside the fabrics is the consequence of the

crack deflections. It is worth to remember that crack deflection is triggered inside the fabrics by the process zone at the crack tip. Thus the weak interfacial resistance between  $C_f/C_f$  and  $C_f/ZrB_2$  (that characterized by a low  $ZrB_2/C_f$  ratio) inside the fabrics is necessary to take full advantage of the toughening mechanisms. The extensive delamination parallel to the  $C_f$  and the propagation of the crack mainly through the matrix leave uncracked-bundles bridges. These bridges should act as intact regions spanning the crack wake to inhibit its progress by further microcracking inside the bundles, and crack deflection along the transverse orientation to the main fracture surface. At the end of the fracture processes, the salami-inspired UHTCMCs should fail under bundle pull-out mode. Some of the footprints leaved by the pull-out of the so called salami are pointed by the white arrows in the Fig.6. In Fig.6 (f) it is clearer how their cross section appears like a slice of salami. In particular, in Fig.6 (f), it can be seen that the strong jagged interface of the fabrics is broken at the same level of the matrix, proving the good stress transmission across these strong interfaces. Moreover, it suggests that the inelastic energy dissipation through the friction interactions during the pull-out of the salami occurs at the weaker interface inside the fabrics. Based on the above discussion, it is reasonable to address the higher  $K_{IC}$  value as due to the higher amount of the footprints left from the pull-out of the salami bundles. The deep holes left by the salami pull-out can be justified by adapting the Kelly-Tyson model [28]:

$$l_c = \frac{\sigma r}{\tau} \quad (1)$$

where  $l_c$  is the critical length and corresponds to the lengths/depth of the fragments/hole formed after the pull-out.  $\sigma$  is the flexural stress of the salami (the EPD  $C_f$  fabrics),  $r$  is the equivalent radius of the projected area of the salami (the footprints leaved by its pull-out), and  $\tau$  is shear stress at the weaker  $C_f/C_f$  or  $C_f/ZrB_2$  interphases. From the Eq.1 it is clear that the pull-out of a bundle of  $C_f$ , due to the weak interphases strength (small  $\tau$ ) and large area ( $r$ ), brings to large value of  $l_c$ , and thus dissipates a large amount of inelastic energy. On the other hand, the pull-out of the single  $C_f$  embedded in the matrix is characterized by a small  $l_c$ , about 10  $\mu m$  (Fig.6

(c)). In any case, the interface debonding did not occur at the strong (jagged) interface, but inside the fiber between weakly bonded inner layers. As it can be seen in Fig.6 (e),  $l_c$  of the single pulled-out carbon fibers inside the fabrics are one order of magnitude larger than those embedded in the matrix. In fact, as said above, the interlocking thickness (*i.e.* the value of  $\tau$ ) between  $ZrB_2$  grains and  $C_f$  is larger along the external matrix/fabric interface rather than  $ZrB_2/C_f$  interfaces inside the fabrics.

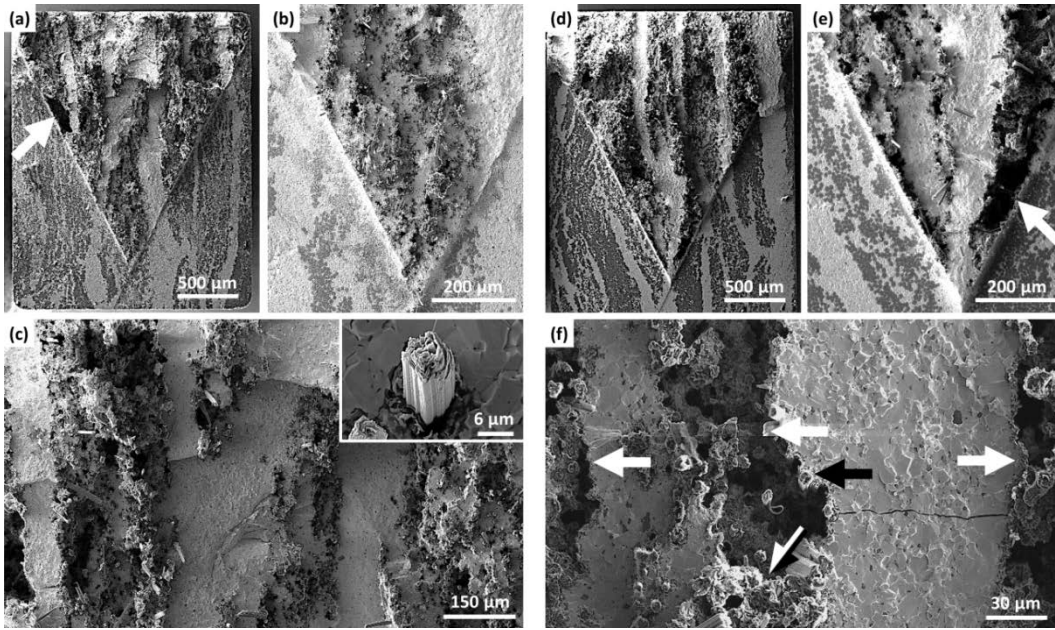


Fig.6 Transversal SEM images of failed CNB under flexural loading. (a)-(c) and (d)-(f) correspond to dotted line ( $K_{IC} = 9.5 \text{ MPa m}^{1/2}$ ) and solid line ( $K_{IC} = 13.8 \text{ MPa m}^{1/2}$ ) in Fig.5, respectively. The white arrows point some of the footprints left by the pull-out of the so called salami. The black arrow and the black and white one point a strong jagged matrix/fabric interface and a weak  $C_f/C_f$  interface, respectively.

In Fig.7 a sketch of the toughening mechanisms produced by the (a) salami-inspired  $C_f/ZrB_2$  UHTCMCs and (b) salami-like particles is drawn. The red line represents the crack pathway. It can be seen how, for both the ceramic (Fig.7 (a)) and polymeric (Fig.7 (b)) composites, the crack tortuosity can be enhanced by microcracking and crack deflection ahead of the crack tip. For this goal, first of all, a strong mechanical coupling between the matrix and the

reinforcement phase is required, as the jagged interfaces and the grafting for  $C_f/ZrB_2$  UHTCMCs and PB-g-SAN, respectively. Then, the good stress distribution should allow the activation of toughening mechanisms inside the reinforcement phase, such as delamination and crazing. These crack pathways leave entire parts of the reinforcement components like the uncracked-bundle bridges for the salami-inspired composites (the cross section appears like a slice of salami), and rubber fibrils for the salami-like particles dispersed in the polystyrene matrix. These latter components give the larger extrinsic contribution that act behind the crack tip and inhibit its propagation.

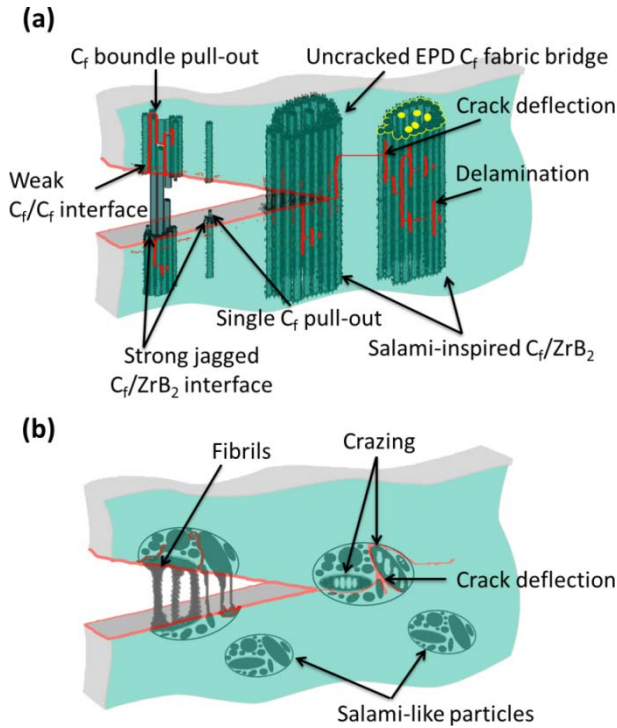


Fig.7 Sketch of the toughening mechanisms produced by the (a) salami-inspired  $C_f/ZrB_2$  UHTCMCs and (b) salami-like particles. The red line and the yellow one represent the crack pathway and the cross section of a salami-inspired reinforcement, respectively.

The resulting damage tolerance,  $c$ , according with the Irwin equation:

$$c = \frac{K_{IC}^2}{\pi \sigma^2} \quad (2)$$

is  $473 \pm 89 \mu\text{m}$ . This value is significantly higher than that of the conventional ceramics of about  $0.1\text{--}1 \mu\text{m}$  [29] and  $\text{ZrB}_2$ -based ceramics of about  $6 \mu\text{m}$  considering typical values of strength ( $\sim 800 \text{ MPa}$  and toughness  $3.5 \text{ MPa m}^{1/2}$  [6]), and approaches the lower bound of the engineering metals (Fig.8). These results suggest that salami-inspired UHTCMCs can be exploited in order to overcome the mutual exclusive properties of strength and toughness and allow to develop strong fiber reinforced ceramic composites with a high resistance catastrophic failure. Finally, although comparison with results available in the literature could be unreliable due to different preforms/matrix composition/process/measurement techniques, it is worthy to notice that our values of strength and toughness are well in agreement with those obtained for other UHTCMCs mostly obtained through enrichment of C/SiC matrix with the UHTC phase [30-32].

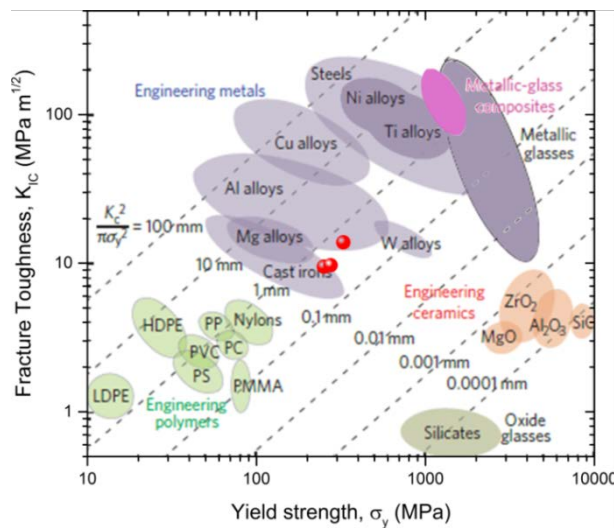


Fig.8 Data of fracture toughness (Fig.5) vs. flexural strength (Fig.3) plotted as red spheres on Ashby map redrawn from ref. [29]. The different levels of damage tolerance are marked with the dotted lines.

## Conclusions

Ultrahigh temperature ceramic matrix composites, based on unidirectional carbon fibers dispersed in a  $\text{ZrB}_2$  based matrix were produced by a first  $\text{ZrB}_2$  coating of the carbon fabrics by electrophoretic deposition followed by slurry impregnation and densification at  $1900 \text{ }^\circ\text{C}$ . The



resulting microstructure consists in electrophoretic coated fabrics dispersed in a fully dense ZrB<sub>2</sub> matrix. The fabrics are characterized by a functionally graded concentration of fibers that is higher at the outer periphery and where the bonding of the fibers with the sintered matrix is strong. The effect of such substructures obtained by EPD was assimilated to that of the salami-like particles in the PB-g-SAN polymer. The salami-inspired bundles increase flexural strength ( $\sigma = 327$  MPa) and enhances the extrinsic crack-tip-shielding mechanisms leading to very high fracture toughness ( $K_{IC} = 13.8$  MPa m<sup>1/2</sup>). The unusual combination of low density ( $\rho = 4.5$  g/cm<sup>3</sup>), strength and high resistance against fracture allows the production of UHTCMC with high damage tolerance ( $c = 570$   $\mu$ m) that can improve the structural component for aerospace applications. Finally, results indicate that the combination of too strong (jagged) outer interfaces and too weak (inner) interfaces can be exploited as an alternative method to achieve an overall ideal weak fiber/matrix interface.

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