Effect of a weak fiber interface coating in ZrB₂ reinforced with long SiC fibers

Laura Silvestroni^{1*}, Diletta Sciti¹, Greg E. Hilmas², William G. Fahrenholtz², Jeremy Watts²

¹*CNR-ISTEC, Institute of Science and Technology for Ceramics, Via Granarolo 64, I-48018 Faenza, Italy*

²*Department of Materials Science and Engineering, Missouri University of Science and Technology, Rolla, MO 65409*

ABSTRACT

This study reports the microstructural analysis and mechanical properties of a ZrB₂ ceramic containing long BN-coated Hi-Nicalon SiC fibers. A composite was produced and thoroughly characterized by transmission electron microscopy to study the interfaces at the nanoscale level. Full densification was accomplished by hot pressing at 1450°C. The fiber in the sintered material retained its pristine aspect, confirming that the coating was effective in preventing degradation due to interactions with the matrix. Pull-out was observed on fractured surfaces, but toughness values were about 4.5 MPaVm, which was comparable to those of ZrB₂ materials with SiC additions in the form of particles or short fibers. However, the composites exhibited a controlled fracture behavior, as confirmed by a notably higher work of fracture, 140 J/m², compared to 20-30 J/m² of unreinforced ZrB₂ or ZrB₂ containing chopped fibers.

Keywords: ZrB₂; fibres; Ceramic-matrix composites (CMCs); transmission electron microscopy; fracture toughness.

1. Introduction

The need for materials able to operate at ever increasing temperatures and for long times, encourages the scientific research of material systems capable of operating in these demanding environments. Components of hypersonic vehicles are exposed to significant heat fluxes as well as aerodynamic and mechanical loads [1]. Therefore, the main requirements that a material for such applications should satisfy are refractoriness at high temperature in oxidizing environments along with

* Corresponding author: Laura Silvestroni
telephone: +39 546 699723
fax: +39 546 46381
e-mail: laura.silvestroni@istec.cnr.it

sufficient mechanical strength and toughness. Ultra-high temperature ceramics (UHTCs), including borides and carbides of transition metals in group IV-V, have been identified as potential candidates for operating in harsh conditions owing to melting points exceeding 3000°C and resistance to ablation [2,3]. Crucial issues for use of UHTCs in severe environments are their low fracture toughness and thermal shock resistance. To overcome these limits, research has focused on fabrication of ZrB₂-based ceramics containing short SiC or C fibers [4-6] and, more recently, the processing of UHTCs reinforced with long fibers has been undertaken [7-10].

When dealing with materials production, the balance between process effort and resulting thermo-mechanical performances is fundamental for industrial applications. Likewise, the debate between the use of short or continuous reinforcement for UHTCs is still open, but studies on the processing and properties of long fiber-containing UHTCs are scarce [7-9]. Evidence demonstrating which route is more effective to obtain the necessary toughness, or more broadly, a set of reliable mechanical properties, is paramount for the development of future advanced composites.

Previous investigations demonstrated that the introduction of up to 40 vol% short Hi-Nicalon or Tyranno SA3 SiC fibers improved the fracture toughness of ZrB₂ [4,5,10], without notably modifying the oxidation properties [11]. However, a toughness plateau was reached after additions in the range of 10 to 30 vol% of short fibers. An alternative strategy to improve the damage tolerance of ZrB₂ could be the use of a weak interphase coating between fiber and matrix or the use of continuous reinforcements.

In this study, a ZrB₂-based composite containing BN-coated long Hi-Nicalon fiber with a 0/90° composite architecture was produced and characterized to test the potential of a UHTC-based ceramic matrix composite (CMC). The coating used throughout this study was Si-doped BN, but will be referred to as simply BN. ZrSi₂ was used as sintering additive, owing to its low melting point enabling densification of ZrB₂ at temperatures right above 1400°C [2,4,5]. Aware of the fact that this silicide is not the best candidate for high temperature applications, we deliberately did not use more refractory silicides, like MoSi₂ or WSi₂, as they promote densification at temperature above 1750°C [2] which could be fatal for preserving the fiber integrity. This study thus explores the effect of starting fiber type on the matrix densification,

fiber/matrix interface and fracture mode behavior. Transmission electron microscopy was used to reveal the microstructure modifications of fibers at the nanoscale level and evaluate the fiber/matrix characteristics.

2. Experimental procedure

A ZrB₂ ceramic composite containing 10 vol% of ZrSi₂ and 25 vol% of long SiC fibers was produced using the following commercial products: ZrB₂ (H.C. Starck, grade B, Germany), specific surface area: 1.0 m²/g, particle size range: 0.1-8 μm, impurities (wt%): C 0.25, O 2, N 0.25, Fe 0.1, Hf 0.2; ZrSi₂ (Japan New Metals Co., LTD, **grade F**, Japan), particle size range: 2-5 μm, impurities (wt%): C 0.15, Fe 0.30, 1.00 O; BN-coated Hi-Nicalon SiC fiber (COI Ceramics Inc., Magna, UT) with a nominal diameter of 15 μm and composition (wt%) Si:C:O= 63.7:35.8:0.5. Prior to mixing, ZrB₂ and ZrSi₂ powders were separately treated in a polymer-coated steel attritor mill with SiC milling media for 2 hours at 500 rpm in acetone to reduce their mean particle sizes. The process for making the composite followed the slurry infiltration method generally used for making fiber-reinforced glass and glass-ceramic composite [12], which consists of winding a slurry impregnated yarn onto a mandrel to form mono-layer tapes as illustrated in Fig. 1a. A viscous slurry was obtained by mixing the powders in solvent consisting of ethanol and methyl ethyl ketone (MEK) with a dispersant (BYK-110, BYK, Wesel, Germany), binder (PVB B79, Maroon Inc., Avon, OH) as binder and a mixture of plasticizers (S-160, Ferro, Walton Hills, OH, and PEG-400, Fisher Scientific, Fair Lawn). The monolayer tapes were cut up to produce plies and then stacked and densified to form the final composite preform in a laminating operation. A schematic of the fiber spool coating process with the ZrB₂-ZrSi₂ slurry and following lamination and sintering is displayed in Fig. 1a and further details on the experimental procedure are provided in [13].

The layup was then loaded into a graphite die and placed in the hot press (HP20-3060-20, Thermal Technology, Santa Rosa, CA). Binder removal was conducted by heating under vacuum (~20 Pa) to 600°C with no applied pressure. The atmosphere was then changed to argon, a uniaxial load of 32 MPa was applied and the furnace was ramped to the sintering temperature at ~25°C/min. The maximum sintering

temperature was set to 1450°C on the basis of previous analysis of shrinkage curves. After 40 min at the sintering temperature, the furnace power was turned off and the specimen was allowed to cool naturally.

The bulk density was measured by Archimedes' method and confirmed by examination of polished cross section. The microstructure was first analysed on fractured and polished surfaces using scanning electron microscopy (FE-SEM, Carl Zeiss Sigma NTS GmbH, Oberkochen, DE). Then a specimen for transmission electron microscopy (TEM) was prepared by cutting a 3 mm disc from the bulk of the sintered pellet. The specimen was mechanically ground to a thickness of about 20 µm and then further thinned by ion beam milling until perforations were observed by optical microscopy. Local phase analysis was performed using TEM (FEI Tecnai F20 ST, Hillsboro, USA) equipped with a Schottky emitter and operating at a nominal voltage of 200 keV, combined with an energy dispersive X-ray spectrometer (EDS; EDAX PV9761/II) that was cooled with liquid nitrogen and equipped with a super ultra-thin window. Scanning Transmission Electron Microscopy (STEM) measurements were also performed with the same TEM in nanoprobe mode providing a point resolution 0.19 nm.

The fracture toughness (K_{Ic}) was evaluated by fracturing chevron notched beams (CNB) in flexure. The test bars were 45 mm x 3 mm x 4 mm (length by width by thickness, respectively) and were notched with a 0.1 mm-thick diamond saw; the chevron-notch tip depth and average side length were about 0.12 and 0.80 of the bar thickness, respectively. The direction of testing is sketched in Fig. 1b. The specimens were fractured using a fully-articulated steel four-point fixture with a lower span of 40 mm and an upper span of 20 mm using a screw-driven load frame (Instron, 6025). Three specimens were loaded with a crosshead speed of 0.05 mm/min. The "slice model" equation of Munz et al. [14] was used to calculate K_{Ic} . Five additional composite specimens were also tested according to ASTM C1421 using a similar, fully articulated four-point fixture at a cross head rate of 0.03 mm/min (Instron mod. 5881). The work of fracture (WOF) was also calculated for the each fracture toughness specimen. The total work was determined by measuring the area under the load deflection curve. The WOF was calculated by dividing the total work by the new surface area produced by fracture (twice the cross sectional area of the chevron portion of the toughness specimens). The room temperature flexural strength (σ_{RT}) was measured

according to the European standard EN 843-1 by fracturing five chamfered bars that were cut along each of the major axes of each composite billet. The bars had dimensions of 25 mm × 2.5 mm × 2 mm (length by width by thickness, respectively).

3. Results

3.1 Microstructural features

Hot pressing at 1450°C was sufficient to fully densify this composite. For comparison, this is 100°C lower than for other $\text{ZrB}_2\text{-ZrSi}_2\text{-SiC}_f$ composites produced with short fibers by conventional ball milling and hot pressing, Table 1 [5,11]. The lower densification temperature is likely due to the use of a finer ZrB_2 powder (mean particle size $\sim 2.1\ \mu\text{m}$) than the previous study (mean particle size $\sim 3.3\ \mu\text{m}$).

The fracture surface of this composite is displayed in Fig. 2a and shows fiber pull-out, which can be an indication of improved toughness. An overview at low magnification of the composite is shown in Fig. 2b, which shows the 0/90° lay-up and confirms that the slurry was able to completely infiltrate the fiber tows with no apparent macrodefects. Away from the fibers, the matrix appears to be fully dense, but contains a high volume fraction of ZrO_2 , Fig. 2c, probably resulting from prolonged exposure to air during processing. No free Si was found, but areas of dendritic SiC and Si-O phases were observed as shown in the inset in Fig. 2c. In addition, microcracking was frequently observed, especially around fibers. Close to the fibers, some porosity was also observed, Fig. 2d. The BN coating survived the processing. The coatings were continuous around each fiber with a thickness of approximately 400 nm, which prevented any interaction between fiber and matrix or sintering additive, Fig. 2e,f.

TEM images collected from the matrix confirmed the presence of ZrO_2 and revealed that the SiO_2 was crystalline, Fig. 3a,b. The grain boundaries in these regions generally appeared to be free of any amorphous phases, Fig. 3b,c. However, amorphous SiO_2 was also found trapped among ZrB_2 and ZrO_2 grains. In addition, the amorphous SiO_2 also contained traces of nitrogen, Fig. 3d-f, probably deriving from dissolution of some of the fiber coating into the glassy phase.

The fiber coating morphology in the composite was investigated by TEM analysis in Fig. 4. The coating had a homogeneous thickness and was composed of BN with scattered dark particles identified as Si_3N_4 and Si-C-B-N-O, Fig. 4c-e. High resolution TEM images of the interfaces between coating and matrix, and between coating and fiber, are reported in Fig. 5. It can be observed that the interface between coating and matrix is sharp and clean, Fig. 5a-c, while an amorphous phase is present at the boundary between fiber and coating, Fig. 5d-f. STEM analyses performed at the fiber-coating interface, Fig. 6, confirmed that Zr had not diffused through the coating or into the fiber. In contrast, Si and C were detected in the coating and oxygen enrichment was observed in the fiber close to the coating, indicating that even though new phases did not form, some diffusion of Si and C species had occurred. Fig. 7 shows the microstructure of the fiber. Comparing the center and the periphery, it is shown that SiC crystallites did not coarsen notably as no significant differences in mean grain size was measured. However, a higher quantity of amorphous phase could be seen in the center, Fig. 7a,c, as compared to the outer zone, Fig. 7b.

3.3 Mechanical properties

The mechanical properties for the ZrB_2 ceramic with long SiC fibers investigated in the present study are summarized in Table I together with some properties of analogous ZrB_2 composites containing various kinds of short SiC fibers previously analyzed [5,11].

The toughness of the composite measured by the slice method was 4.5 MPa $\sqrt{\text{m}}$, which is similar to conventional ZrB_2 -SiC ceramics, but lower than composites containing a discontinuous reinforcement that range from 5 to 6 MPa $\sqrt{\text{m}}$. However, when measured according to ASTM 1421, the toughness was 6.4 MPa $\sqrt{\text{m}}$, which correlates to the upper end of the range of toughness reported for discontinuous reinforcements. A typical load displacement curve for a composite is displayed in Fig. 8. The failure is characteristic of damage-tolerant ceramics. Hence it is reasonable to hypothesize that the composite toughness should be higher than conventional ceramics. One complication with testing the fracture toughness of these types of composites is that the crack paths deflect around and along the reinforcing fibers, which means the crack is no longer traveling in Mode I. As such, calculating K_{Ic} from such tests may

not be meaningful. Instead, calculation of the work of fracture may give a more reasonable estimate of the damage tolerance of the composite. While the K_{Ic} values measured by the slice method were lower than those measured by the ASTM method, the slice measurements exhibited a higher inelastic response and, therefore, a higher total WOF, Table I. This is likely due to the difference in strain rates of the two methods. Regardless of test method, the long fiber containing samples exhibited both total and inelastic WOF values that were more than three times those measured for short fiber composites. The inelastic WOF is a measure of the amount of energy required to propagate a crack after it has been initiated. Thus, while not a measure of K_{Ic} , the higher inelastic WOF indicates that the continuous fiber composites are more resistant to catastrophic failure than other ZrB₂-based ceramics or composites.

The strength values were about 190 MPa for bars cut in the A direction and 130 MPa for bars cut in the B direction, which is comparable to values obtained for other long-fiber reinforced CMCs [15]. Interestingly, higher strength values were associated with specimens that fractured completely, whilst lower strength was associated with non-separated bars.

4. Discussion

4.1 Fiber coating: BN vs naked

The interposition of a weak interface between fiber and matrix, such as BN or pyrolytic carbon, is a common technological expedient used in CMC production to retard reactions between fiber and matrix during high thermal treatments and to trigger relevant toughening mechanisms, such as fiber pull-out [15,16]. However, deposition of a BN coating is an expensive procedure and not all the coatings are suitable for these composites. Indeed previous tests performed on chopped BN-coated fibers revealed that amorphous BN coatings tend to detach from the fiber during milling and crystallize during sintering, forming phases that weaken the resulting composite. Similarly, previous experiments on pyrolytic carbon-coated fibers did not show any benefits over uncoated fibers. In the present study, the BN-coating not only survived the processing and sintering, but also effectively hindered fiber degradation. Examples of uncoated Hi-Nicalon

or Tyranno SA3 fiber in ZrB_2 are shown in Fig. 9b,c. The efficacy of a smooth, continuous coating with homogeneous thickness has clearly protected the fiber during processing, Fig. 9a.

Although no fiber damage was observed for composites with long reinforcement and fiber pull-out was observed on fracture surfaces, the resulting fracture toughness value was not notably different than particulate or short fiber composites, probably owing to the combination of fiber/matrix properties, as will be discussed in the next [section](#).

4.2 Fracture behavior: brittle vs graceful

In order to have efficient load transfer, the Young's modulus of the fiber needs to be higher than that of the matrix. In the present case, the ZrB_2 matrix has a modulus around 500 GPa [17], compared to about 270 GPa for Hi-Nicalon fiber [18]. Unlike a previous report of uncoated chopped Hi-Nicalon fibers in a ZrB_2 matrix [5], the fibers in the present study did not show signs of degradation during processing, so the modulus value should be similar before and after processing.

Two distinct kinds of composites are recognized in CMC technology: Weak Interface Composites (WIC) and Weak Matrix Composites (WMC) [19]. In the former, the crack resistance of the fiber/matrix interface is low, which allows debonding between fiber and matrix. During fracture of WICs, debonding occurs between the fiber and matrix, which enables toughening due to fiber pull-out. On the other hand, for WMCs, the matrix is weak, which causes it to fracture preferentially and allow fiber debonding. For WMCs, the bonding between fiber and matrix is of minor importance due to the weak matrix. For both WICs and WMCs, the modulus of the fibers (E_F) needs to be higher than the modulus of the matrix (E_M) to promote load transfer to the fibers. Chopped fiber composites do not belong to either of these two classes. Typically, the matrix/fiber interface is very strong for chopped fiber composites [4,5] and the matrix has a very high stiffness and strength, i.e. the condition for load transfer ($E_M < E_F$) is not satisfied. As a result, the composites are brittle and strength is sensitive to the notch size, as verified by mechanical testing.

In the present case of continuous fiber composites, a weak interface was obtained using the BN layer. Hence, the composite fails in a non-brittle manner, even though $E_F \cong E_M$. The materials in the present

study were tested according to methods used for the determination of fracture toughness and flexural strength of monolithic ceramics. Being aware that the load transfer mechanisms are different in ceramics with non-brittle behavior, further studies on the mechanical characterization of such composites are in progress.

Considering the results as a whole, it is evident that the combination of a high ratio between the Young's modulus of the matrix and fiber, along with the weak fiber/matrix interface, results in low strength and moderate toughness of the continuous fiber composites produced in the present study.

In the previous studies of composites with chopped fibers, the increase in fracture toughness relative to monolithic ceramics was attributed to the positive contribution of crack pinning by the fibers, which overcame the negative effect due to residual thermal stresses [4,5,11]. Thermal residual stresses in composites arise due to the coupling of different phases with different thermo-elastic properties. The magnitude of the residual stresses depends on the difference of elastic properties and the mismatch in the coefficients of thermal expansion (CTE) between matrix and reinforcements multiplied by the temperature difference over which elastic stresses develop (ΔT). Tensile stresses in the matrix are particularly important for composites processed at high temperatures, since ΔT for these types of composites is high enough to generate residual stresses on the order of the tensile strength of the matrix itself. Evaluation of residual stresses in such composites is complex and the results from different calculations are not always in agreement. Previous studies measured residual stresses in ZrB_2 reinforced with SiC particles using neutron diffraction, Raman spectroscopy and x-ray diffraction [20,21]. These pointed out that stresses began to accumulate at $\sim 1400^\circ\text{C}$ during cooling from the processing temperature. Because of the fact that the CTE of the ZrB_2 matrix, $7.45 \times 10^{-6}\text{K}^{-1}$ [17], is higher than that of SiC fibers ($3.5 \times 10^{-6}\text{K}^{-1}$ for Hi-Nicalon fiber or $4.5 \times 10^{-6}\text{K}^{-1}$ for Tyranno SA3 fiber [18,22]), the ZrB_2 matrix shrinks faster than the SiC fibers as the composite is cooled from the processing temperature. The result is a tensile stress state in the matrix, σ_m , and a corresponding compressive stress state in the reinforcing phases, σ_r , as calculated with Taya et al.'s model using the following relationships [23], plotted in Fig. 10.

$$\sigma_r = -\frac{(1-f)\epsilon^*}{f} \sigma_m \quad (6)$$

$$\sigma_m = E_m \frac{2f\beta\epsilon^*}{(1-f)(\beta+2)(1+\nu_m) + 3\beta f(1-\nu_m)} \quad (7)$$

where f is the reinforcement volumetric fraction and

$$\beta = \frac{1+\nu_m}{1-2\nu_r} \frac{E_r}{E_m} \quad (8)$$

E_r , E_m , ν_r and ν_m are Young's moduli and Poisson's ratios of reinforcement and matrix, respectively, and ϵ^* is the thermal expansion misfit strain given by:

$$\epsilon^* = (\alpha_r - \alpha_m)\Delta T \quad (9)$$

where the α_r , α_m are the thermal expansion coefficients of reinforcement and matrix, respectively and ΔT is the difference between the zero stress temperature and the final temperature, for this case 1400°C and room temperature [21].

In the materials in the present study, the combination of ZrB₂ with SiC fibers implies a negative contribution to toughness due to the residual tensile stress in the matrix which should be overcome by other positive toughening mechanisms in order to achieve an increase of fracture toughness. **Although Taya's model is valid for particle or short fiber-reinforced composites**, the plot in Fig. 10 gives indications that tensile stress in the matrix increases with an increasing amount of reinforcing phase.

4.4 Fiber length: short vs continuous

Although little data has been published on long fiber-ZrB₂ composites, the present experiments do not support the superiority of long-fiber composite over short-fiber in terms of flexural strength or fracture toughness values. Examples of load-displacement curves during fracture toughness tests of unreinforced ZrB₂ along with long- and short fiber-reinforced composites are displayed in Fig. 8a. These curves show typical features of materials having good chevron notch failure behavior: pop-in, slow crack growth, and then catastrophic failure.

In the case of long continuous fiber composite, non-brittle failure is clearly observed: the load-deflection curves show a nonlinear slope, achieve a maximum in applied load followed by a reduction, which reflects stable crack growth up to final fracture of the composite. The behavior of the bar following the initial

fracture results in both total and inelastic WOF values that are significantly improved over monolithic materials or short fiber composites. The inelastic WOF was around 9, 17 and 78% of the total WOF for unreinforced ZrB₂ and ZrB₂ with short or long fiber, respectively.

The fracture surface of a broken bar is shown in Fig. 8b where fiber pull-out is evident. Although the higher amount of fiber, 25 vol%, the quality and efficiency of the coating in protecting the fiber and promoting relevant toughening mechanisms, the fracture toughness values measured by CNB testing were in the same range as short-fiber composites. Some of the discrepancy between observed fracture behavior and measured fracture toughness might be due to the testing method. Evidence of fiber pull-out and a crack path that travels out of the plane of the fracture surfaces is evidence that failure was not purely mode I. The calculations for the CNB methods assume mode I failure. Since this is not the case, the calculated K_{Ic} values are questionable. However, the resulting composite had superior WOF values, indicating non-brittle failure was achieved.

4.5 Toughness and strength trade-off and future perspectives

Properties like high strength and toughness are vital requirements for structural materials, but these are generally mutually exclusive. Therefore the development of a damage tolerant material will always be a compromise between hardness, dictating the strength, and ductility, expressed by the toughness [24]. Also in the present case, a controlled failure behavior is coupled to a dramatic strength decrease: unreinforced materials possess strength in the scattered range 600–840 MPa [2,3], whilst long-fiber reinforced composites have a narrower range, but around only 100-200 MPa [15].

When combining fiber and matrix to increase the toughness, not only are their fundamental properties important, but interface characteristics assume an added importance in the case of brittle matrix composites, so the choice of the coating material is crucial in getting the desired effect. Fracture in brittle matrix/brittle filament composite, where the interfacial bond between fiber and matrix is strong, often results in fast matrix crack propagation perpendicular to the filaments. Usually such an energetic crack breaks through all filaments in the path of the crack and complete brittle fracture ensues [25,26]. This is for

example the case of UHTCs reinforced with chopped Hi-Nicalon fibers [4,5,10]. By introducing a suitable coating, if the interfaces are sufficiently weak, there could be the possibility to introduce an additional contribution to toughness, namely Cook/Gordon tensile debonding ahead of the crack [27]. Such mechanisms may blunt and slow down cracks or even arrest them. However, a weak interface throughout the composite can reduce the strength quite significantly.

High tensile strength characteristics of strong interfacial filament/matrix bonding can be combined with the high fracture toughness of weak interfacial bonding, when the fibers are arranged to have alternate sections of high and low shear stress. Such weak and strong bonds can be achieved by appropriate intermittent coating of the fiber, [25] or mixing coated and non-coated filaments. The strong regions ensure that the filament is picked up, weak areas randomly dispersed along the running crack path serve to blunt them, by producing pull-out length with an associated large contribution to toughness.

Moving from this concept and from the outcomes of the present study combined with the experience on strong matrix/fiber interface composites, one could play with several combinations of layups to find the best compromise between high strength and controlled failure.

5 Conclusions

A ZrB_2 ceramic containing continuous BN-coated SiC fibers was produced and characterized. TEM was used to examine the microstructure at the nanoscale level inside the fiber, in the fiber coating and at the interface between the fiber coating and the matrix. The use of a BN-coating for Hi-Nicalon fiber was effective in hindering fiber degradation during processing. However, the measured fracture toughness values were similar to monolithic ZrB_2 ceramics owing to an unfavorable ratio between Young's modulus of the matrix and the fibers, which did not allow efficient load transfer from the brittle matrix to the high strength fibers. Nonetheless, the use of the BN-coated long continuous fibers resulted in a more damage tolerant composite compared to monolithic ZrB_2 or ZrB_2 reinforced by particles or short fibers. The composite containing the continuous fibers exhibited total and inelastic WOF values that were more than 3

times higher than those for the short fiber composites demonstrating the enhanced controlled failure behavior of the continuous fiber composites.

Acknowledgements

Part of this activity has been performed through NSF grant “Materials World Network Program, Cooperative activity in materials research between USA and Italy: Dual composite ceramics for improved properties”. We also acknowledge the financial support of the US Air Force Research Laboratory for TEM characterization through Grant No. FA8655-12-1-3004, with Dr. Ali Sayir as contract monitor.

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Tables' captions

Table 1: Composition, sintering parameters, relative density and mechanical properties of SiC fiber-reinforced ZrB₂ ceramics.

Label	s.a. vol%	Fiber, vol%	Type	Sintering, °C, MPa, min	Rel. density %	K _{IC} , MPa·Vm	Total WoF J/m ²	Inelastic WOF J/m ²	σ _{RT} , MPa	σ ₁₂₀₀ , MPa	Ref.
ZBZ-iH	10 ZrSi ₂	25 (BN)Hi-Nicalon	long	1450,32,40	98.0	4.5±0.5* ^S 6.4±0.4* ^{#B}	140±11 ^C 100±14 ^D	108±21 ^C 57±11 ^D	192±53 ^A 127±55 ^B	-	This work
ZBZ-H		20 Hi-Nicalon	short	1650,50,8	99.0	6.2±0.4	114±12 ^C	30±8 ^C	385±13	379±15	5
ZBZ-T		20 Tyranno SA3	short	1600,50,11	99.0	5.1±0.2	75±1 ^C	20±8 ^C	375±15	-	11

*40 mmx 3 mmx 4 mm

^S Measured according to CEN/TS 14425-3

[#] Measured according to ASTM C1421

^A bar cut along A side, Fig. 1b

^B bar cut along B side, Fig. 1b

^C Measured from chevron notch bars tested according to CEN/TS 14425-3

^D Measured from chevron notch bars tested according to ASTM C1421

Figure captions

Figure 1: a) Sketch of the experimental procedure for the fabrication of 0/90° long-fiber ZrB₂ composite. b) Sketch of test directions for mechanical characterization of composites containing long or short fibers.

Figure 2: a) Fracture surface and b)-f) polished surfaces of ZrB₂ composite containing long BN-coated Hi-Nicalon fiber and ZrSi₂ as sintering additive. b) Overview of the material architecture, c) magnification of the matrix showing ZrO₂ and SiC aggregates, d) fiber distribution with trapped porosity, e) homogeneous BN coating around the fibers and f) efficient blockage of secondary phases at the coating interface.

Figure 3: Examples of HR-TEM images of the matrix showing the interfaces between ZrB₂-SiO₂-ZrO₂ with EDS spectra of SiO₂ and ZrO₂ containing N traces.

Figure 4: TEM images of fiber matrix interfaces at a) low and b) high magnification. c) Morphology of the coating with d) HR-image of BN with diffraction pattern and e) EDS spectra of the particles trapped within the coating.

Figure 5: HR-TEM images of fiber-coating-matrix interfaces. a)-c) coating-ZrB₂ interfaces and d)-f) coating-fiber interfaces.

Figure 6: STEM image of a fiber /matrix interface with EDS elemental mapping.

Figure 7: Morphology of a SiC fiber a) in the core and b) in the edge with corresponding diffraction patterns showing similar crystallinity degree and mean grain size. c) HR-TEM of crystallites and partially amorphous C-rich phase in the fiber core.

Figure 8: a) Load-displacement curves recording during CNB tests of unreinforced, chopped- or long-fiber reinforced ZrB₂ composites and b) fiber pull-out after flexural testing.

Figure 9: Examples of fiber section in ZrB₂-based composites sintered with ZrSi₂ as additive and containing various fiber types. The sintering temperature and the fracture toughness is reported for each composite.

Figure 10: Calculated thermal residual stresses [23] in the ZrB₂-based composites, considering $\Delta T=1400^{\circ}\text{C}$.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10