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Combined effect of SiC chopped fibers and SiC whiskers on the toughening of ZrB_2

Diletta Sciti*, Laura Pienti, Daniele Dalle Fabbriche, Stefano Guicciardi, Laura Silvestroni

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

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Abstract

ZrB_2-based composites were toughened by the simultaneous additions of SiC chopped fibers and SiC whiskers. The fracture toughness measured by Chevron Notched Beam in flexure was of the order of 6 MPa $m^{1/2}$ and the 4-pt flexural strength around 500 MPa. The values of mechanical properties are compared to those of unreinforced ZrB_2 and composites reinforced by solely fibers or whiskers in order to understand whether a synergistic whiskers-fibers toughening action is present or not in these composites. The combination of two different reinforcing agents is a successful strategy to obtain a super reinforcement provided that densification, reinforcing agents chemical integrity and secondary phases composition and amount are properly controlled.

Keywords: B. Whiskers; C. Mechanical properties; Fibers; ZrB_2; Microstructure

1. Introduction

Zirconium diboride (ZrB_2) is currently considered among the most appealing materials for aerospace applications owing to its high melting temperature and better performances over metal components in high-temperature environments, including low creep rate and high strength at elevated temperatures. In the last decade, research has focused on fabricating high density composites possessing good strength (500–1000 MPa) [1–6]. One aspect that deserves investment of efforts regards the low fracture toughness of these compounds which ranges from 2.5 to 4.5 MPa $m^{1/2}$. The possibility to produce transition metal borides with higher defect tolerance would open a wider scenario of uses and expand the market for this class of compounds. The simplest approach for increasing fracture toughness is the addition of discontinuous elongated reinforcements that are able to activate toughening mechanisms, such as crack pinning, crack deflection, crack bridging, microcracking and thermal residual stress. It has been reported that the addition of short fibers, nanotubes, whiskers or flakes gives promising results for the increase of the fracture toughness [7–12]. Addition of short carbon fibers led to an increase of toughness up to 6.6 MPa $m^{1/2}$ [7]. Fracture toughness values up to 6.7 MPa $m^{1/2}$ were reported by single edge notched beam (SENB) for SiC whiskers additions [8–12] or in the range of 5–6.2 MPa $m^{1/2}$ by chevron notched beam (CNB) in flexure for SiC chopped fibers [13–15].

The aim of the present study is to explore the effect of simultaneous addition of fibers and whiskers, thus exploiting a synergistic effect from both the reinforcing phases. In the past a few attempts were carried out on the basis of this approach. Becher et al. [16] suggested that coupling of two or more toughening mechanisms, such as addition of whiskers or platelets combined with microstructural tailoring, offers the potential to achieve fracture toughness values in excess of 10 MPa $m^{1/2}$. He reported that the fracture toughness of a fine grained Si_3N_4 matrix exhibits lower toughness than when elongated matrix grains are formed. Studies on mullite materials reinforced by 20 vol% SiC whiskers and 20 vol% ZrO_2 particles showed that the combined toughening effects were equal to, or greater than, the sum of individual toughening effects [17]. In the work of Kodama et al. [18] a notable increase of fracture toughness was obtained adding SiC particles and SiC whiskers to a silicon nitride matrix: when a 10 vol% of particles was combined with 20 vol% of SiC whiskers, the toughness changed from 7 MPa $m^{1/2}$, for the addition of only whiskers, to 10.5 MPa $m^{1/2}$.

*Corresponding author. Tel.: +39 546 699748; fax: +39 546 46381.
E-mail address: diletta.sciti@istec.cnr.it (D. Sciti).

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More recently, Chen et al. [19] have studied the combined effect of SiC whiskers and SiC particles on a ZrB_2 matrix, reporting a maximum increase of fracture toughness (6.9 MPa m$^{1/2}$) for addition of 7 vol% particles and 20 vol% whiskers. Finally, Lin et al. studied the effect of simultaneous addition of ZrO_2 short fibers and SiC whiskers and reported notable increments of toughness (8.0 MPa m$^{1/2}$) due crack deflection by whiskers and transformation toughening by ZrO_2 [20].

In this work, the joint effect of SiC whiskers and SiC chopped fibers on the mechanical properties of ZrB_2 is analyzed. The synergistic effect should be in principle ensured by the fact that short fibers and whiskers toughen the boride matrix through different mechanisms (crack bowing and crack deflection, respectively [13–15]). Moreover, that addition SiC reinforcing phases should ensure better high temperature stability compared to systems containing oxide phases, such as ZrO_2. To assess whether combinations of whiskers and fibers really have the potential to promote a super reinforcement, the properties of the hybrid composites are compared to those of composites reinforced by solely chopped fibers or whiskers.

2. Material and methods

Commercial raw materials were used to prepare the ceramic composites: ZrB_2 Grade B (H.C. Starck, Germany), specific surface area 1.0 m^2/g, impurity max content: C 0.25 wt%, O 2 wt%, Fe 0.1 wt%, Hf 0.2 wt%, particle size range 0.1–8 μm; SiC chopped fibers (HI-Nicalon, Nippon Carbon), diameter 14 μm, length 1 mm, wt% Si:C:O=62:37:0.5; SiC whiskers (American Matrix, Inc. Knoxville, TN), diameter 0.8 μm, length 30 μm, impurities Ca 1.7 at%, Mg 1.2 at%, Fe 0.4 at %. As sintering additives the following powders were used: α-Si_3N_4 Baysind (Bayer, Germany), specific surface area 12.2 m^2/g, impurity max content: O 1.5 wt%; $ZrSi_2$-F (Japan New Metals Co., LTD, Osaka, Japan), impurity max content: C 0.11 wt%, O 1.00 wt%, Fe 0.09 wt%, particle size range 2–5 μm. The compositions are summarized in Table 1. The poly-reinforced systems contained 10 vol% or 20 vol% whiskers (w) combined with 10 vol% fibers (f). The sintering additives were added in amounts comprised between 5 and 10 vol%. The compositions (in vol%) were labeled as follows:

- 75 ZrB_2 + 10 SiCw + 10 SiCf + 5 Si_3N_4,ZS1010
- 70 ZrB_2 + 10 SiCw + 10 SiCf + 10 $ZrSi_2$, ZZ1010
- 65 ZrB_2 + 20 SiC w + 10 SiCf + 5 Si_3N_4, ZS2010

The powder mixtures were ball milled for 24 h in absolute ethanol using silicon carbide media. Subsequently the slurries were dried in a rotary evaporator. The powder mixtures were sintered in a graphite mold using a hot pressing machine at 1650 °C for $ZrSi_2$ additions and at 1700 °C for Si_3N_4, with applied pressure of 40–50 MPa and holding time of 10 min. The bulk densities were measured by Archimedes' method. The microstructures were analyzed using scanning electron microscopy (SEM, Cambridge S360, Cambridge, UK) and energy dispersive spectroscopy (EDS, INCA Energy 300, Oxford

Table 1
Compositions, sintering additive and properties of the hybrid composites. K_{Ic} fracture toughness, σ 4-pt flexural strength. f= fibers, w= whiskers. Mean ± 1 standard deviation when appropriate.

Label	Composition (vol%)	Sintering Aid (vol%)	Sintering Temperature (°C)	Theoretical density (g/cm^3)	Experimental density (g/cm^3)	Relative density (%)	K_{Ic} (MPa m$^{1/2}$)	σ (MPa)	Matrix mean grain size (μm)
ZS1010	ZrB_2+10SiCf+10SiCw	5 Si_3N_4	1700	5.33	5.14	96.4	6.1 ± 0.3	430 ± 71	1.8 ± 1.0
ZS2010	ZrB_2+10SiCf+20SiCw		1700	4.71	4.38	93.1	4.3 ± 0.3	–	1.6 ± 1.0
ZZ1010	ZrB_2+10SiCf+10SiCw	10$ZrSi_2$	1650	5.36	5.27	98.4	6.1 ± 0.2	520 ± 30	1.9 ± 1.1

Instruments, UK) on fractured and polished surfaces. The fracture toughness (K_{Ic}) was evaluated using the method of chevron notched beam (CNB) in flexure. The test bars, $25 \times 2 \times 2.5$ mm^3 (length by width by thickness, respectively), 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 specimens were fractured using a semi-articulated SiC four-point fixture with a lower span of 20 mm and an upper span of 10 mm on a universal testing machine Zwick mod. Z050. The specimens, three for each composite, were loaded with a crosshead speed of 0.05 mm/min. The "slice model" equation of Munz et al. [21] was used to calculate K_{Ic}. On the same machine and with the same fixture, the flexural strength was measured at room temperature with a crosshead speed of 1 mm/min on machined bars $25 \times 2.5 \times 2$ mm^3 (length by width by thickness, respectively) with the long edges chamfered. For each material, five specimens were broken.

3. Results and discussion

3.1. Microstructural features of hybrid composites

Microstructural features of hybrid composites are shown in Figs. 1–3. SEM inspection confirmed a low level of porosity in ZS1010 and ZZ1010 composites (~ 3 and 1%, respectively) (Figs. 1 and 3). On the contrary, a significantly higher fraction of porosity was found for ZS2010 (Fig. 2). Typical fracture surfaces are shown in Figs. 1a, 2a and 3a.

In the polished microstructure of ZS1010, fibers with maximum length of 300 μm can be recognized (Fig. 1b), whilst whiskers with length lower than 10 μm can be visualized in Fig. 1c. The matrix grains are surrounded by a glassy phase that is the residue of the liquid Si–B–O–N phase formed during sintering due to the addition of the sintering aid, Si_3N_4 (Fig. 1d). BN small platelets are embedded in the glassy phase and form upon re-precipitation from the liquid phase during cooling down from the sintering temperature. Whiskers are generally surrounded by BN platelets, zirconia or residues of the Si–O–B–N liquid phase (Fig. 1d). It is apparent that some local porosity can be found in areas where the whiskers are agglomerated (Fig. 1e) or inside the fiber themselves (Fig. 1d). In the SEM picture at higher magnification (Fig. 1d), a multilayered microstructure of the fiber is evident, explained as follows. Hi-Nicalon fibers are composed of nanograins of SiC (5–10 nm), amorphous Si–C and free carbon [22]. During sintering, SiC grain growth, recrystallization of Si–C and carbon outward migration occur. Moreover, external regions of the fiber may react with localized oxides such as zirconia, react with the liquid phases generated by silicon nitride o zirconium silicide additives and/or incorporate $ZrO_2/ZrSi_2$ particles. The final result is a multilayered structure, very different from the original fiber morphology. The inner part (core) is constituted of nanosized 30 nm SiC, surrounded by a rim of coarsened SiC crystallites (50 nm). In the rim, $ZrSi_2$ and ZrC particles can be observed, as well as contamination of Ni and Fe which are thought to derive from SiC whiskers [23]. The fracture surface of the composite ZS2010 is shown in Fig. 2a and b and is similar to that of the ZS1010 composite apart from some residual porosity. Very likely the higher content of whiskers favored the formation of SiC weak bondings or hindered densification. Moreover, the high volumetric amount of whiskers (20 vol%) probably enhanced the amount of glassy silica introduced in the system, that was generally found in proximity of the whiskers: clusters

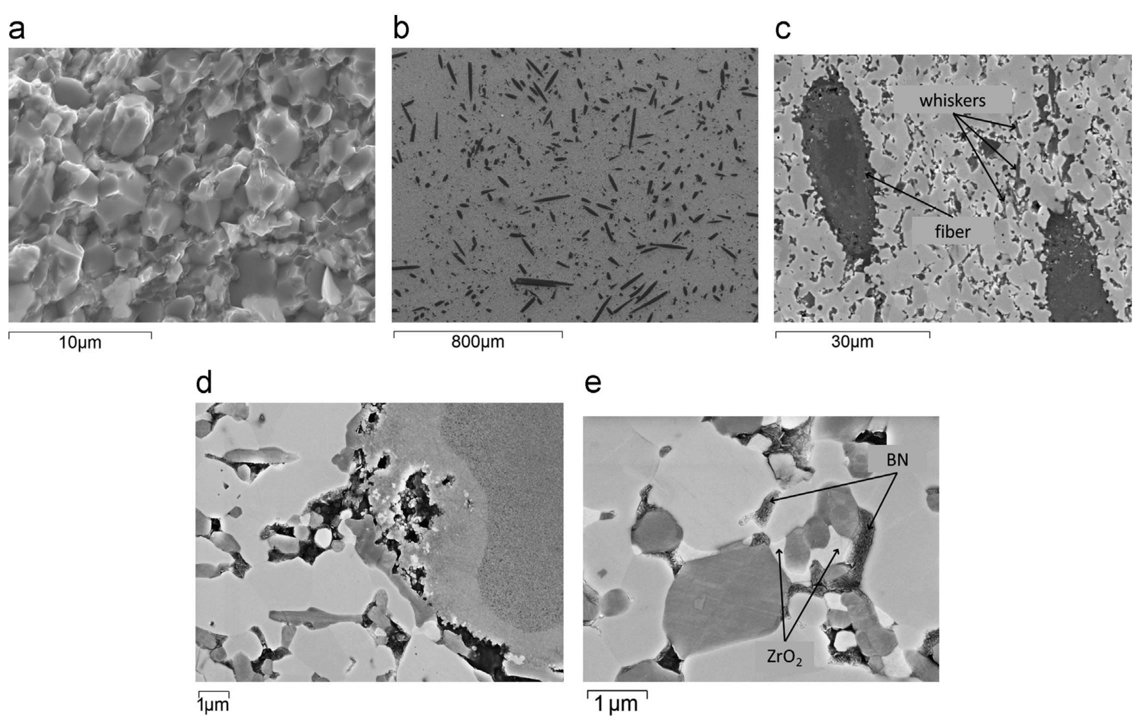

Fig. 1. Microstructural features of material ZS1010 reinforced by both 10 vol% whiskers and 10 vol% fibers: (a) fracture surface, (b) polished section at low magnification, (c) polished section at higher magnification, (d) chemical damage of a fiber and (e) secondary phases near the whiskers.

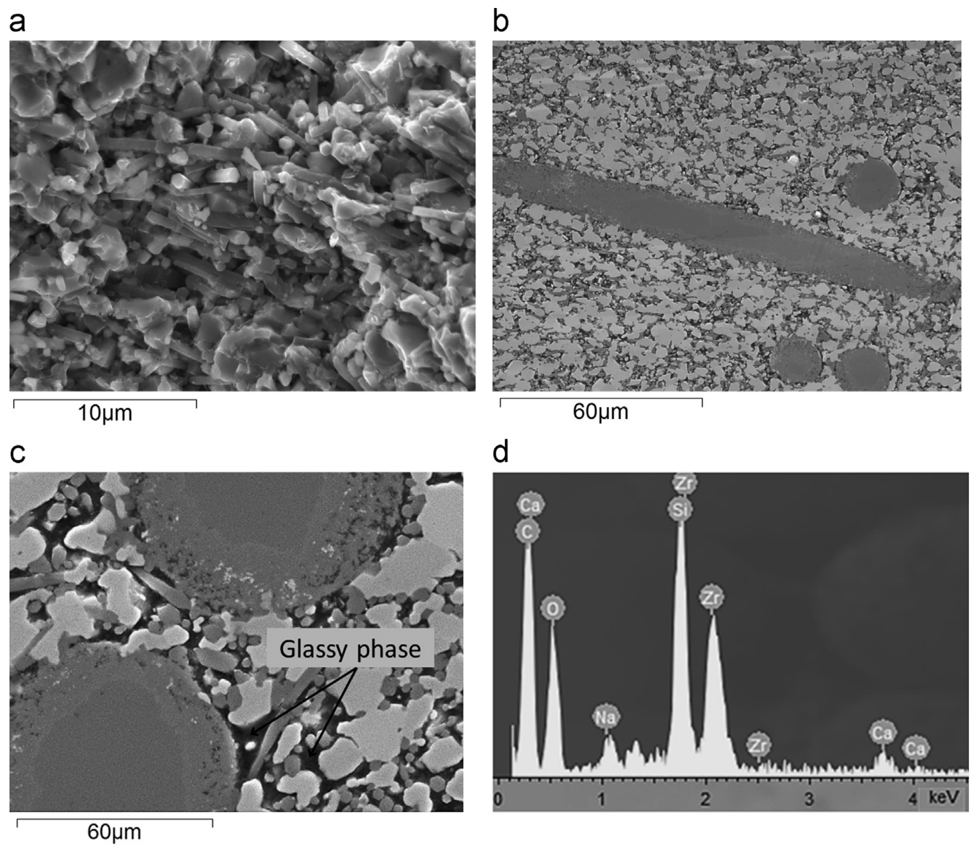

Fig. 2. Microstructural features of material ZS2010 reinforced by both 20 vol% whiskers and 10 vol% fibers: (a) fracture surface, (b) polished section at low magnification, (c) polished section at higher magnification and (d) EDS spectrum showing impurities of Na, Ca and Mg in the glassy phase.

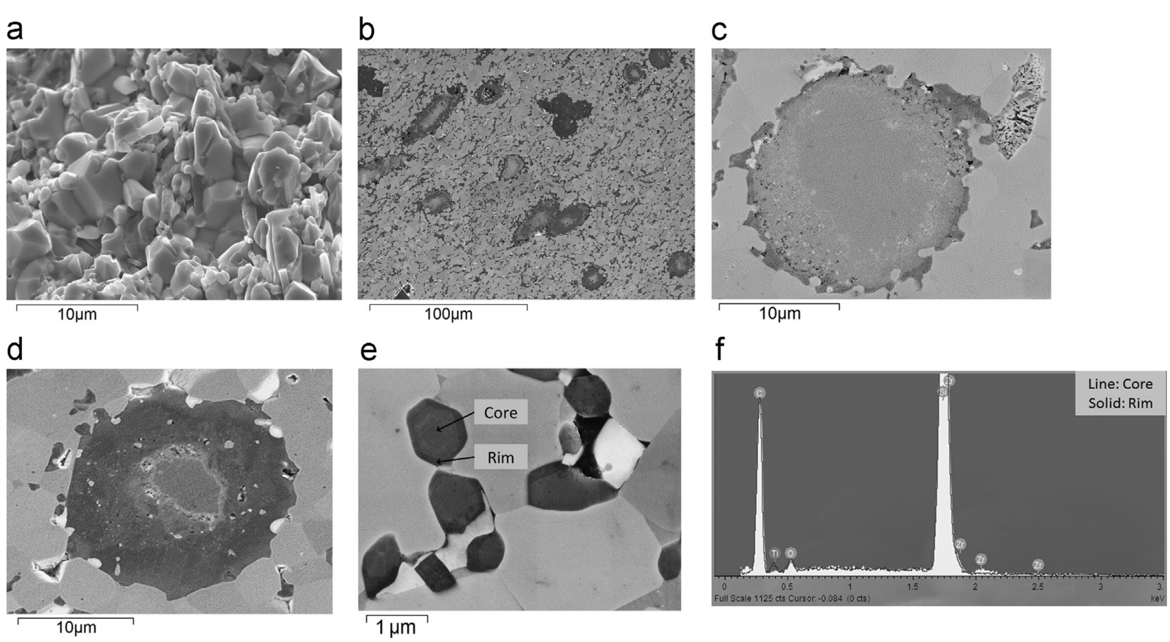

Fig. 3. Microstructural features of material ZZ1010 reinforced by 10 vol% whiskers and 10 vol% fibers with $ZrSi_2$ as sintering aid: (a) fracture surface showing whiskers pull out, (b) polished section at low magnification, (c) typical cross section of a fiber partially and (d) heavily altered, (e) whiskers section showing core rim structures and corresponding EDS spectra in (f).

of whiskers embedded in the SiO_2 based phase were frequently observed (Fig. 2c). EDS analysis in the glassy phase revealed also the presence of alkaline and alkaline earth metals, such as Na, Mg and Ca (Fig. 2d), probably deriving from whiskers fabrication [23]. The fracture surface of the composite labeled ZZ1010 (Fig. 3a) reveals cleaner grain boundaries compared to the silicon nitride doped systems and some whisker pull out is also apparent. In the polished microstructure (Fig. 3b), the reinforcing phases are homogeneously distributed. Looking in more detail it is evident that two main fiber morphologies were observed in the composite sintered with $ZrSi_2$, one, more frequent, with features analogous to ZS1010 (Fig. 3c), and another one shown in Fig. 3d where the fiber is mostly composed by recrystallized SiC. The reasons leading to these different features are at the moment still under investigation, however it could be related to the presence of metal impurities which locally alter the chemistry and interact with the fiber in selective way [24]. Overall, this fiber transformation was generally more pronounced than that observed in a composite containing the same sintering additive, $ZrSi_2$, and only 20 vol % of fibers, hot pressed at 1650 °C [15]. Whiskers also underwent microstructural modification, developing a core–shell microstructure (Fig. 3e). According to EDS analysis in Fig. 3f, the SiC whisker core contained some impurities, such as Ti, Ca and O probably deriving from precursors used for synthesis. In the rim, Si and C and traces of Zr were found.

3.2. Mechanical properties

The mechanical properties of hybrid composites are summarized in Table 1. The fracture toughness reached values of 6.1 MPa $m^{1/2}$ for both ZS1010 and ZZ1010. On the contrary, the toughness of ZS2010 was remarkably lower and close to that of unreinforced ZrB_2. In Table 2, the fracture toughness of similar composites are reported for comparison. As can be seen, for ZS1010, the fracture toughness values were higher than that of composites reinforced by solely 10–20 vol% of whiskers or fibers. In the case of ZZ1010, the fracture toughness was significantly higher than composite containing 20% whiskers but just the same as the composite containing 20 vol% fibers (Tables 2, 6.2 MPa $m^{1/2}$ [15]). SEM inspection of cracks generated by 98.1 N indentations confirmed that the crack passed through the fibers and was deflected by the whiskers (Figs. 4a–c). This suggests that a crack deflection mechanism is active when the crack encounters SiC whiskers. This has been already observed in composites reinforced solely by whiskers [13,14]. Fracture surfaces also suggest some potential crack bridging phenomena, due to whisker pull out however this mechanism was not clearly identified on SEM inspection of the crack path. On the other hand, the toughening contribution from fibers can be ascribed to crack pinning, due to absence of bridging and deflection phenomena. In previous works the separate effect of whiskers and fibers was analyzed and compared to existing models. For additions of 10–20 vol% whiskers, typical toughness values were in the range 5–5.7 MPa $m^{1/2}$ [13,14]. For addition of 10–20 vol% fibers, toughness values were in the same range, 5.3–5.6 MPa $m^{1/2}$ [13,14]. In the case of whiskers addition, the model of Faber and Evans for crack deflection was applied [25]. In the case of fibers addition, the model for crack pinning was considered [26]. For both kinds of composites, the contribution from residual stresses was also taken into account. The incorporation of reinforcing elements (SiC) with a thermal expansion coefficient lower than the matrix (ZrB_2) leads to the development of tensile residual stresses in the matrix itself, which results in a negative contribution to the overall fracture toughness [27]. Keeping this in mind, the overall toughness for whiskers-reinforced composites was described as

$$K_{Ic}^{reinforced} = K_{Ic}^{matrix} + \Delta K^{deflection} + \Delta K^{residualstress} = K_{Ic}^{matrix} + \Delta K' \quad (1)$$

and for fiber-reinforced ones as:

$$K_{Ic}^{reinforced} = K_{Ic}^{matrix} + \Delta K^{pinning} + \Delta K^{residualstress} = K_{Ic}^{matrix} + \Delta K'' \quad (2)$$

Table 2
Compositions and fracture toughness values (K_{Ic}) of previously produced reinforced composites. f=fibers, w=whiskers. Mean ± 1 standard deviation when appropriate.

Composition (vol%)	Add. (vol%)	K_{Ic} (MPa $m^{1/2}$)	Ref.
ZrB_2	$5Si_3N_4$	3.8 ± 0.3	13
ZrB_2+10 SiCf		5.3 ± 0.3	13
ZrB_2+20 SiCf		5.6 ± 0.3	13
ZrB_2+10 SiCw		5.0 ± 0.1	13
ZrB_2+20 SiCw		5.3 ± 0.3	13
ZrB_2	$10ZrSi_2$	4.2 ± 0.3	15
ZrB_2+20 SiCf		6.2 ± 0.3	15
ZrB_2+20 SiCw		5.0 ± 0.1	This work

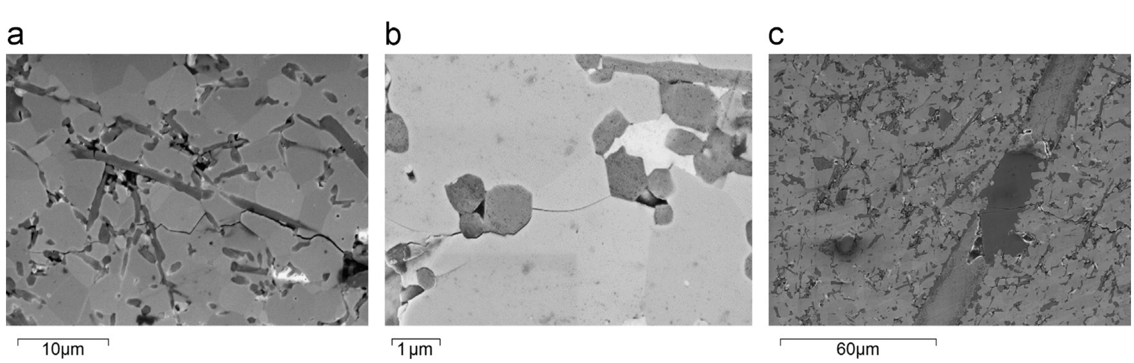

Fig. 4. Crack paths generated by 98.1 N indentation deflected by whiskers. Examples of whisker deflection in (a) ZS1010, (b) ZZ1010, in (c) a crack passes through the fiber.

Experimental data collected from unreinforced (matrix) and reinforced composites were overlapped to theoretical values and good agreement was found in both cases [14,15].

Thus, toughness of the hybrid composites can be interpreted as the sum of the unreinforced matrix toughness plus the increment due to toughening mechanisms exerted by the fibers and/or whiskers

$$K_{Ic}^{\text{hybrid}} = K_{Ic}^{\text{matrix}} + \Delta K^{\text{fiberpinning}} + \Delta K^{\text{residual stress (fiber)}} + \Delta K^{\text{whiskerdeflection}} + \Delta K^{\text{residual stress (whisker)}} = K_{Ic}^{\text{matrix}} + \Delta K' + \Delta K'' \quad (3)$$

A rough estimation of the expected increase of toughness K_{Ic}^{hybrid} can be performed using Eq. (3), where: K_{Ic}^{matrix} is the toughness measured for unreinforced ZrB_2 with Si_3N_4 as sintering aid (3.8 MPa m$^{1/2}$ [6,15]), and ΔK′, ΔK″ are the toughness increments due to each single reinforcement. Considering the toughness value of Table 2, for example, we see that ΔK′ = 1.5 MPa m$^{1/2}$ for a composite containing 10 vol% of SiC whiskers and ΔK″ = 1.2 MPa m$^{1/2}$ for a composite containing 10 vol% of SiC fiber, so that the total increment due to the concomitant introduction of 10 vol% of fibers and whiskers is 2.7 MPa m$^{1/2}$. For a composite containing 20 vol % of SiC whiskers and 10 vol% of SiC fibers the expected total increment is 3 MPa m$^{1/2}$.

According to this simple calculus, K_{Ic}^{hybrid} should be about 6.5 and 6.8 MPa m$^{1/2}$ for ZS1010 and ZS2010, respectively. The experimental value of ZS1010 is lower, but not too far from the expected value (6.1 vs. 6.5 MPa m$^{1/2}$) on the other hand, the experimental value of ZS2010 was remarkably lower (4.3 vs. 6.8 MPa m$^{1/2}$). These results suggest that just for one system (ZS1010), there is partial synergistic effect of the two types of reinforcement as the hybrid composite has a toughness higher than composites containing the same overall amount of reinforcement (20 vol%). In the case of ZZ1010, the calculations just performed cannot be applied as we do not know the individual contribution of the addition of 10 vol% of reinforcement (either whiskers or fibers). At the light of the results reported in Table 2, however, it can be said that there is no indication of a synergistic effect as the toughness of the composite containing 10% whiskers and 10% fibers (ZZ1010) is the same as the composite just containing 20% of fibers. Just as an indication of the importance and complexity of the sintering aid effect, it is possible to see that when $ZrSi_2$ is used, the fracture toughness of the composite with 20 vol% of SiC fibers is higher than the corresponding composite in which Si_3N_4 was used; vice versa holds true when the reinforcement was 20 vol% of whiskers, see Table 2.

The reason for the mismatch between the experimental fracture toughness of the hybrid composites and the expected values can have several explanations:

(1) the fracture toughness of the ZrB_2 matrix with double reinforcement could be lower than the toughness of the matrix with one reinforcement;
(2) one or both toughening contributions could be less efficient than in composites containing just one type of reinforcement;
(3) the residual stress terms in the hybrid composite could be higher than in composites containing one type of reinforcement.

According to hypothesis (1), the matrix could have been weakened by: (i) a reduction of matrix mean grain size, (ii) residual porosity and (iii) a change of secondary phases chemistry (Fig. 2d). For (i), no significant variation of matrix mean grain size was recorded for hybrid composites, as compared to previous ones [13–15]. In contrast (ii), composites containing whiskers showed the tendency to retain more porosity [13], as whiskers limited grain boundary movement making densification more difficult. Moreover, significant fractions of low density phases were found due to addition of whiskers (iii). Even in successful densification cases, say ZS1010 and ZZ1010, relative densities were 1–2% lower than corresponding composites containing equivalent amount of reinforcement, but just fibers. In case of ZS2010, moreover, densification was largely incomplete (final relative density 93%) and sizable areas of amorphous phase were detected. These two factors could explain the lack of expected toughness increase.

According to hypothesis (2), one or both reinforcements are not completely effective in the hybrid composites. Looking at the crack path, it is apparent that whiskers can actively deflect the crack, as previously seen (Fig. 4a and b). In contrast, the toughening increment due to crack bowing is proportional to the fiber fracture strength and fiber radius. The fact that in the composite ZZ1010 the fibers are more damaged from the chemical point of view (see Fig. 4d) suggests that in this hybrid system the tensile strength could have been reduced from the original value, thus becoming only partially effective. In turn, this higher degree of damage can be due to either impurities, but also to the densification temperature (1650 °C), well above the melting point of the sintering aid, $ZrSi_2$. At this temperature, the formation of excessive liquid phase should have enhanced diffusion of metallic impurities and fiber degradation.

As for hypothesis (3), the negative contribution to fracture toughness that comes from residual stress developed in the matrix due to the difference in moduli and thermal expansion coefficients of ZrB_2 and SiC fibers or whiskers could be not captured by the used model. It was in fact seen that the microstructure and the chemistry of both matrix and reinforcement are rather involved and this is the result of the simultaneous presence of fibers and whiskers. In this case the matrix and reinforcement properties used for the calculation of residual stresses could be not representative of the composite at hand. Thus the contribution from residual stress could be higher than expected, and this could be also a reason why even in the most successful case, ZS1010, toughness increment was lower than expected.

Finally, as a general conclusion, the results showed that the microstructures of the composites with fibers and whiskers are very complex, containing glassy phases and other newly formed phases between ZrB_2 matrix and SiC reinforcements. Thus, even the proposed pinning and deflection toughening mechanisms could not operate in the way depicted by the proposed models, which could lead to discrepancies between experimental and predicted values.

As for the strength, on-going specific studies have shown that this property is mainly dictated by the fiber maximum length, given also the similar ZrB_2 mean grain size, around 2 μm [28]. As previously observed, strength of fiber-reinforced composites is generally halved compared to unreinforced composite, with values around 400 MPa [13,15]. In contrast, addition of whiskers can raise the flexural strength. For instance it was found that strength of composites containing 10 or 20 vol% of whiskers was higher (700 MPa) or similar to that of pure ZrB_2 (600 MPa) [13,14]. In the hybrid systems, the strength was 430 and 520 MPa for ZS1010 and ZZ1010, respectively. These values are similar to those generally obtained for materials just containing fibers, confirming that addition of fibers, rather than addition of whiskers, controls this property.

4. Conclusions

The aim of the present study was to explore the effect of simultaneous addition of whiskers and fibers on the toughness of a ZrB_2 ceramic matrix, thus exploiting a synergistic effect from both the reinforcing phases. Results obtained demonstrate that the toughness of the hybrid composites overpasses 6 MPa $m^{1/2}$ and is higher than the toughness of composites reinforced by an equivalent amount of reinforcement, either in form of fiber or whisker, that was generally found to below 6 MPa $m^{1/2}$. However, the synergistic effect can be only obtained if both matrix and reinforcement do not undergo degradation due to the sintering process. The combination of two different reinforcing agents has the potential to be a successful strategy to obtain a super reinforcement provided that densification, final porosity, secondary phases type and amount and chemical integrity of the reinforcing agents are properly controlled. In spite of the presence of fibers, a good level of strength (up to 520 MPa) was measured in the hybrid composites.

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