

Joining ZrB₂-SiC composites using glass interlayers

LAURA ESPOSITO, ALIDA BELLOSI*

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

E-mail: bellosi@istec.cnr.it

A joining technique, based on the use of a glass powder as a bonding interlayer between two ceramic pieces, is tested for a ZrB₂-SiC composite. At the bonding temperature, the glass melts, wets the ceramic and flows through the interface driven by the capillary pressure that builds up between the two contacting ceramic surfaces, promoting their adhesion. The behaviour of three glasses is compared: two in the system Ca-Al-Si-O (melting temperatures 1400 and 1210°C) and one in the system Y-Al-Si-O (melting temperature 1440°C). The ceramic-glass interfacial characteristics depend mainly on the temperature, on the composition of the glass and on the phenomena influencing the adhesion, such as the partial dissolution of the ceramic grains when the glass wets them. The 3-point flexural strength values of the joints obtained by the system that resulted with the more homogeneous interface are also reported.

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1. Introduction

Zirconium diboride (ZrB₂) is an ultra-refractory material of particular interest because of the excellent and unique combination of high melting point, high electrical and thermal conductivity, chemical inertness against molten metals or non basic slag and superb thermal shock resistance [1]. These properties make it an attractive candidate for high temperature applications where corrosion-wear-oxidation resistance are demanded.

Zirconium diboride is currently used as a refractory in foundry or electrical devices (heaters, igniters). Other applications have been recently developed in aerospace for the thermal protection of leading edges or other sharp parts on hypersonic re-entry spacecrafts [2–4].

High density ZrB₂-based materials can be obtained through liquid phase sintering at temperatures lower than those necessary for undoped ZrB₂ [1, 5–8]. However, the grain boundary phases deriving from the sintering aids sometimes deteriorate the properties of this class of material [6, 8–11], in particular when metal sintering aids (Ni, Fe) are used. Ceramic additives have been tried recently and these improve significantly both the sintering and microstructure of ZrB₂ [12–14]. The fracture toughness and strength of monolithic ZrB₂ ceramics can be improved by introducing a secondary reinforcing phase [13].

Potential applications of ZrB₂-based materials can be widened further by developing reliable joining techniques which would overcome the problems associated with the fabrication of complex shaped components

[15, 16]. No literature has been found on the joining of ZrB₂ materials and related composites. Thus, the present study aims to evaluate the possibility of joining two parts of ZrB₂, in the light of high temperature applications, even under oxidizing conditions. Recent studies on the oxidation behaviour of ZrB₂ and ZrB₂-SiC composites showed that these materials can withstand very high temperatures (up to 1600°C) without evident degradation, due to the growth of a protective silica layer which inhibits the further oxidation of the diboride matrix [11, 13, 17].

Among the numerous bonding techniques developed for ceramics, the use of a thin glass interlayer placed between two ceramic pieces is suitable for several oxide and non-oxide ceramics [16–24]. The key factors controlling the adhesion are the wetting and compatibility of the glass with the ceramic crystalline phases and the intergranular phase. If these conditions are fulfilled, at $T > T_{\text{glass melting}}$ when the glass viscosity is sufficiently low, the capillary force arising between the two ceramic surfaces drives the wetting and adhesion processes. The microstructure of the joint region is the result of the modified equilibrium of the forces acting among the grains when these come into contact with a liquid glass. This technique does not need any applied pressure and is also suitable for ceramic pieces with complex shapes.

In this study the suitability of glasses as interlayers to produce bonds between zirconium diboride-based pieces is evaluated by means of preliminary tests on chemical compatibility and wetting ability of several silicate glasses with a ZrB₂-SiC composite particularly

*Author to whom all correspondence should be addressed.

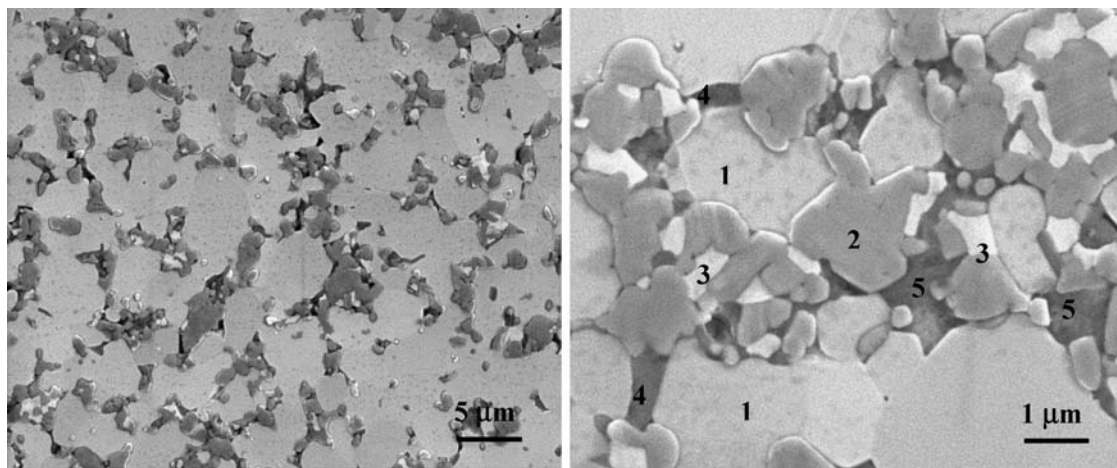


Figure 1 Secondary electron SEM micrographs of a polished section of ZrB₂-SiC composite. The following phases were identified: 1:ZrB₂; 2:SiC; 3:ZrO₂; 4:BN, 5:B-N-O-Zr-Si glassy phase.

suitable for high temperature applications [13]. This material contains 20 vol% of silicon carbide particles and a grain boundary phase formed by amorphous Si-Zr-O-N-B compounds located at triple points. These phases are compatible with several silicate glasses, which therefore are used in the present study to evaluate the interaction with the ZrB₂-SiC composite. For this purpose, the glasses were applied as coatings on the ceramic material and thermally treated at properly selected temperatures. The resulting coatings have been evaluated in terms of reaction and interdiffusion between the glass and the ceramic components, devitrification and/or dissolution/precipitation phenomena and mechanical compatibility among the involved phases.

On the basis of the results, symmetrical joints have been also prepared using as interlayers the glasses which exhibited the best chemical and mechanical compatibility when used as coatings.

In addition, the ability of the ZrB₂-SiC composite to oxidize at high temperature to form a pore-free silica layer (with a thickness that is a function of the oxidizing temperature and time) has been exploited to form symmetrical joints between two oxidized ceramic parts.

The flexural strength of the more homogeneous, pore free joints has been measured.

2. Experimental

2.1. Ceramic material: Processing and characteristics

ZrB₂ powder (grade B, H.C. Starck, Germany) was selected as the raw material. This powder has a specific surface area of 1 m²/g, a particle size in the range 0.1–8 μm and irregular shaped particles. The elemental impurities are (wt%): O 1.0, C 0.25, N 0.25, Hf 0.2, Fe 0.1. The oxygen content corresponds to 1.5 wt% of B₂O₃, due to surface oxidation of the powder particles during production and handling. The SiC used as a reinforcing phase (BF 12, H. C. Starck, Germany) has a specific surface area of 11.6 m²/g and oxygen impurity of 1.65 wt%. The Si₃N₄ powder (Baysinid, Bayer, Germany) used as a sintering aid has a specific surface area of 12.2 m²/g and an oxygen content of 1.5 wt%.

The starting powder mixture, ZrB₂-3.8 Si₃N₄-20 SiC (wt%) was hot pressed at 1850°C, 30 MPa and the resulting material exhibited the best mechanical properties of various compositions previously tested [1–13].

The final density was 5.85 g/cm³, which corresponds, in accordance with the rule-of-mixtures, to a relative density of 98%. The microstructure is rather regular, mean grain size is 3 μm and the residual porosity is very sparse (Fig. 1a). The SiC particles generally exhibit a clustered distribution and are often in contact with products derived from the reactions occurring during the sintering process between the sintering aid (Si₃N₄) and B₂O₃ present on the ZrB₂ particles and SiO₂ present on the SiC particles [12]. The newly formed phases, i.e. BN, t-ZrO₂ and a glassy phase, in the system Zr-Si-B-N-O, locate randomly at triple points or at grain boundaries of the two main constituents: ZrB₂ and SiC particles. The majority of darker regions in Fig. 1a and b consist of low density secondary phases such as boron nitride and glassy silicates.

The flexural strength of the hot pressed composite at room temperature is 730 ± 100 MPa, at 1000°C it is 430 ± 110 MPa and at 1200°C it decreases to 250 ± 10 MPa. Values of fracture toughness (about 4.6 MPa m^{1/2}) and hardness (20.4 GPa) were measured. The thermal expansion coefficient in the temperature range 20–1300°C is 7.50 · 10⁻⁶°C⁻¹. Details on processing and characteristics of this composite have been reported in a previous paper [13].

2.2. Glasses used as interlayers

The compositions and physical characteristics of the three glasses used as surface coatings and/or bonding interlayers are listed in Table I.

The selected glasses are silicates which, from previous studies [23, 24], were found to be compatible with and to wet most of the phases forming the ceramic material, in particular SiC and ZrO₂, and the amorphous intergranular phase [13].

The compositions of glass 1 and 2 fall in the CaO-Al₂O₃-SiO₂ ternary diagram and are near two eutectic points, which occur at 1380 and 1170°C, respectively

TABLE I Compositions and physical properties of the glasses. α coefficient of thermal expansion; ρ density; T_{trans} transition temperature, T_{soft} softening temperature, T_{liq} liquidus temperature

| Glass | Composition wt% | | | | $\alpha \cdot 10^{-6} (^{\circ}\text{C}^{-1})$ | ρ (g cm ⁻³) | T_{trans} (°C) | T_{soft} (°C) | T_{liq} (°C) |
|-------|------------------|--------------------------------|-------------------------------|------|--|------------------------------|-------------------------|-------------------------|---------------------------|
| | SiO ₂ | Al ₂ O ₃ | Y ₂ O ₃ | CaO | | | | | |
| 1 | 34.0 | 39.8 | | 26.2 | 6.6 | 2.76 | 930 (833) | 970 (856) | 1400 |
| 2 | 61.8 | 14.9 | | 23.2 | 5.5 [§] | 2.66 | 900 | 935 | 1210 (1139 [§]) |
| 3 | 32.5 | 25.0 | 42.5 | | 5.3 [*] | 3.48 | (884 [*]) | 950 (934 [*]) | 1440 (1353 [#]) |

Ref. 27,[§] Ref. 28, ^{*} Ref. 29, [#]Ref. 30.

[25]. The composition of glass 3 is near the eutectic point of the Y₂O₃-Al₂O₃-SiO₂ ternary phase diagram, which occurs at 1370°C [26]. Studies of the three glasses using a microscope with a hot stage showed that the liquidus temperatures are close to those of the ternary phase diagrams and that the transition, softening and liquidus temperatures are close to those reported in the literature for similar glass compositions (Table I).

The density of all the glasses is lower than that of the ceramic material and therefore buoyancy effects during the bonding cycles, when one ceramic piece is placed on top of the other one coated with the glass, cannot be excluded. Under such conditions, poorly bonded grains from the upper ceramic part may detach and move toward the other ceramic part, which is in a lower position.

The coefficients of thermal expansion of all the glasses, shown in Table I, are lower than that of the ceramic composite ($7.5 \times 10^{-6} \text{ } ^{\circ}\text{C}^{-1}$). During the cooling step of the bonding cycles, therefore, compressive stresses may form within the glass interlayer, leading to the formation of cracks or of other defects.

2.3. Coating and joining cycles

The interaction between the ceramic and the glasses was studied by coating the upper surfaces of small ceramic pieces (1 cm × 1 cm × 0.2 cm), previously polished with diamond pastes down to 1 μm, with the glass pow-

ders. The glass powder (sieved below 25 μm) was deposited through a fine sieve (below 40 μm). The amount of glass was controlled by weighting the sample before and after each subsequent sieving step until the desired quantity was reached. The amount of glass needed to obtain a final glass layer thickness of 50 μm was calculated as a function of the surface area of the ceramic piece and the density of the glass. With this technique more homogeneous glass powder layers were obtained, compared to other deposition techniques [24].

Preliminary tests to evaluate the compatibility of the glass and the ceramic were carried out at temperatures ranging from the softening point up to the melting point of the glass. During the thermal treatments the glass deposited on the ceramic surface at first softens, then melts and interacts with the ceramic; these phenomena depend on the characteristics of the glass and on the temperature. In the tested samples, no evident reaction between the ceramics and the glasses occurred at temperatures in the range from the softening point to the melting point of the glass. As an example, Fig. 2 reveals the interface between the ceramic and glasses 1 and 2 after a thermal cycle of 950°C for 1 h under vacuum. Glass 2, characterized by a lower softening temperature, gives rise to a uniform layer that exhibits good adhesion but almost no interaction with the ceramic; no chemical reactions, interdiffusion or matter transfer took place. On the contrary Glass 1, with a higher softening temperature, wets the ceramic surface only partially.

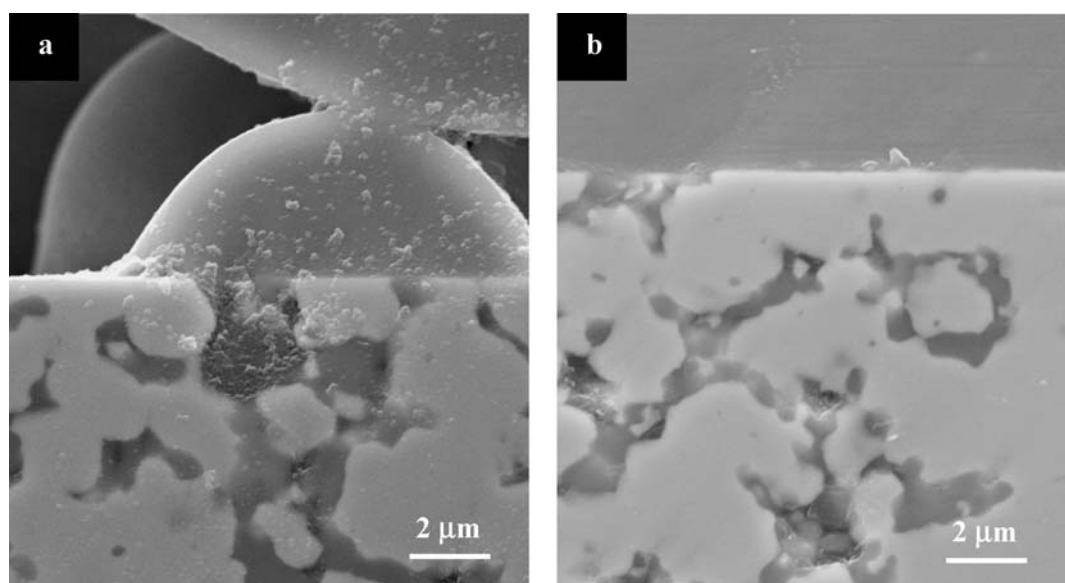


Figure 2 Interface between the ceramic composite and the glass after a thermal cycle of 950°C for 1: (a) ceramic/glass 1; (b) ceramic/glass 2.

On the basis of these results, the coating cycles were conducted in a furnace with graphite heating elements and under flowing nitrogen ($pO_2 < 2.10^{-1}$ Pa), at a temperature of 1440°C for 30 min, for all glasses.

The bonding cycles were carried out in the same furnace using the coated samples with another ceramic slice on top. In order to obtain adhesion between the ZrB₂-SiC composite and the glasses, the temperature of 1440°C was selected for all three glasses as the processing condition.

Bonding tests were also performed on samples previously oxidized at 1120°C for 20 h. The two oxidized surfaces were put in contact and treated at 1300, 1400 and 1500°C for 30 min.

Finally, on the basis of the obtained results, two bonding cycles were conducted using larger ceramic samples which were suitable for testing the mechanical properties of the bonds. In these cases the two halves of a ceramic pellet with a diameter of 3.2 cm were used.

The interfacial microstructure between the ceramic and the glass after the thermal treatments was analysed by optical microscopy (OM), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). The flexural strength of the bonds was evaluated at room temperature in 3-point bending on bars 14.0 × 2.0 × 1.5 mm on a jig of 11 mm span with a crosshead speed of 0.5 mm/min and calculated with the usual bending formula.

3. Results and discussion

3.1. System ZrB₂-SiC composite/glass 1

In this system during the coating tests the glass wets the ceramic extensively and homogeneously and forms a coating of about 50 μm, corresponding to the thickness calculated from the amount of glass powder deposited on the ceramic surface. No crack is found at the interface (Fig. 3a and b). The morphology at the interface and the EDS spectra (Fig. 3c) reveal that both the crystalline phases SiC and ZrB₂ strongly interact with the glass. The SiC grains oxidize forming silica. This oxidation involves the SiC grains located at the ceramic surface, therefore in contact with the glass at the beginning of the test, as well as the SiC grains in the ceramic bulk, that come into contact with the oxygen diffused subsequently into the bulk. The glass penetrates the bulk of the ceramic composite through the channels formed by the silica resulting from the SiC oxidation and the grain boundary amorphous phase originally present in the ceramic. In these areas, besides oxygen, Al and Ca cations are also present due either to mass transfer of glassy phase from the upper regions or to diffusion along the grain boundaries. The massive oxidation of SiC particles, as well as the presence of Al and Ca, is revealed up to a depth of about 120 μm from the upper ceramic surface.

In addition, the contact of the ceramic with the glass involves a reaction of ZrB₂ grains with the glass,

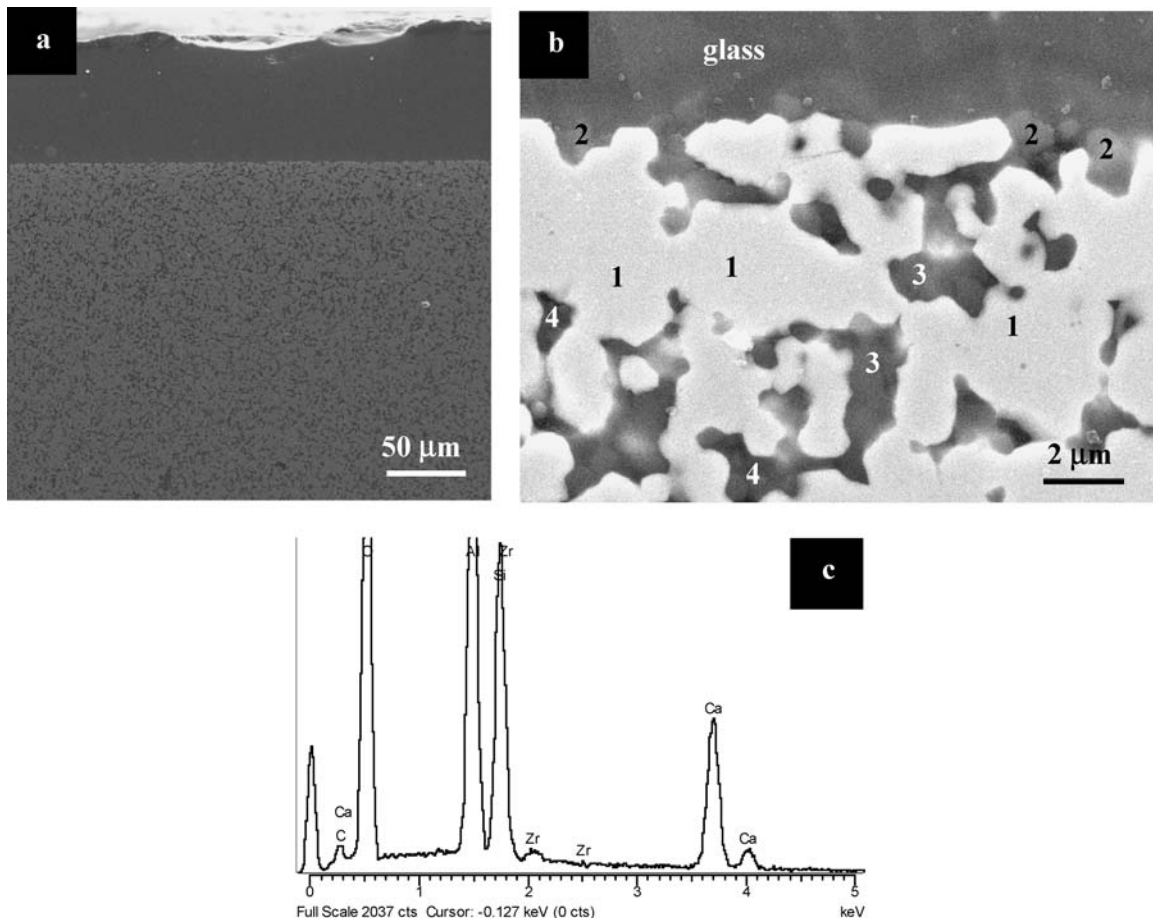


Figure 3 (a) Microstructure of sample formed by ZrB₂-SiC composite coated with glass 1 at 1440°C for 30 min under flowing N₂; (b) glass/ceramic interface: the following phases are identified: 1: ZrB₂, 2: Zr-Si-O phase, 3: Silica due to SiC oxidation, 4: residual SiC particles; (c) EDS spectrum of the elements in the glass.

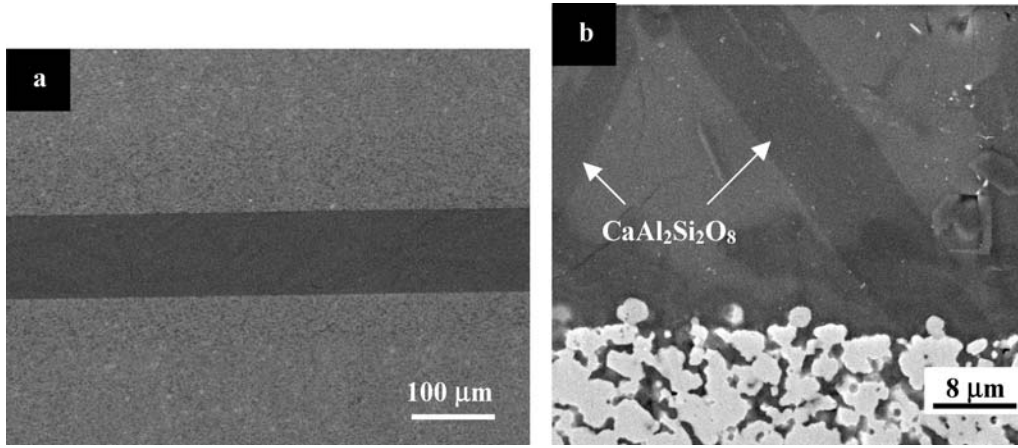


Figure 4 (a) Microstructure of sample formed by two pieces ZrB_2 -SiC composite with glass 1 as interlayer and bonded at 1440°C for 30 min; (b) interface morphology.

leading to a progressive formation of intermediate compounds containing Zr-Si-O at the boundary of ZrB_2 grains (Fig. 3b). Thereafter the so formed compounds dissolve within the glass, as confirmed by the presence of zirconium within the whole glass thickness (Fig. 3c). No ZrB_2 grain detachment and migration is evidenced.

During the bonding cycle neither pores nor cracks form at the interface (Fig. 4a). The glass/ceramic interaction is the same previously described. The glass

interlayer has a constant thickness of $35\ \mu\text{m}$ and crystallizes extensively. The main new crystalline grains have a morphology similar to elongated platelets (Fig. 4b) and the composition, determined by EDS, corresponds to the phase $\text{CaAl}_2\text{Si}_2\text{O}_8$.

3.2. System ZrB_2 -SiC composite/glass 2

The microstructure and elemental analysis of the coated sample are shown in Fig. 5.

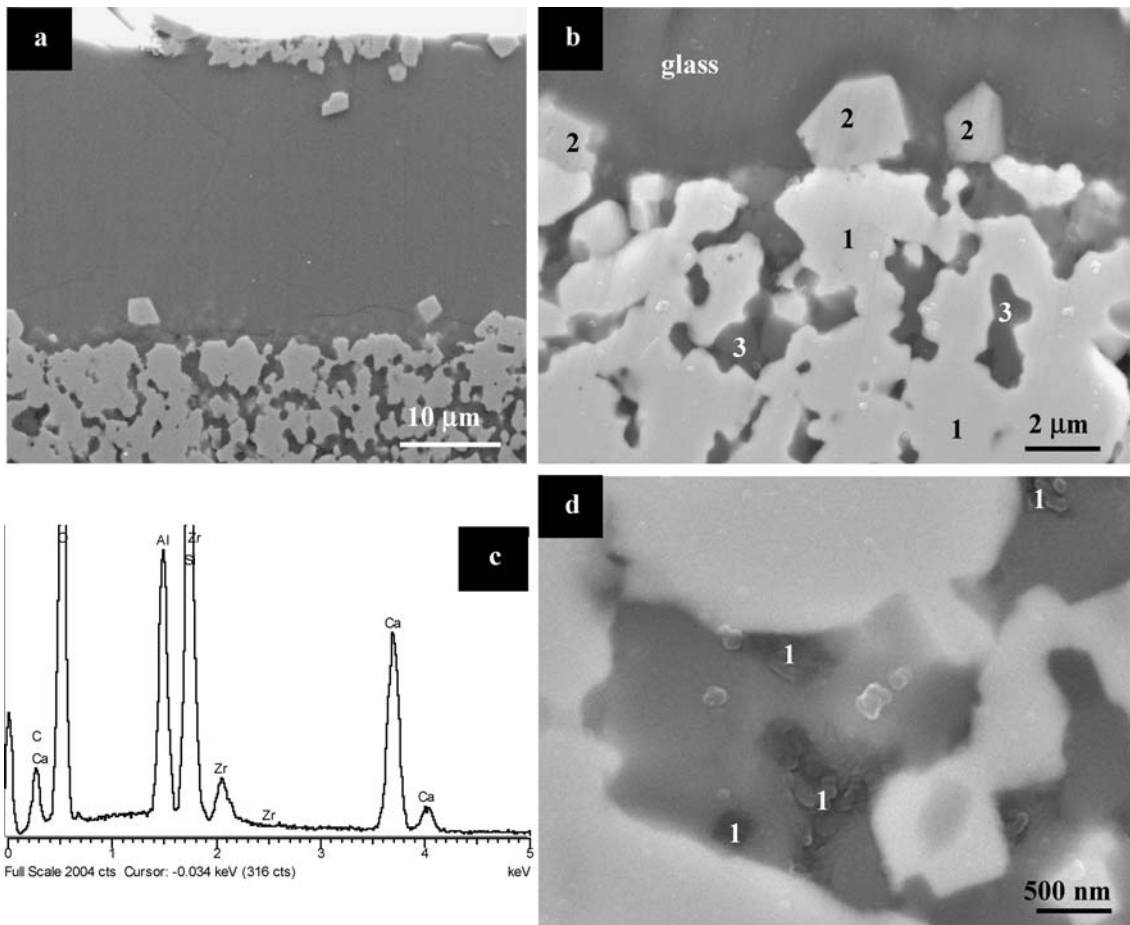


Figure 5 (a) Microstructure of sample formed by ZrB_2 -SiC composite with glass 2 treated at 1440°C for 30 min. under flowing argon; (b) glass/ceramic interface: The following phases are identified: 1: ZrB_2 , 2: Zr-Si-O phase, 3: Silica due to SiC oxidation; (c) EDS spectrum of the elements in the glass; (d) microstructure at about $50\ \mu\text{m}$ from the surface, showing the intergranular pockets where some residual SiC particles are still evident (1): These particles are embedded in a silica-rich glass deriving from the mixing of the original grain boundary phase with the reaction products.

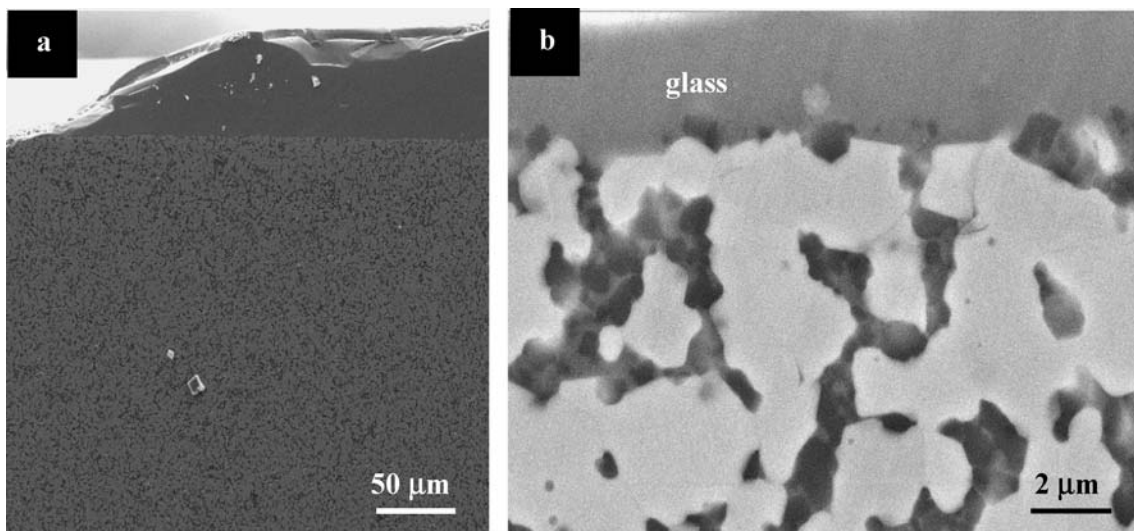


Figure 6 Microstructure of sample formed by ZrB_2 -SiC composite with glass 3 treated at $1440^\circ C$ for 30 min.

The glass wets the ceramic with a contact angle of $10\text{--}20^\circ$ and no cracks form at the ceramic/glass interface (Fig. 5a). The EDS elemental analysis shows the presence of carbon and zirconium within the glass coating, coming from the dissolution of ZrB_2 and SiC grains (Fig. 5b). The morphology of the interface and EDS analyses indicate that the dissolution of ZrB_2 grains through intermediate Zr-Si-O phases is more appreciable than in the previous case when Glass 1 is used. It is possible to observe Zr-Si-O grains detached from the original ZrB_2 grains and floating in the glass; afterwards these grains undergo total or partial dissolution, with the not dissolved parts migrating towards the free surface of the glass (Fig. 5a). This can be explained by the hypothesis that the viscosity of this glass at the test temperature is lower than the viscosity of Glass 1 (the melting point of Glass 2 is $1210^\circ C$, whereas for Glass 1 is $1400^\circ C$), and this feature enhances the glass penetration, favouring either the oxidation of SiC, or the partial reaction and dissolution of ZrB_2 grains. Also in this case the elements present in the glass (oxygen, aluminium and calcium) migrate towards the bulk: they are found up to a depth of about $70\ \mu m$. Oxygen reacts with SiC grains which progressively disappear (Fig. 5d) allowing the production of silica and, therefore, increasing the amount of glassy phase. This glassy phase fills the intergranular voids left among the ZrB_2 grains and progressively induces the reaction at the boundary of these grains giving rise to Zr-Si-O compounds.

The coating thickness however is not homogeneous and part of the ceramic surface is not wet. Presence on the ceramic surface of regions with no glass leads, during the bonding cycle, to the formation of pores at the interface.

3.3. System ZrB_2 -SiC composite/glass 3

The interfacial microstructure of this sample is shown in Fig. 6. Glass 3 coats the ceramic surface in an irregular way, leaving a few, non-wetted islands. No crack forms at the ceramic/glass interface. The dissolution of the ceramic in the glass is poor, as shown by the EDS

spectrum, in which no zirconium and a small amount of carbon are present and by Fig. 6b, in which SiC grains are still present at the interface. Their conversion to silica is much slower than in the cases previously examined. In addition, ZrB_2 grains are less affected by leaching at the boundaries, as confirmed by their sharp edges. The cation migration from the surface glass towards the bulk is very limited (up to about $20\ \mu m$).

This behaviour can be related to the relatively high viscosity of the glass, since its melting temperature is the same as the test temperature.

No bond forms when this sample is heat treated in a sandwich-like way with another piece of ceramic composite. The two ceramic pieces do not adhere to each other.

3.4. Oxidized ZrB_2 -SiC bonded to itself

When the ZrB_2 -SiC composite is treated at high temperature in air a silica layer containing some boron forms on the surface. The thickness, homogeneity and density of this layer depend on the temperature and soaking time, and in general it works as a protective coating against further oxidation in case of applications of the material at high temperature.

The goal of the following set of tests was to exploit this silica layer to bond two pieces of the same material, by putting the two oxidized surfaces in contact. The selected combination of oxidation temperature and time was $1120^\circ C$ for 20 hours, because under these conditions a homogeneous silica layer of $20\ \mu m$ (Fig. 7) forms on the ceramic surface, as shown in a previous study [17], without the formation of bubbles, cracks and spalling, usually found after oxidation at higher temperatures.

Three different bonding temperatures were tested: 1300 , 1400 and $1500^\circ C$ under flowing argon. The soaking temperature was in all cases 30 min. The bond obtained at $1300^\circ C$ exhibited numerous pores. The interfacial microstructures obtained at 1400 and $1500^\circ C$ are shown in Figs 8 and 9, respectively. At $1500^\circ C$ a consistent amount of silica penetrated the ceramic

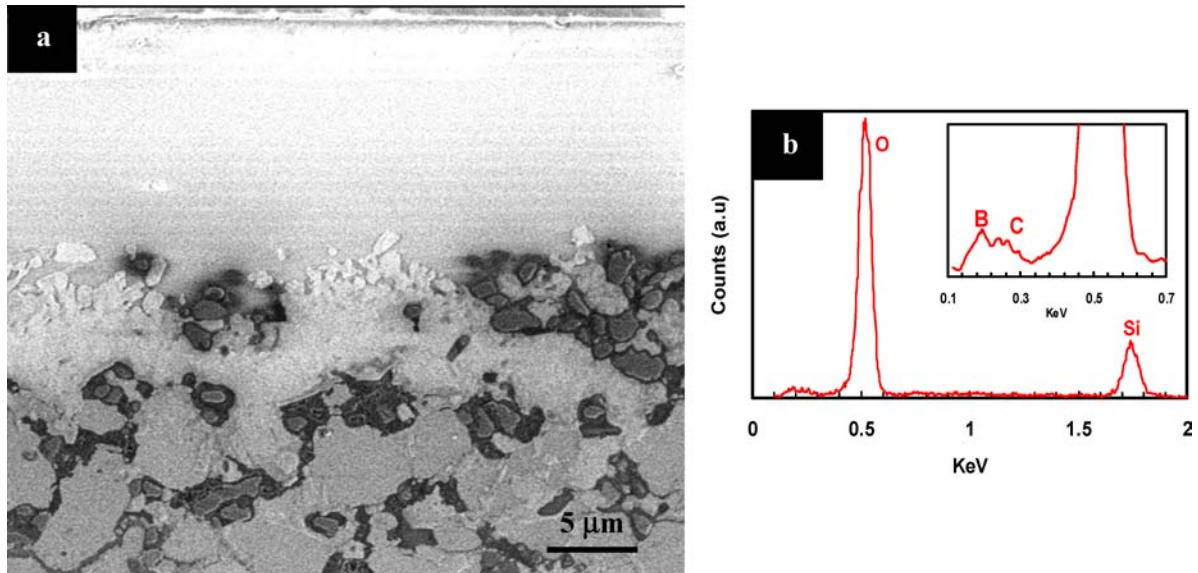


Figure 7 (a) Cross section of the ZrB_2 -SiC sample oxidized at $1120^\circ C$ for 20 h; (b) EDS spectra of the surface oxide scale.

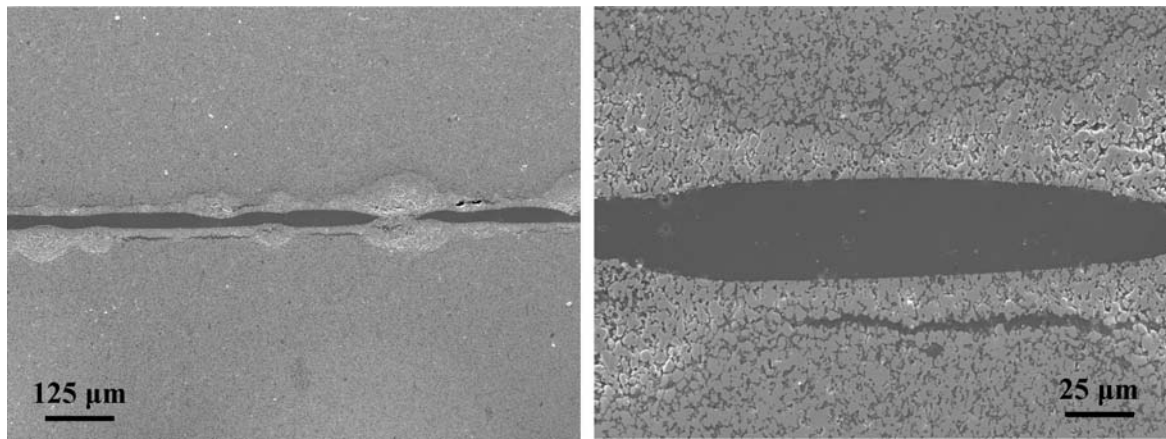


Figure 8 Interfacial microstructure of two ZrB_2 -SiC samples bonded at $1400^\circ C$ for 30 min after being oxidized in air at $1120^\circ C$ for 20 h.

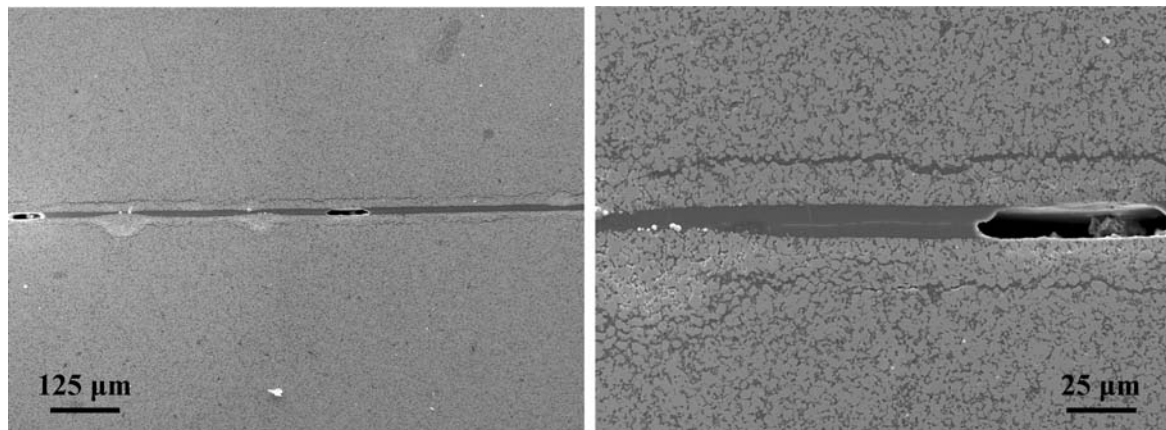


Figure 9 Interfacial microstructure of two ZrB_2 -SiC samples bonded at $1500^\circ C$ for 30 min after being oxidized in air at $1120^\circ C$ for 20 h.

material, thus decreasing the total amount of silica at the interface and promoting pore formation. The resulting mean thickness of the silica layer was about $15 \mu m$. At $1400^\circ C$ the thickness of the silica layer was about $40 \mu m$, as expected from the starting thickness of the coating. In some regions, however, it was not regular, since the liquid glass partially penetrated the ceramic.

This penetration results from the structure of the oxidized sample, that consists of a multilayered structure formed by a surface oxide scale, a reaction interface and a sub-layer affected by partial oxidation of SiC and ZrB_2 . The partial oxidation of the sub-layer gives origin to some porosity and microcracks due to gaseous products that form by the reactions of the constituent phases with oxygen. These voids are filled with

silica-based glassy phases. The subsequent bonding treatment at 1300–1500°C enhances the penetration of the silica-rich glass present at the interface towards the bulk through the defects and open channels previously formed during oxidation. During this penetration, the liquid glass reacts with other oxides deriving from the previous oxidation and reaches the boundary of the oxidation front between the unreacted bulk ceramic and the portion of the material that underwent partial oxidation. In this boundary some microcracks had previously formed by thermal expansion mismatch between the oxidation products (zirconia and Zr-B-O phases) and the original ZrB₂ matrix. In these cracks the molten glass concentrates and forms the thin layers that mark the interface between the partially oxidized material and the starting ceramic composite (Figs 8 and 9).

Due to these characteristics, the interface of the bonded samples is not regular and exhibits some pores and defects.

3.5. Bonding tests on large samples

On the basis of the above results glass 1 was selected to prepare larger samples for the mechanical tests because it gave the best results in terms of interfacial characteristics. Glass 1 has a higher softening and melting temperature than Glass 2 and it induces a more limited dissolution of the phases constituting the ceramic composite. Glass 1 also wets well and coats the ceramic homogeneously. Another positive factor of Glass 1 is the lower thermal expansion mismatch with the ceramic.

These features addressed the activity for the joining of large pieces toward two sets of tests. In the first set Glass 1 was used as interlayer, and in the second set of tests the oxidized samples were bonded together.

In both the cases, the microstructural features are similar to those described for the smaller samples. The following 3-point bending strengths of the joints obtained using Glass 1 as interlayer were measured: at room temperature (277 ± 20 MPa), at 800°C (195 ± 13 MPa) and at 1000°C (88 ± 16 MPa). The most remarkable aspect is the very low standard deviation of the results, indicating that the interface is homogeneous with few defects. This means that this technique can be used to bond components that have to be used at temperatures up to about 1000°C, also under oxidizing environments. Brazed joints cannot be used under these conditions.

The joint produced by putting two oxidized surfaces in contact did not survive to the cutting operations for the preparation of the flexural strength bars. The interfacial defects and glass penetration towards the bulk limited the adhesion between the two parts in contact. This is related to the difficulties in obtaining surface oxide layers with an homogeneous composition and thickness during the oxidation treatments.

4. Conclusions

The joining of ZrB₂-SiC composites using glassy interlayers was successful. By properly selecting the glass

composition, optimal interaction among the phases present in the ceramic and the glass can be achieved: the SiC particles oxidize to silica and the reaction product mixes with the grain boundary phase and penetrates towards the bulk inducing good adhesion. At the same time a partial reaction of ZrB₂ grains also occurs. The key factor is the control of the glass composition and of the processing parameters in order to favour the partial reactions and to avoid excessive interaction.

Using a glass of composition in the system Ca-Al-Si-O with a melting point of about 1400°C, bonded samples obtained at 1440°C exhibited a room temperature strength of 277 MPa. The strength degradation at high temperature is relatively low: at 800°C a value of about 200 MPa was measured.

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