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Microstructure and shear strength of self-joined ZrB_2 and ZrB_2–SiC with pure Ni

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Monolithic ZrB_2 ceramic and ZrB_2–20 vol.% SiC composite were joined to themselves using pure nickel powder. The interfacial phenomena were observed and analyzed. The joining effects were evaluated by shear strength. Resulting from the special interfacial microstructure, the shear strength of ZrB_2/Ni/ZrB_2 system was as high as 59.7 ± 5.3 MPa. In the ZrB_2–SiC/Ni/ZrB_2–SiC system, the reaction between Ni and SiC resulted in a homogeneous joint composition, which was beneficial to the joining effects.

Keywords: Ultra-high-temperature ceramics (UHTCs); Nickel; Joining; Interfacial phenomena

The increasing interest in ultra-high-temperature materials can be traced to the desire for hypersonic flight such as ballistic missiles, re-entry vehicles and hypersonic cruise aircraft [1,2]. Ultra-high-temperature ceramics (UHTCs) are a family of materials with melting temperatures beyond 3000 °C, which mainly include several borides, carbides and nitrides of the group IVB and VB transition metals. As an important UHTC, zirconium diboride possesses some excellent properties, such as high melting temperature (3245 °C), high hardness (23 GPa), high thermal ($\sim 60\ W\ m^{-1}\ K-1$) and electrical ($\sim 10^7\ S\ m^{-1}$) conductivity, low thermal expansion coefficient ($5.9 \times 10^{-6}\ K^{-1}$) and relatively low density ($6.09\ g\ cm^{-1}$). The material is considered as a potential candidate for applications in the fields of refractory materials, electrodes and spaceflight [3,4].

Usually, zirconium diboride is fabricated by hot pressing or pressureless sintering. The addition of SiC can inhibit ZrB_2 grain growth, improve sinterability, and increase the mechanical properties and oxidation resistance [5,6]. However, the difficulty in fabricating UHTCs with complex shapes or large size limits their application. Therefore, great interest has been generated in assembling complex shapes or large sizes from small pieces of ceramics via joining techniques. Consequently, the ability to join the UHTCs to metals and alloys or to themselves using suitable brazes is a very important aspect to consider when exploiting their applications.

To the best of our knowledge, studies on the wetting and spreading of liquid metals or glasses on ZrB_2-based ceramics and the joint properties of these ceramics are quite scarce. Esposito and Bellosi [7] joined ZrB_2–SiC composites using Ca–Al–Si–O glass as interlayers at 1440 °C, obtaining a bending strength of 277 MPa at room temperature. Muolo et al. [8,9] studied the wetting behavior of ZrB_2-based materials in contact with the liquid Cu, Ag, Au and their alloys with active elements. They concluded that optimal results were obtained when silver-based alloys were used, and the quite sharp metal/ceramic interface resulted in much better mechanical properties in the joining process. Nevertheless, the temperature the joint could endure would be no higher than 1000 °C due to the low melting points of these solders. Subsequently, Asthana and Singh studied the joining of the ZrB_2-based UHTCs with some commercial brazes [10] and Pd-based braze alloys [11], but did not report the joining strengths.

Nickel is an important element in the fabrication of high-temperature alloys, and is considered as a potential candidate for high-temperature brazes due to its relatively high melting temperature, low vapor pressure and low price. Furthermore, it has been reported that nickel wets ZrB_2 and HfB_2 ceramics well [12,13], and nickel alloys have been used as braze to join ZrB_2-based

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UHTCs [14]. In the present work, the joint properties of monolithic ZrB_2 ceramics and ZrB_2–20 vol.% SiC composites joined to themselves were studied. The shear strengths of the joints were measured using a stainless steel mould to evaluate the joining effects. The microstructures of the interfaces were examined and the interfacial interactions were analyzed based on thermodynamics. The relationship between the microstructures of the interfaces and the mechanical properties of the joints are discussed.

Commercially available ZrB_2 (14 μm, 99%, Gongyi Sanxing Ceramics Materials Co. Ltd., Gongyi, China) and SiC powders (0.45 μm, 98%, Changle Xinyuan Carborundum Micropowder Co. Ltd., Changle, China) were used as starting materials. They were first mixed in plastic bottles using anhydrous alcohol as the medium, and then dried by rotary evaporation. After that, the mixed powders were sieved through a 200-mesh screen. Subsequently, the composites were hot pressed at 1900 °C for 90 min under a pressure of 30 MPa. Fully dense monolithic ZrB_2 was difficult to fabricate from the commercially available powders. In the present work, fine ZrB_2 powder was first synthesized based on the reaction between ZrO_2 (0.2 μm, 99%) and B_4C (2 μm, 99%), $7ZrO_2 + 5B_4C \rightarrow 7ZrB_2 + 5CO + 3B_2O_3$, at 1600 °C in vacuum, with 15% excess B_4C relative to the stoichiometric composition. The as-synthesized ZrB_2 powder has an average particle size of about 1 μm, and was hot pressed at 2000 °C/30 MPa for 60 min. The relative densities of the hot-pressed ZrB_2–20 vol.% SiC (designated ZS for simplicity) and ZrB_2 (designated ZB) ceramics were about 97.2% and 99%, respectively. The samples above were machined into Φ9.0 mm plates, subsequently ground and polished with diamond paste of 1.5 μm. Pure Ni powder (2.68 μm, 99.9%, Boyle Chemical Co. Ltd., Shanghai, China) was selected as braze.

The ZS and ZB plates were cleaned by ultrasound in acetone and air-dried just prior to each joining experiment. A certain amount of Ni powder was deposited on the polished surfaces like snowing through a 200-mesh screen. The other same plate was put upon the braze very carefully, forming a sandwich structure. A specific weight was put on the upper plate to supply a pressure of 10 kPa, as shown in Figure 1a. The assembly was placed in a graphite furnace for the joining process. The furnace was first evacuated to about 5 Pa at room temperature, and then heated at 10 °C min^{-1} to 1400 °C, followed by dwelling for different times. The samples were cooled down to room temperature at a rate of 5 °C min^{-1}.

The joined specimens were embedded in an epoxy resin and sectioned perpendicular to the joint interface, then ground and polished with 1.5 μm diamond paste. The microstructures of the interfaces were examined by scanning electronic microscopy and energy-dispersive spectrometry (EDS). After carefully removing the residual braze outside the specimens, shear strength was measured using a stainless steel mould (Fig. 1(b)), where the crosshead speed was 0.5 mm min^{-1}. The strengths were calculated from the maximum value of load divided by the overlap area, and the reported value was an average of three measurements. The phase compositions of the joints were analyzed by X-ray diffraction (XRD).

The cross-sections of ZB/Ni/ZB joints after joining at 1400 °C for 40 and 80 min are shown in Figure 2a and b, respectively. They revealed a good contacting, characteristic of Ni on the surface of ZrB_2 ceramic, which resulted in an intimate joining. During the cooling process, the metal interlayer is under tension and the ceramic under compression. The elastic thermal strain, $\Delta\alpha\Delta T$ ($\Delta\alpha$: CTE mismatch, ΔT: temperature interval) may exceed the yield strain of the interlayer and cause plastic flow within the braze. The CTE of Ni and hot-pressed monolithic ZrB_2 are 1.3×10^{-5} and 7.5×10^{-6} °C^{-1}, respectively [14,15]. A slow cooling rate (decreasing ΔT) was effective for releasing the elastic thermal strain, and no cracks were found for the joint with short holding time.

The designed thickness of the interlayer was 100 μm. However, a smaller interlayer thickness was noted in joined samples. To understand this, a separate wetting experiment was conducted in which Ni powders were first placed on the surface of ZrB_2 substrate and then heated to the joining temperature. As a result, the powders melted and formed a liquid droplet below the melting point of nickel. It was possibly caused by the solid-state diffusion prior to melting and the formation of low-melting phases (the phase diagram of the Ni–Zr–B system could not be found). So, part of the melted nickel was extruded under an applied pressure of 10 kPa during the joining process.

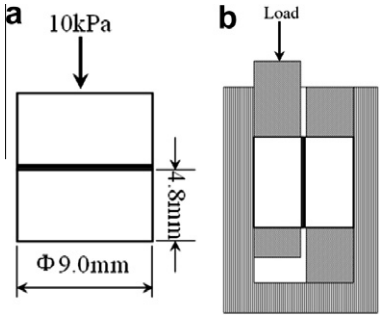

Figure 1. Schematic diagram of the sandwich structure for joining experiments (a) and the stainless steel mould for shear strength tests (b).

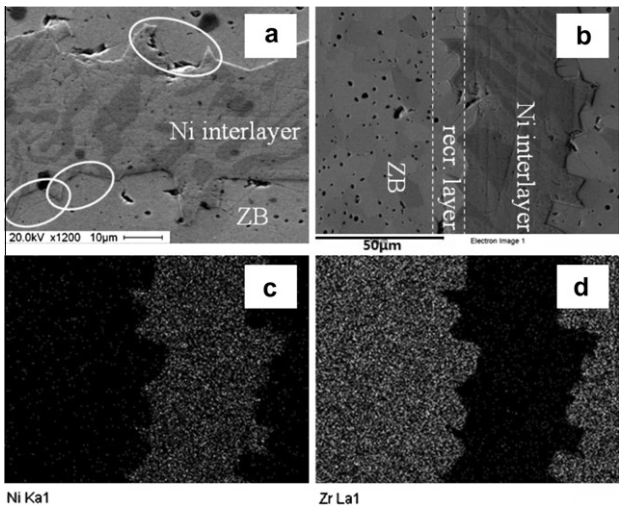

Figure 2. Cross-section of monolithic ZrB2 ceramic after joining at 1400 °C for (a) 40 min and (b) 80 min, and the element distribution maps ((c) Ni and (d) Zr) for (b).