Spark Plasma Sintering of ZrB_2-Based Ceramic Reinforced with SiC Particles and Whiskers

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1-Introduction

Materials based on the transition metals nitride, boride, and carbide possess immensely high melting temperatures and are classified as ultra-high temperature ceramics. Zirconium diboride has shown better combination of features including moderate density, extreme melting temperature and considerable thermal conductivity. This summation of characteristics has converted boride materials candidates for engineering applications such as melted metals crucibles, furnace elements, electronics, industrial tools, and aerospace technology. Anyway, due to the covalent strong bondings and negligible coefficient of self-diffusion, it is hard to densify these materials with no applied external pressure and/or high temperature. On the other hand, the high-temperature oxidation resistance of ZrB_2 (at >1000 °C) and its mechanical properties (such as fracture toughness) are not suitable. Therefore, the many studies have done to improve this limitations of ZrB_2. Various additive parts such as disilicides, carbides, nitrides and metals are employed to upgrade the sinterability and properties of diboride ceramics. The introduction of SiC, as the most common phase in zirconium diborides, not only encourage the sintering mechanism but also increase the bending strength of composite ceramic because of the stoppage of ZrB_2 coarsening over the manufacturing processes.

Up to now, few researchers have focused on the role of the silicon carbide phase morphology on the microstructure, densification and mechanical performance of ZrB_2-based parts manufactured by the field assisted sintering method. For this purpose, a baseline monolithic ZrB_2 and 3 ceramics reinforced with 25 vol% silicon carbide in different morphologies (particulate, whisker and particulate/whisker mixture) were manufactured for 7 min at 1900 °C under 40 MPa by spark plasma sintering process.

2-Experimental

Commercially available ZrB_2 powders (purity>99.9%, Xuzhou Hongwu Co., particle size < 2 μm), SiC particulate (SiC_P: purity>99.0%, Xuzhou Hongwu Co., particle size < 500 nm) and SiC whiskers (SiC_w: purity>99.0%, Xuzhou Hongwu Co., 500 nm< D < 1000 nm, L < 20 μm) were bought as starting materials. The powders were weighted and the slurries of mixed powders were mixed ultrasonically, then dried by hot stirrer plate. The dried powder mixtures were milled using agate mortar and then passed through a sieve. After inserting the mixture into the selected die with an inner diameter of 30 mm, lined with foils of graphite, the field assisted sintering was completed at a temp. of 1900 °C for a hold time of 7 min under a loading of 40 MPa.

The bulk density of the as-SPSed samples were calculated by means of the Archimedes formula with distilled water as the medium. The relative densities of the specimens were computed as the ratio of the bulk per the theoretical densities determined by the rules of mixtures. Microstructures of the fractured/polished sections and the phase investigations of the samples were done by a Mira3 field emission Tescan scanning electron microscope and a PW1800 X–ray Philips diffractometer, respectively. The harnesses values of the sintered samples were obtained via a ZHV10 Zwick Roell Vickers indenter. The fracture toughness of the composites were also estimated by the indentation method of direct crack measurements.

3-Result and discussion

Measured relative densities of as-SPSed samples are displayed in Figure 1. A density of 96% was measured for monolithic ZrB_2 specimen. A near fully dense ZrB_2-based composites with a relative density value of 99.9% were achieved by field assisted sintering under 40 MPa at 1900 ºC in 7 min. It seems that the sintering conditions are desirable to achieve a fully dense samples. The simultaneous addition of the SiC_w and SiC_p leads to the fabrication of the composites with their theoretical densities.

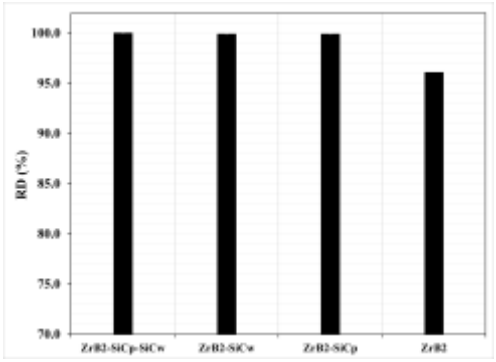

Figure 1. Relative density of spark plasma sintered samples (Reproduced and reused with permission from Y. Pazhouhanfar et al., Ceramics International 46 (2020) 5773–5778).

Figure 2 demonstrates the XRD results of the as-SPSed ZrB_2-based parts. As it can be seen for ZrB_2-SiC_p sample, the detected crystalline lattice of the silicon carbide phase is "hexagonal", on the foundation of the XRD test. This observation confirms that no fresh phase has created in the SPS process. Therefore, the composite manufacturing process can be considered as non-reactive sintering.

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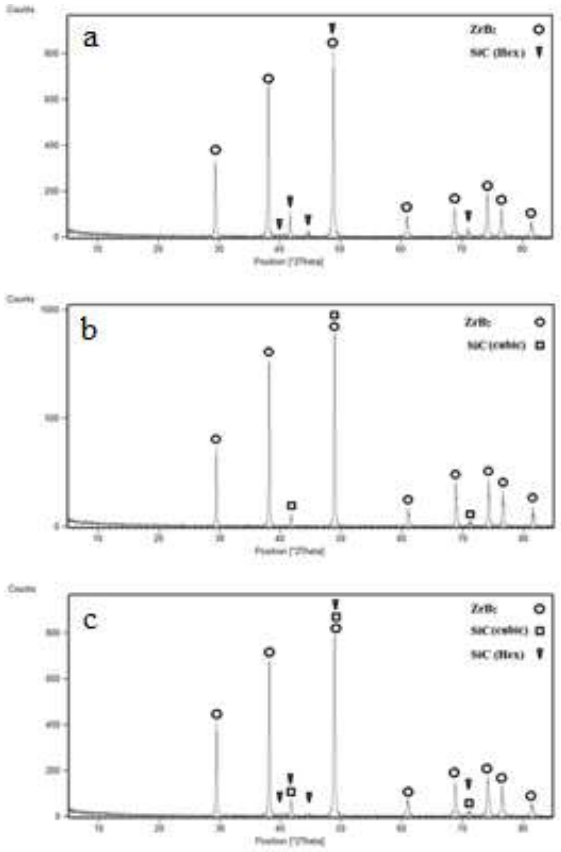

Figure 2. XRD maps of ZrB_2 ceramics reinforced with (a) SiC_p, (b) SiC_w and (c) SiC_p/SiC_w (Reproduced and reused with permission from Y. Pazhouhanfar et al., Ceramics International 46 (2020) 5773–5778).

The result of XRD pattern for the ZrB_2-SiC_w sample is a little different. In addition to the ZrB_2 phases peaks, the β-SiC peaks with cubic crystalline structure are observed that indicates this reinforcement is whisker. The XRD analysis of ZrB_2-SiC_p/SiC_w, indicates the peaks of α-SiC and ZrB_2 as well as β-SiC. In all the samples, SiC is a non-reactive additive. There is no difference between the phase composition of SPSed samples and initial powder mixture, therefore, the sintering process is non-reactive.

A Vickers hardness value of 13.1 GPa was measured for the additive free ceramic. Vickers hardness of SiC reinforced ZrB_2 composite is higher than those additive free one. Measured hardness value for ceramics reinforced with SiC_p, SiC_w and SiC_p/SiC_w were 19.5, 21.9 and 23, respectively. The simultaneous presence of SiC_p and SiC_w in the sintered microstructures, led to the increase in the hardness value. It seems that the more effective inhibitory role of SiC_w on dislocation motion (compered to SiC_p) is a reason for such an observation. Therefore, SiC_w may resist in a great trend than the SiC_p against the deformation over the hardness testing.

Fracture toughness of ceramics reinforced with SiC_p, SiC_w and SiC_p/SiC_w were estimated 4.3, 4.7 and 6.2 MPa $m^{½}$, respectively. These values is higher than measured fracture toughness for Z sample (3.2 MPa $m^{½}$). The FESEM results of indentation-created cracks on the polished ZrB_2-SiC_p are depicted in Figure 3. Deflections have been induced by the interaction of the initiated crack with secondary grains as reinforcement. In addition to the deflections, other toughening mechanisms including the crack bridging, branching and the defragmentation of a big SiC can also be observed. In ZrB_2-SiC_w, whiskers may pull out or fracture over the propagation of cracks or reactivate other mechanisms e.g. deflection or bridging. In the ZrB_2-SiC_p/SiC_w, an upgrade in the fracture toughness is attributed to the simultaneous toughening roles of silicon carbide particles and whiskers.

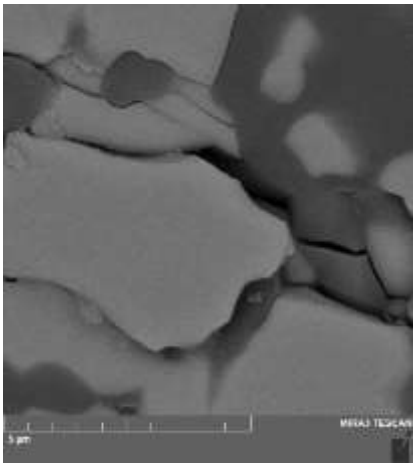

Figure 3. FESEM image of an indentation-created path of crack in the polished section of ZrB_2-SiC_p composite.

4-Conclusion

To investigate the role of silicon carbide morphology on densification and mechanical response of ZrB_2-matrix composites, a monolithic ZrB_2 ceramic and 3 ZrB_2-based ceramics strengthened with 25 vol% silicon carbide in several morphologies (particulate, whisker and particulate/whisker mixture) were field assisted sintered at 1900 °C for 7 min under 40 MPa. Compared to the monolithic part (with a relative density of 96%), the other materials reached their complete densities.

The mechanical performance (hardness and fracture toughness) of carbide reinforced samples were better than those for the monolithic one. Synergistic influence were observed on the improvement of mechanical efficiency of composite by the simultaneous addition of SiC particulates/whiskers.