Materials and Design 104 (2016) 43–50

Contents lists available at ScienceDirect

Materials and Design

journal homepage: www.elsevier.com/locate/matdes

Densification and characterization of hot-pressed ZrC-based composite doped with Nb and CNT

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ARTICLE INFO

Article history:
Received 6 March 2016
Received in revised form 28 April 2016
Accepted 1 May 2016
Available online 4 May 2016

Keywords:
ZrC
Nb
CNT
Microstructure
Mechanical properties

ABSTRACT

ZrC-based composite doped with 20 vol.% niobium (Nb) and 3 vol.% carbon nanotubes (CNT) was prepared by hot pressing. Due to the addition of Nb and CNT, the sinterability of ZrC was significantly improved, resulting in highly dense matrix (99.28%) at reduced sintering temperature (1600 °C). The flexural strength was 590 MPa at room temperature and 563 MPa at 800 °C, respectively. The fracture toughness was 7.23 MPa·m$^{1/2}$, which increased by 80% compared with the monolithic ZrC (4 MPa·m$^{1/2}$). In addition, the work of fracture was calculated to be 267 J/m^2. Based on the microstructure characterizations, the improved fracture properties could be attributed to crack deflection, crack bridging and crack branching, which consumed more fracture energy during the fracture process.

1. Introduction

Owing to the high hardness (25 GPa), high Yong's modulus (390 GPa) as well as high melting point (3420 °C), zirconium carbide (ZrC) has been considered as the candidate material for cutting tools, jet engines and leading edges of re-entry space aircraft [1–3]. Nevertheless, ZrC is also well known for its poor sinterability due to strong covalent bonding characteristic and low self-diffusion coefficient. Therefore, the densification of ZrC was typically accomplished by applying pressures (30–40 MPa) at high sintering temperature (2000–2300 °C). For example, it was shown by Barnier et al. [4] that ZrC could be sintered to a relative density of 98% by hot pressing (HP) at 2300 °C with an applied pressure of 40 MPa. Moreover, on account of the intrinsic brittleness of ZrC ceramics, their toughness is in the range of 3–4 MPa·m$^{1/2}$, which is not high enough to show the high reliability during application. Recently, Acicbe et al. [5] studied the mechanical properties of spark plasma-sintered (SPS) ZrC ceramics, revealing that the fracture toughness was as low as 3.3 MPa·m$^{1/2}$, despite the high relative density of ~96%.

To solve the problems mention above, the preparation of ZrC-based composites (by adding a second phase) has become one of the most promising approaches in recent years. For example, high strength ZrC-Al composites with relative density above 98% were prepared by reactive hot pressing (RHP) of ZrC and Al at 1900 °C [6]. The reaction between ZrC and Al resulted in the formation of ZrC_{1-x}, $Zr_3Al_3C_5$ and Al-Zr compound, which could improve the densification behavior and mechanical properties of ZrC-Al composites. In addition, through the addition of 40 vol.% Mo into ZrC, highly dense ZrC-Mo composites could also be fabricated at 2200 °C by pressureless sintering (PS) [7]. The improved sinterability of ZrC-Mo composites was attributed to the formation of Mo_2C and its subsequent eutectic reaction with Mo. Most recently, other metals or nonmetals, such as Zr, C, Si, ZrO_2, etc., were separately doped to prepare dense ZrC-based composites with improved fracture toughness [8–12]. However, the optimized sintering temperature of these ZrC-based composites were still in the range of 1800–2000 °C. Furthermore, disilicides, such as $TaSi_2$ [13] and $MoSi_2$ [14], were added into ZrC in order to reduce the sintering temperature. Owing to the formation of liquid phase during sintering, the sintering temperature of ZrC-$TaSi_2$ or ZrC-$MoSi_2$ composites was significantly reduced to ~1700 °C. Whereas, the fracture toughness of the resulting composites was only ~3.6 MPa·m$^{1/2}$, with no sign of toughening effect as compared to the monolithic ZrC ceramics.

To obtain dense ZrC-based composites with satisfied fracture toughness, the addition of Nb may be more suitable due to its outstanding effectiveness in the improvement of densification behavior and fracture toughness [15–19]. Sun et al. [15–16] reported that Nb was conducive to the sintering process of ZrB_2-based ceramics on account of its ductile deformation at high temperature. This could help the ZrB_2 grains align under the applied pressure during sintering. As a result, highly dense ZrB_2–Nb composites (~99%) with a high fracture toughness of 6.19 MPa·m$^{1/2}$, were prepared by hot pressing at 1800 °C. The addition of a ductile phase into a brittle ceramic matrix was shown to be an effective method in the improvement of fracture toughness [19–21]. Because the ductile phase can dissipate the energy of crack initiation and propagation through plastic deformation, consequently making a large

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http://dx.doi.org/10.1016/j.matdes.2016.05.003

contribution to the increment of toughness for brittle ceramic materials. Nevertheless, the Nb content in the matrix of ZrC-based composites should be kept in a reasonable scope. The reason is that excessive residual Nb would deteriorate the high temperature mechanical properties of ZrC-based composites. Therefore, the co-addition of Nb and CNT may be a win-win approach because the residual Nb can react with CNT to form NbC, which is a refractory carbides with good thermal-mechanical properties. In addition, owing to the large specific surface area and high surface energy, CNT would react more easily with Nb when compared with other carbon sources, such as carbon black and graphite powder. Furthermore, CNT was shown to be an effective reinforcement for ZrB_2-based ceramics, on account of its multiple toughing mechanisms such as crack bridging and crack deflection [22–24]. In view of the successful utilization of Nb or CNT in ZrB_2-based composites, the similar mechanisms should, in principle, apply to the ZrC-based composites.

Therefore, ZrC–Nb–CNT ternary composite was designed in this paper in order to prepare highly dense ZrC-based composites with high fracture toughness. The purpose of this study is to investigate the densification behavior, microstructure evolution and mechanical properties of ZrC–Nb–CNT composite. As far as we know, the relevant research has rarely been reported.

2. Experimental procedure

2.1. Materials fabrication

Commercial powders of ZrC (purity: >99%, average particle size: 80 nm, supplied by Alfa Aesar Co., Ltd., China), Nb (purity: >99%, average particle size: 325 mesh, supplied by Alfa Aesar Co., Ltd., China) and CNT (purity: >97%, average diameter: 30 nm, average length: 10 μm, supplied by Shenzhen Nanotech Port Co., Ltd., China) were used as the raw materials in this work.

Based on previous sintering tests, the composition of the composite was designed as follows (in vol.%):

ZrC–20Nb–3CNT (hereafter, it is referred as ZNC).

To get homogenized and fine powder mixtures, the ZrC–20Nb powder mixtures were ball-milled at a speed of 250 RPM for 24 h by using WC balls (diameter: 3 mm) and ethanol as the milling media. In order to minimize the aggregation of the doped CNT, the CNT was firstly immersed into acetone for about 24 h and then was ultrasonically dispersed for 3 h. After the dispersion, the CNT was mixed with the ball-milled ZrC–20Nb slurry by magnetic agitation for 10 h. Again, a ball milling was applied to the final ZrC–20Nb–3CNT mixtures at a speed of 250 RPM for 12 h for further mixing. After that, the powder mixtures were dried by rotary evaporator under vacuum condition and then were sieved to 60 mesh. Finally, the resulting powder mixtures were placed in a BN-coated graphite die (inner diameter: 30 mm) and hot-pressed at 1600 °C under vacuum condition (<25 Pa). The applied pressure of 30 MPa was adjusted to the powder at RT and kept constant throughout the hot pressing process. The pressure was applied at the beginning of the sintering process because high green density is favorable for better densification by reducing the pores prior to densification during heating. The heating rate was about 10 °C/min and the holding time at terminal temperature was 60 min. The temperature was measured by an infrared pyrometer through a hole opened in the graphite die. Furthermore, in order to monitor the densification process, the shrinkage of the powder compact was measured by recording the displacement during hot pressing. The hot-pressed composite was about 30 mm in diameter and 5 mm in thickness.

2.2. Characterization

The bulk density and open porosity of the hot-pressed composite were measured by the Archimeds methods with distilled water. The theoretical density was calculated according to the rule of mixtures. According to the ASTM: C1327-15, the hardness was tested by Vickers indentation with 10 N as the applied load for 15 s on a polished section. The reported Vickers hardness was the mean values of 10 measurements.

The composite was cut by wire-electrode cutting in order to get the standard bars for mechanical tests. The dimensions of the bars were 25 mm × 2 mm × 1.5 mm for the flexural strength test and 25 mm × 2 mm × 4 mm for the fracture toughness test, respectively. The flexural strength was measured by means of 3-point bending test according to the ASTM: C1161-13. The support span was 20 mm and the crosshead speed was 0.5 mm/min. The flexural strength was also tested at 800 °C in atmosphere environment. During the testing, a heating rate of 10 °C/min and a holding time of 60 min were applied, in order to reduce the non-uniform temperature distribution in the test chamber. The fracture toughness (K_{IC}) was measured by means of the single edge notched-beam (SENB) test following the ASTM: C1421-10. The support span was 20 mm and the crosshead speed was 0.05 mm/min. For each test, at least five samples were used. Besides the fracture toughness, the work of fracture was calculated to evaluate the toughness of the hot-pressed composite.

The phases of the raw powders and hot-pressed composite were characterized by X-ray diffraction (XRD) with Cu Kα radiation. The morphologies of polished surface and fracture surface were observed by optical microscopy and scanning electron microscopy (SEM) equipped with energy dispersive spectrum (EDS) analysis.

3. Results and discussion

3.1. Densification

Fig. 1 shows the SEM micrograph of the ball-milled ZNC powder. It was found that the doped CNT was uniformly distributed in the powder mixtures without any agglomeration. Generally, the CNT is prone to aggregation during mixing due to the high aspect ratio. The prepared ZNC powder exhibit fine morphology and high homogeneity, indicating that the mixing procedure in this study is very effective. Typically, the homogeneous and fine powder is conducive to the densification process of ceramic composites.

Fig. 2 shows the densification curve of ZNC composite during hot pressing. As indicated by the arrows, the densification process can be divided into three stages. In stage 1, the relative density of ZNC remained at about 61% without obvious densification until the sintering temperature reached to 1200 °C. In stage 2, with the further rising of sintering temperature, a rapid densification was displayed in the range of 1200–1600 °C. At the end of this stage, a relative density of 96.75% was achieved when the sintering temperature reached to 1600 °C. In

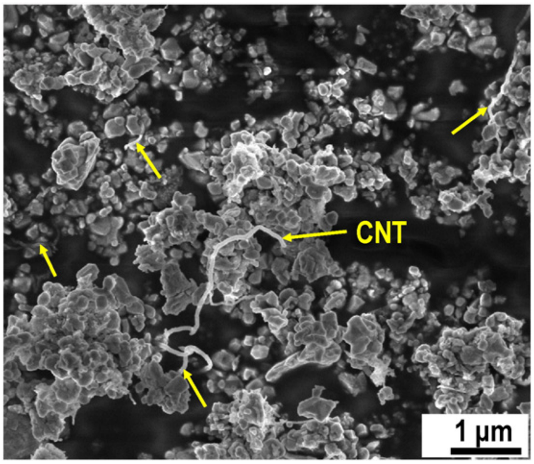

Fig. 1. SEM micrograph of the ball-milled ZNC powder.