Materials and Design 110 (2016) 340–345

Contents lists available at ScienceDirect

Materials and Design

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

Effect of WC or ZrC addition on thermal residual stresses in ZrB_2—SiC ceramics

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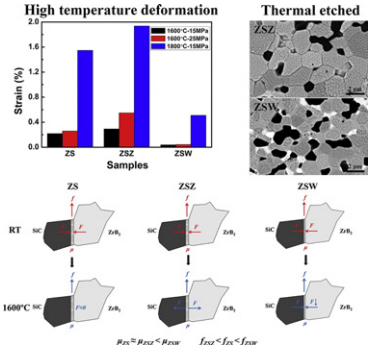
HIGHLIGHTS

- Residual stresses in ZrB_2—SiC with addition of WC or ZrC were measured.
- High-temperature resistance to deformation of ZrB_2—SiC-based ceramics was evaluated.
- Relationship between mechanical properties and residual stresses was analyzed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 22 June 2016
Received in revised form 31 July 2016
Accepted 1 August 2016
Available online 3 August 2016

Keywords:
ZrB_2
Residual stresses
High-temperature deformation
High-temperature mechanical properties

ABSTRACT

The residual stresses in ZrB_2—SiC ceramics with the addition of WC or ZrC were measured using Raman spectroscopy (RS) and X-ray diffraction (XRD). The temperatures at which the residual stresses began to accumulate were calculated. The resistance to high-temperature deformation of ZrB_2—SiC-based ceramics was evaluated via four-point flexure test under a static load (15, 25 MPa) for 5 h at 1600 °C and 1800 °C. The results indicate that a compressive residual stress existed in SiC particles and a corresponding tensile stress applied in ZrB_2 matrix. The values of thermal residual stresses increase in order of ZSZ (ZrB_2—SiC—ZrC) < ZS (ZrB_2—SiC) < ZSW (ZrB_2—SiC—WC). The temperature composite begin to accumulate the residual stresses also increases in the same order. The apparent different behaviors are resulted from their dissimilar grain boundary state and third phase nature in three ceramics. The phenomenon was explained by a proposed model. The results provide a path to design material compositions with an ideal mechanical properties and guidance role for applications.

1. Introduction

Ultra-high temperature ceramics (UHTCs), such as zirconium diboride (ZrB_2) and hafnium diboride (HfB_2), have received significant attention, because of their potential applications in thermal protection systems [1]. The addition of silicon carbide (SiC) to ZrB_2 increased its strength [2,3], fracture toughness [4,5] and oxidation resistance [3,6].

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http://dx.doi.org/10.1016/j.matdes.2016.08.009
0264-1275/

In order to promote the densification and improve the properties of ZrB_2—SiC-based UHTCs further, different additives such as WC [7], VC [8], ZrC [7,9], B_4C [10], were studied.

Previous research [8] indicated that ZrB_2—SiC—ZrC (ZSZ) ceramics had very excellent bending strength at room temperature (>1 GPa). However, the strength degraded seriously when temperature increased to 1600 °C. Compared to ZrC, WC had the opposite effect on the mechanical properties of ZrB_2—SiC ceramics, i.e. ZrB_2—SiC—WC (ZSW) ceramics had lower room temperature strength, but the flexural strength significantly increased as temperature rises to 1600 °C. This is because the ZrB_2—SiC—WC ceramics had cleaned grain boundaries at elevated temperature. However, the stress states of grain boundaries also influence the high-temperature mechanical properties (bending strength and creep resistance) [11]. Due to the mismatch in coefficient of temperature expansion (CTE) between ZrB_2 (~5.2 ppm/K [12]) and SiC (~3.3 ppm/K), the matrix (ZrB_2) tries to shrink at a faster rate than the SiC particles during cooling down from the densification temperature to room temperature. As a result, the residual stresses were generated and developed in the ZrB_2 matrix and the SiC particulate phase after cooling down to room temperature. The effect of the residual stresses on the mechanical properties of ZrB_2—SiC ceramics at room temperature has been studied [13,14]. However, there is lack of research on influence of the residual stresses on mechanical properties of the ceramics at various temperatures.

In this present work, the residual stresses generated in the hot pressed ZrB_2—SiC (ZS), ZSZ and ZSW composites during cooling from the densification temperature were measured using both Raman spectroscopy (RS) and X-ray diffraction (XRD). According to the residual stress values, the temperatures at which the stress started to accumulate were calculated. Then, four-point flexural creep deformation of these samples in high purity argon atmosphere under a static load was investigated. The relationship between residual stresses and high-temperature mechanical properties of these composites were studied. A mechanism model was proposed to explain the results. Based on the results, the composition of the composite materials with the ideal mechanical properties is able to be designed. The understanding on the residual stresses in ceramics parts is helpful for the applications in the future.

2. Experimental procedure

Self-synthesized ZrB_2 powder (D_{50} = 1.05 μm, purity 98%, O 0.46 wt.%), ZrC powder (D_{50} = 0.85 μm, purity 98%, O 0.88%), commercial α-SiC (D_{50} = 0.45 μm, purity 98.5%, Changle Xinyuan Carborundum Micropowder Co. Ltd., China) and WC powder (D_{50} < 1 μm, Hard alloy Co., Ltd., Zhuzhou, China) were used as the starting materials. ZrB_2 powder was synthesized through a boron/carbon thermal reaction between ZrO_2 and B_4C in vacuum. An appropriate amount of each powder was used to prepare 80 vol.% ZrB_2 and 20 vol.% SiC for ZS and 80 vol.% ZrB_2, 20 vol.% SiC and additional 5 vol.% WC or ZrC for ZSW or ZSZ. The starting powders were mixed for 24 h in a polyethylene jar using ethyl alcohol and Si_3N_4 balls, then the slurry was dried by rotary evaporation. The dried powders were sieved through a 200-mesh screen and then were placed in a graphite die (37 × 30 mm) with an h-BN coating. The mixtures were heated to 1600 °C and held at this temperature for 30 min, then a pressure of 30 MPa was applied and the furnace was backfilled with argon gas. Subsequently the samples were heated to the final temperature 2000 °C and held for 1 h. Specimens prepared for high-temperature creep test and residual stress measurements were polished to a 0.5 μm diamond finish.

2.1. Raman spectroscopy method

In crystalline materials without strain, interatomic force constants as well as the vibrational frequencies correspond to the equilibrium atomic spacing [15]. Both cooling process after sintering and mechanical machining (such as finish and polish) generate residual stresses in materials, which will change equilibrium atomic spacing and interatomic force constants [16]. Therefore, Raman Spectrum (RS) can be employed to measure residual stress in materials, based on the shifts of characteristic Raman band positions when the material is subjected to a stress/strain field [17]. However, ZrB_2 could not be detected by RS since it is not Raman active. Therefore, Raman patterns are acquired only from SiC particles for ZS-based ceramics. This method has been used by Watts et al. [13,18] and Stadelmann et al. [14,19] to measure the residual stress in ZrB_2—SiC composites.

In the present work, the RS measurements were made using a Raman spectrometer (RenishawinVia Raman microscope) with 514.5 nm Ar^+ laser. Prior to collecting data, the instrument was calibrated using a silicon standard and the main silicon peak at 520.7 cm^{-1}. Raman measurement for ZS, ZSZ and ZSW was repeated at least 15 individual SiC points for getting a highly reliable data.

2.2. X-ray diffraction method

X-ray diffraction (XRD) is extensively used to measure the residual stresses, especially for metals and alloys. Zhang et al. employed this method to detect the residual stresses in TiB_2/SiC ceramic composites [20]. In the present work, XRD analysis was performed using CuKα radiation at 40 kV and 200 mA (λ = 1.540562 A, D/max 2550 V, Japan). Slid-inclination method was chosen to measure the residual stresses and the average stress was calculated from:

$$\sigma_\phi = -\frac{E}{2(1+\mu)}\frac{\pi}{180}\frac{\partial 2\theta_{\phi\psi}}{\partial \sin^2\psi}\cot\theta_0 \quad (1)$$

Where E, μ are Young's modulus and Poisson's ratio for the particular phase, $2\theta_0$ is the diffraction angle of a peak in a non-stressed sample and its theoretical datum can be used here. Ψ is the tilt degree of samples and $\partial 2\theta_{\phi\psi}/\partial \sin^2\psi$ is the slope of the line $2\theta_\psi - \sin^2\psi$.

As the fraction of SiC in the ZrB_2—SiC composites is <20 vol.% and Si is an element with lower atomic weight, compared with Zr, the intensities of peaks of SiC phase are quite low, especially in the high angle. Therefore, only ZrB_2 peaks were used to measure the residual stress. For ensuring accuracy of the measured values, three conditions must be taken into account: (1) The diffraction angle should be high; (2) The intensity of the peak should be strong; (3) The peak should be in good shape. However, the first condition and the last two are contradictory. In this work, the (211) peak of ZrB_2 at 2θ = 101.438°. was selected by comprehensive considering of the three conditions. Accordingly, the scan range was chosen from 100.400° to 102.600° with scan speed of 0.500°/min. In order to determine the value of the slope, seven ψ values (i.e. ψ = 0, 15, 25, 30, 35, 40, 45°.) were acquired.

2.3. Resistance to high-temperature deformation

The resistance to high-temperature deformation was evaluated using four-point flexure test with outer span of 30 mm and inner span of 10 mm under an applied static loads (15, 25 MPa) for 5 h at 1600 °C and 1800 °C provided by the gravitation of a tungsten, as reported in Guo's work [21]. The samples with dimensions of 3 × 4 × 37 mm for load of 15 MPa and 2.3 × 4 × 37 mm for load of 25 MPa were heated at a rate of 20 °C/min to the test temperature and held for 5 h in the graphite element furnace (MRF3338, Materials Research Furnaces Inc., Suncook, USA) in a high purity argon atmosphere. The samples were cooled down to room temperature under the applied load. The deformation displacements of the samples were measured at room temperature. Based on the creep displacement, the strain (ε) in four-point