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Pressureless sintered in situ toughened ZrB_2–SiC platelets ceramics

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Abstract

ZrB_2–SiC composite ceramics were densified by pressureless sintering with addition of Si_3N_4 or $MoSi_2$ at temperatures that induced SiC anisotropic growth from particles to platelets, within a ZrB_2 matrix with rounded grains. Si_3N_4 addition resulted in the formation of large amounts of liquid phase which enhanced mass transfer mechanisms in terms of matrix grain growth and homogeneous distribution of SiC platelets having an aspect ratio of 3. On the contrary, $MoSi_2$ helped the densification with local formation of liquid phases leading to a finer matrix with finer SiC platelets, though more agglomerated and with a lower aspect ratio (about 2). These different microstructures had very different fracture properties values, namely a toughness of 3.8 MPa $m^{1/2}$ and a strength of 300 MPa for the Si_3N_4-doped composite; toughness of 5 MPa $m^{1/2}$ and strength of 410 MPa for the $MoSi_2$-doped one.

Keywords: Borides; Platelets; Sintering; Microstructure; Toughness and toughening

1. Introduction

Zirconium diboride-based materials are currently considered a class of promising materials for several applications, in particular in the aerospace sector. In the last five years, research has focused on the fabrication of dense composites possessing high strength (500–1000 MPa).[1–4] However, the low fracture toughness remains one of the major concerns for the application of these materials under severe environmental conditions. Commonly, the fracture toughness of various ZrB_2-based composites is hardly higher than 4.5 MPa $m^{1/2}$. This can be seen in Fig. 1 (white columns) which shows the fracture toughness of several ZrB_2-based materials produced in our labs. They embrace both monolithic ZrB_2, i.e. only containing sintering agents below 5 vol%, and composites containing particulates of SiC.[4–7] The fracture toughness of these materials was measured with the same chevron notched beam (CNB) technique. As it can be seen the values range from about 2.9 to 4.0 MPa $m^{1/2}$ for unreinforced materials and from 3.8 to 4.6 for SiC particle reinforced ZrB_2.[4–7] Other toughness values reported in the literature were not included in the comparison as they were very often obtained with a different testing technique, and it is widely recognized that the testing technique can have a large impact on the measured toughness value.[8]

From Fig. 1, it is particularly evident that often the addition of particles does not represent an effective strategy for a major toughness improvement. In case of SiC particles, for example, it has been shown that residual tensile stresses are developed in the ZrB_2 matrix, due to the difference of thermal expansion coefficient between SiC and ZrB_2.[9] As a result, particle-reinforced ZrB_2–SiC materials are often as brittle as other ZrB_2-based composites even if they display significant increase of hardness and strength.

Spherical reinforcement can be efficaciously substituted by elongated reinforcement. The potential advantages of elongated secondary phases over particulate-reinforced systems include more effective toughening mechanisms such as enhanced crack deflection and load-carrying capability. In addition, other toughening mechanisms, such as crack bridging and pullout, are possible. Indeed, significant increases of fracture toughness have been recently obtained through addition of SiC whiskers[10–12] or carbon fibers.[13] Also for the SiC whisker-reinforced ZrB_2 composites and SiC chopped fiber-reinforced composites produced in our labs a significant toughness improvement has been obtained[14,15] especially when the content of whisker or fiber was around 20 vol%, see Fig. 1 (dark grey columns). However, it must be mentioned that processing this kind of composites requires special care, as the reinforcement can be severely

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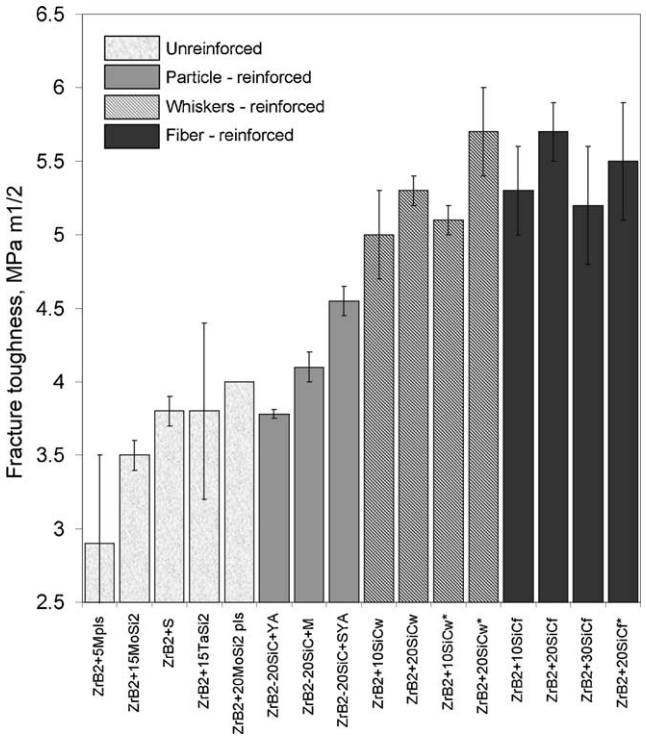

Fig. 1. Comparison of the fracture toughness values of several ZrB_2-based materials produced in our labs, un-reinforced (from Refs.[4–7]), particle-reinforced (from Refs.[4–7]), whiskers reinforced (from Refs.[14,15]) and chopped-fibers reinforced composites (from Refs.[14,15]). All the values were obtained by the chevron notched beam technique. Error bars represent ±1 standard deviation.

degraded if the sintering temperature is higher than 1750 °C: SiC whiskers tend to agglomerate and transform into particles, SiC chopped fibers undergo decomposition and progressive detachment from the matrix. This implies that only pressure-assisted techniques (hot pressing, spark plasma sintering) can be used to effectively sinter these composites, which means that the possibility to obtain reinforced materials by pressureless sintering is highly reduced or very difficult when these kinds of reinforcement are introduced. On this line, it is worth mentioning the notable increase of fracture toughness that has been recently obtained through development of elongated ZrB_2 grains by pressureless sintering at $T = 2200$ °C.[16]

In this work, the main objective was to explore the possibility to obtain tough ZrB_2–SiC composites in which SiC platelets, an intermediate reinforcement geometry between particles and fibers, are developed in situ by pressureless sintering. The main advantage of pressureless sintering over pressure-assisted sintering is the possibility to produce near-net shaped components. The direct incorporation of commercially available SiC platelets would in fact require the use of pressure-assisted techniques, as these large reinforcements would hinder the matrix densification.

ZrB_2 materials containing 20 vol% SiC platelets were produced by starting either from α- or β-SiC particles. The pressureless sintering cycle was set in order to obtain coalescence and anisotropic growth of SiC starting particles, which normally occurs at temperatures higher than 1900 °C. This anisotropic growth offers the possibility to obtain an in situ reinforcement and, potentially, an increase of fracture toughness.[17] Different sintering aids, such as Si_3N_4 and $MoSi_2$, are used and their effect on microstructure and fracture properties is compared.

2. Experimental procedure

The following compositions were selected for the present study:

$ZrB_2 + 5$ vol% $MoSi_2 + 2$ vol% α-SiC particles, labeled as ZMα.
$ZrB_2 + 5$ vol% $MoSi_2 + 20$ vol% β-SiC particles, labeled as ZMβ.
$ZrB_2 + 5$ vol% $Si_3N_4 + 20$ vol% β-SiC particles, labeled as ZSβ.

Commercial powders were used to prepare the ceramic composites:

ZrB_2 Grade B (H.C. Starck, Germany), specific surface area 1.0 m^2/g, impurities: 0.25 wt% C, 2 wt% O, 0.25 wt% N, 0.1 wt% Fe, 0.2 wt% Hf, particle size range 0.1–8 μm; α-SiC (Starck UF-25, Germany), specific surface area 23–26 m^2/g, impurities: 2.5 wt% O, mean particle size 0.45 μm; β-SiC (Starck BF-12, Germany), specific surface area 11–13 m^2/g, impurities: 0.88 wt% O mean particle size 0.60 μm; tetragonal $MoSi_2$ (Aldrich, Germany), specific surface area 1.60 m^2/g, impurities: 1 wt% O, mean particle size 1 μm; α-Si_3N_4 Baysind (Bayer, Germany), specific surface area 12.2 m^2/g, impurities: 1.5 wt% O, mean particle size 0.15 μm.

The powder mixtures were ball milled for 24 h in absolute ethanol using ZrO_2 media. Subsequently the slurries were dried in a rotary evaporator. The pellets were prepared by uniaxial pressing followed by cold isostatic pressing under 250 MPa. These specimens were subsequently pressureless sintered in a resistance-heated graphite furnace (Onyx Furnace 22001 C, LPA DVM, Seyssinet, France) under a flowing argon atmosphere (∼0.1 MPa) with heating rate of 600 °C/h at temperatures of 2100–2150 °C and holding times of 120 min. After the dwelling time, free cooling was set.

The bulk densities were measured by Archimedes' method. Crystalline phases were identified by X-ray diffraction (Siemens D500, Germany). The fractured and polished surface of the samples were analyzed by scanning electron microscopy (SEM, Cambridge S360, Cambridge, UK) and energy dispersive spectroscopy (EDS, INCA Energy 300, Oxford Instruments, UK). TEM samples were mechanically polished to a thickness of about 150 μm and punched out 3 mm in diameter by an ultrasonic cutter. After mirror polishing on both the surfaces, it was created a dimple to about 10 μm and then further ion beam thinned until small perforations were observed by optical microscopy.

The Vickers hardness (HV1.0) was measured on polished surfaces with an applied load of 9.81 N. The fracture toughness (K_{Ic}) was evaluated using chevron notched beam (CNB) in flexure. The test bars, 25 mm × 2 mm × 2.5 mm (length by width by