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Microscopic, mechanical and thermal properties of spark plasma sintered ZrB_2 based composite containing polycarbosilane derived SiC

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ABSTRACT

ZrB_2-SiC_p (w/w 80:20) composites were spark plasma sintered at 1900, 2000 and 2100 °C with t_{on} = 50 ms and t_{off} = 5 ms conditions under 50 MPa pressure for 15 min. SiC was obtained by in situ pyrolysis of polycarbosilane during sintering. The FTIR spectra of semi-pyrolysed ZrB_2-SiC_p powder showed that pre-ceramic PCS polymeric bands such as Si-CH_2-Si, Si-CH_3 and Si-H weakened and few characteristic bands like Si-C, Si-O and C = C peaks appeared strong in the spectra. In ZrB_2-SiC_P composition, uniform distribution of ZrB_2 and secondary SiC phases were found in the sintered sample. The interfaces between hexagonal ZrB_2 and needle shaped SiC were found in high resolution bright field TEM images. The Vickers' micro-hardness, fracture toughness (measured by DCM) of ZrB_2-SiC_p composite sintered at 2000 °C achieved up to 16.22 GPa and 3.69 MPa√m, respectively. The critical energy release rate (G_{IC}) value was 27.46 $J \cdot m^{-2}$ implying that the composite resists fracture during indentation. Wear resistance coefficient and wear rate values of all the composites were found to be very low. Thermal conductivity values of all the composites varied from 78.09 to 57.20 W/m·K in 100 °C to 1000 °C range.

1. Introduction

The family of ultra high temperature ceramics (UHTC) is basically founded on transition metal based carbides and borides like ZrB_2, HfC, TiB_2, ZrC, TaC, TaB_2 etc. and their composites [1,2]. Among them, ZrB_2-SiC composite has some unique properties like outstanding high temperature structural properties, low theoretical density, high thermal and electrical conductivity and good oxidation resistance in adverse (include individually or in combination of effect of temperature, chemical reactivity, radiation, mechanical stress and wear) condition that make it a potential and promising material in structural, aerospace and other conventional fields like refractory crucible, electrode, thermal and reactor plants etc. [3–6]. It is well known that structural properties of any composite depend not only on compositions but also on other parameters like particle morphology, impurities, densification process parameters and microstructures. Recently, researchers are using SiC in different forms and shapes, including bulk, sub-micron, micron and nano-size powders, foams, fibres (continuous and chopped), platelets, whiskers and pre-ceramic organic polymer precursors like polycarbosilane (PCS), polydimethylsilane (PDMS), polydimethyl-methylvinylsilane (PDMMVS) etc. [7–9]. Among these, polycarbosilane is widely used as a precursor of SiC due to its high ceramic yield, low-price and also slow decomposition rates of polymeric groups that led to rearrange the stable stoichiometric SiC structure at high temperature [10,11]. Moreover, the major reports stated that for improvement of mechanical and other structural properties of ZrB_2-SiC composite, the particle sizes of both ZrB_2 and SiC powders should be preferably in between 1 and 10 μm range. Zou et al. showed that hardness and flexural strength values of hot pressed ZrB_2-SiC (20 vol.%) composite were achieved up to 17.82 GPa and 462 MPa [12]. Akin et al. reported that the highest fracture toughness (4.1 MPa·$m^{1/2}$) was observed for spark plasma sintered ZrB_2-50 mass% SiC composite at 1900-2100 °C [13]. Asl et al. stated that hot pressed ZrB_2-30 vol.% SiC composite at 2000 °C showed the highest hardness (21.3 GPa) and fracture toughness (4.7 MPa $m^{1/2}$) values [14]. In these studies, the processing temperature was the main variable for densification and superior structural properties. In general, densification occurs at initial stage of hot consolidation under pressure by particle fragmentation and their rearrangement. In the later stage, diffusion, creep by dislocation movement can play a vital role for densification [15]. However, no systematic study is available on sintering and densification of ZrB_2-SiC (PCS derived) composite by spark plasma sintering technique at different temperatures and also the effect of microstructural defects between ZrB_2 and SiC grains and their interfaces towards densification, structural and thermal properties.

In this work, ZrB_2-SiC_p composites, with polycarbosilane (PCS) as a precursor of SiC were spark plasma sintered in argon atmosphere at three different temperatures (i.e., 1900 °C, 2000 °C and 2100 °C) for

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15 min under 50 MPa pressure. The effects of temperature during spark plasma sintering on microstructure, mechanical, tribological and thermal properties were investigated in details.

2. Experimental

2.1. Materials

For ZrB_2-SiC_P composition under study, DMSRDE, Kanpur, has supplied the composite powder after semi-pyrolysing ZrB_2 with PCS at 650 °C. The detailed powder processing steps were reported elsewhere [16].

2.2. Spark plasma sintering

ZrB_2-SiC_P batch powders were sintered in a spark plasma sintering furnace (HP D 25, FCT Systeme GmbH, Germany) at 1900-2100 °C in argon atmosphere under 50 MPa pressure for 15 min. In this study, we used t_{on} of 50 ms and t_{off} of 5 ms and kept the total pulse cycles (n) fixed in 1. The heating and cooling rates of the furnace were kept at 100 °C/min and 50 °C/min, respectively. The temperature of the sample during operation was measured by optical pyrometer focused on the bottom surface of the top plunger of the graphite die. The shrinkage of the sample was calculated from the piston displacement. The details of SPS operation schedule is plotted in Fig. 1. The diameter and thickness of the sintered compacts were around 20 mm and 4 mm, respectively.

2.3. Characterization

Powder morphology was studied by scanning electron microscope (800–07334, PHENOM-WORLD, The Netherlands) in backscattered mode. The particle size distribution of the ZrB_2-SiC_p powder was determined by laser diffraction particle size analyser (LS13 320, Beckman Coulter. Inc, USA) after ultrasonically dispersing the powder in water. Surface area of the powder is calculated by surface area analyser (NOVA 4000e, Quantachome, USA). The infrared spectra analysis of the precursor polycarbosilane (both solid and liquid) and semi-pyrolysed ZrB_2-SiC_p powder was done by FTIR spectrometer (Cary 660, Agilent Technologies, Singapore) from 500–4000 cm^{-1} range. The phase analysis was done by the X-ray diffraction technique (X'Pert Pro MPD; PanAnalytical, The Netherlands) using X'Celerator operating at 40 kV and 30 mA with CuKα radiation (α = 1.54 Å) at room temperature. The sintered ZrB_2-SiC_P samples were ground and polished by a grinder (NKT6, ELB-Scliff, Germany) and surface polisher machine (Spectrum System 1000, LECO Corporation, USA), respectively [16]. The microstructure and also the elemental analysis (EDS) of the ZrB_2-SiC_P composites were done by Field Emission Scanning Electron Microscope (FESEM) (AXIOS; PanAnalytical, The Netherlands). Specimen for TEM study was prepared by conventional polishing and ion-thinning. Bright field (BF) images and SAED patterns were taken using transmission electron microscope (HRTEM) (Tecnai G2 30ST, FEI, USA). The details of microhardness, tribological and thermal conductivity tests were reported elsewhere [16].

3. Results and discussion

3.1. Powder morphology

Fig. 2(a) shows the morphological characteristics of the ZrB_2-SiC_P powder after semi-pyrolysis at 650 °C. The specific surface area obtained from BET surface area measurement gives 88.23 m^2/g. It is clearly visible by the SEM image that polycarbosilane-derived SiC particles are adhered on the hexagonal ZrB_2 grains. Some small grains of SiC are overlapped and agglomerated on the large ZrB_2 grains. From the EDS spectra, it is found that Zr and Si elements in the form of ZrB_2 and SiC phases and oxygen are also present in the powder. This powder shows a wide particle size distribution leading to average particle size (d_{50}) close to 15.85 μm.

3.2. FTIR analysis

Fig. 3 shows the FTIR spectra of both liquid and solid PCS and the ZrB_2-SiC_p powder after semi-pyrolyzed at 650 °C. The strong absorption around 1261 cm^{-1} and the relatively weak absorption around 2962 cm^{-1} are attributed to the stretching vibrations of Si-C and C-H bond in Si-CH_3, respectively. The absorption peaks at around 1065 cm^{-1} and 2897 cm^{-1} correspond to CH_2 bending and C-H stretching in Si-CH_2-Si, signifying the presence of polycarbosilane backbone (Si-CH_2-Si) [17]. In general, maximum liquid polycarbosilanes were synthesized by Grignard coupling reaction between triethoxysilane and organomagnesium halide (Grignard reagent) and subsequently formed hyperbranched polycarbosilanes

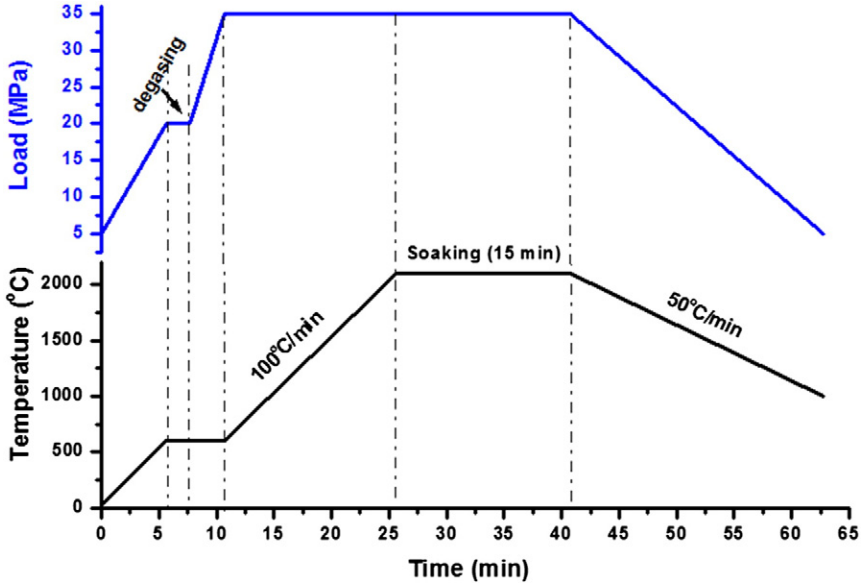

Fig. 1. Thermomechanical cycle applied during spark plasma sintering of ZrB_2-SiC_p composite at 2100 °C.