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Densification and properties of transition metal borides-based cermets via spark plasma sintering

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Abstract

Engineering borides like TiB_2 and ZrB_2 are difficult to sinter materials due to strong covalent bonding, low self-diffusion coefficient and the presence of oxide layer on the powder particles. The present investigation reports the processing of hard, tough and electrically conductive transition metal borides (TiB_2 and ZrB_2) based cermets sintered with 6 wt.% Cu using spark plasma sintering (SPS) route. SPS experiments were carried out with a heating rate of 500 K/min in the temperature range of 1200–1500 °C for a varying holding time of 10–15 min and the optimization of the SPS conditions is established. A maximum density of ∼95% ρ_{th} in ZrB_2/Cu and ∼99% ρ_{th} in TiB_2/Cu is obtained after SPS processing at 1500 °C for 15 min. While the optimized TiB_2/Cu cermet exhibits hardness and fracture toughness of ∼17 GPa and ∼11 MPa m$^{1/2}$, respectively, the optimized ZrB_2/Cu cermet has higher hardness of ∼19 GPa and fracture toughness of ∼7.5 MPa m$^{1/2}$, respectively. High electrical conductivity of ∼0.20 MΩ^{-1} cm^{-1} (TiB_2/Cu) and ∼0.15 MΩ^{-1} cm^{-1} (ZrB_2/Cu) are also measured with the optimally sintered cermets.

Keywords: TiB_2; Sintering; Electron microscopy; Hardness; Toughness and toughening; Electrical conductivity; Spark plasma sintering

1. Introduction

Transition metal borides, an important class of advanced structural ceramic materials, are candidate materials for various applications, i.e. armor materials, aluminum evaporation boat, cathode material for hall-heroult cell, cutting tool, electro discharge machining (EDM) electrode, wear parts, high temperature applications, electrical devices, in rockets nozzles, in foundry or refractory applications, etc.[1–5] This is due to the fact that the borides like TiB_2 and ZrB_2 are characterized by high melting point (>3000 °C), high hardness (TiB_2: ∼25–32 GPa, ZrB_2: ∼22–25 GPa), elastic modulus (TiB_2: 510–575 GPa, ZrB_2: 440–460 GPa), wear resistance, good oxidation resistance, excellent thermal and electrical properties. Although having excellent properties, the borides have low to moderate fracture toughness (4–5 MPa m$^{1/2}$), primarily because of the inherent bonding nature. Furthermore, low self-diffusion coefficient and the presence of oxide layers (B_2O_3 and TiO_2 on TiB_2 particles, B_2O_3 on ZrB_2 particles) poses additional difficulties in the sintering of these TiB_2 and ZrB_2 transition borides.[1–5] Therefore, major research largely focused on using various sintering additives/binders to attain maximum densification and to improve the toughness of borides.

As far as the densification is concerned, considerable research activity is directed towards optimizing (a) processing parameters and (b) proper amount binder addition (metallic or ceramic binders). Hot pressing as well as dynamic compaction (DC) is reported to be quite effective in achieving maximum densification at lower temperature in the range of 1800 °C, while conventional pressureless sintering requires high temperature of ∼2000 °C to obtain better densification, which is typically attained in the presence of binders.[6,7] Sintering additives play a major role in triggering sintering kinetics and thus helps in achieving maximum densification.

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Moreover, some sintering aids also improve specific properties, i.e. toughness, oxidation resistance, electrical properties, in addition to obtain better densification. Various metallic binders, investigated widely, are Ni, Cr, Fe, etc.[6,7] Cemented borides with a metallic binder have recently been developed in the TiB_2-Fe system. TiB_2-based cermets typically contain TiB_2 as a major phase, bonded with metallic phase (Co/Ni).[8] These materials are expected to be a novel lower density substitute for the WC/Co system. In recent times, $MoSi_2$ has also been used as sinter-additives in developing TiB_2-based high temperature materials. Both the hot processing as well as SPS processing parameters to obtain dense TiB_2–$MoSi_2$ ceramic composites are optimized and reported elsewhere.[9,10]

Another serious problem with high temperature sintering of ceramics like TiB_2 and ZrB_2 is the exaggerated grain growth, which in turn leads to the formation of micorcraks due to thermal anisotropy during cooling.[2,3] This leads to the degradation in mechanical properties (strength, hardness). To this end, faster sintering techniques like SPS can produce dense borides while restricting the grain growth and thereby enhancing mechanical properties, like hardness. The spark plasma sintering (SPS), a variant of activated sintering, is characterized by the application of electric current in addition to applied pressure. SPS process is reported to trigger superfast densification of nanomaterials without considerable grain growth.[10–13] In the present investigation, the densification study on the TiB_2 and ZrB_2 is conducted with the use of the metallic binder addition (Cu) in SPS route. The aim of the present investigation is to illustrate the influence of Cu binder on the densification behavior of two different borides in an electric field assisted sintering process. The optimization of SPS temperature to obtain maximum densification and better mechanical and electrical properties in TiB_2 and ZrB_2 is reported in the current work.

2. Experimental procedure

2.1. Starting powders and densification

Commercial TiB_2 and ZrB_2 were used as the major bulk phase in our composites. Both the boride powders are procured from Aldrich, USA and have average particle size <5 μm. The commercially available high purity copper (<5 μm, Aldrich, Korea) is used as a sintering aid for both TiB_2 and ZrB_2. During the preparation of cermets, TiB_2:Cu and ZrB_2:Cu in the weight ratio of 94:6 was mixed in a mixer for 24 h in 1 l of toluene in a polyethylene bottle. To break the agglomerates and to ensure better dispersion, WC balls were used during the mixing process, followed by drying in the oven.

The dried premixed powders are placed inside the graphite mold, ensured with proper insulation around the inside wall of the graphite mold (10 mm internal diameter) using thin graphite sheet to avoid contamination during sintering. The graphite punches are inserted into the mold and the graphite mold is placed between the graphite electrodes of SPS chamber. The SPS chamber is closed firmly and high vacuum of 70 mtorr is maintained throughout the experiment. During SPS experiments, DC current of 1–1.5 kA, DC voltage of 5–10 V and pulse frequency of 30–40 kHz are applied and variation in this range depends on the final holding temperature. The experiments are carried out in the temperature range of 1200–1500 °C with a heating rate of 500 K/min with the varying holding period of 10 and 15 min. A constant pressure of 40 MPa is maintained during the heating and holding period. The current flow is stopped and pressure is released as soon as the holding at sintering temperature is over. The final thickness of the sintered discs was about 2–3 mm.

2.2. Characterization

After complete removal of protective graphite insulating layer around the specimen, the density of spark plasma synthesized samples was measured in water following Archimedes principle. The theoretical densities of the corresponding composites were calculated by rule of mixture, taking density of TiB_2, ZrB_2 and Cu as 4.52, 6.06 and 8.9 g cm^{-3}, respectively. Further, phase identification was performed using X-ray diffraction using Cu Kα radiation (Rich-Seifert, 2000 D). The Vickers indentation is carried out on smoothly polished surface to measure hardness and toughness at indent load of 10 kg with a dwelling time of 15 s on a universal hardness tester. The fracture toughness is evaluated by measuring crack length measurement (2c) of the radial crack pattern formed around Vickers indents, adopting formulation proposed by Anstis et al.[14] The reported values are the average of five indentation tests. Detailed Microstructural investigation of the polished and fractured composites was performed using Scanning Electron Microscopy (FEI QUANTA SEM, Philips). Elemental compositional analysis of different phases are examined using EDS analysis and X-ray mapping on SEM. Room temperature electrical resistivity (dc) was measured by standard four probe method at room temperature with appropriate silver epoxy-coating on the flat materials, followed by hardening at 150 °C.

3. Results and discussion

3.1. Densification

At the first stage of the present work, the SPS experiments were carried out on TiB_2/Cu system and the SPS parameters were optimized. In the later experiments with ZrB_2/Cu, the SPS parameters were selected based on our experience in densifying TiB_2/Cu materials. The densification data of the TiB_2–6 wt.% Cu and ZrB_2–6 wt.% Cu cermets, Spark Plasma Sintered at various sintering temperature (1200–1500 °C) and various holding period (10 and 15 min) is presented in Fig. 1. Fig. 1a reveals the densification behavior of the TiB_2–6 wt.% Cu composites, indicating that the developed