Development of ZrB2 Reinforced Eutectic Ceramics
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Abstract

SiC-B4C-ZrB2 eutectic composites were prepared in arc melting furnace under the Ar atmosphere. Button shaped melts, containing irregular eutectic structures of ‘Chinese script’, with interpenetrated ternary and binary phases were achieved by rapid cooling. Pulverized fine powders of eutectic were then consolidated by the spark plasma sintering (SPS) technique, applying 3 min dwell time at 1800°C for ternary composition, 5 min dwell time at 1850°C for binary composition under a uniaxial pressure of 15 MPa. The measured Vickers hardness was around 18 GPa and 11 GPa for ternary and binary compositions, respectively. The fracture toughness of the samples was around 5 MPa m^{1/2}. It was observed that fracture toughness values are higher compared with oxide eutectics although the phase formed are distributed not homogeneously in the material.

1. Introduction

The development of hypersonic-atmospheric re-entry vehicles and nuclear facilities increased the demand for materials, which will work under extremely high temperatures and oxidizing environments. Ultra-High Temperature Ceramics (UHTC) based on transition metal borides meets the working as mentioned above conditions regarding their extreme melting temperature and good thermo-physical properties. ZrB2 is a transition metal boride which belongs to a member of UHTC takes more attention due to its high melting point temperature of around 3500 K, high hardness, high electrical and thermal conductivity and excellent corrosion resistance [1]. Although it provides excellent properties, the utilization of ZrB2 has been greatly limited by its poor sinterability, low mechanical strength, and low fracture toughness. To overcome these disadvantages, ceramic oxide and non-oxides with binary and/or ternary eutectic compositions, produced by particular single crystal growth and melting processes, have been investigated extensively over the last decade [2-5]. Of all the eutectic ceramics, ZrB2-reinforced eutectics present superior oxidation resistance, high temperature mechanical properties retention up to their eutectic temperature makes these eutectics an important candidate for high-temperature applications above 1500°C.

Eutectic ceramics were generally fabricated by cooling a melt with a eutectic composition with unidirectional and directional growth techniques like Bridgman Methods, infrared heating by halogen or xenon lamps, laser beam heating, inductive heating, arc melting etc. Unfortunately, scalability of these processing methods is limited by thermal gradients during processing which lead to inconsistent eutectic microstructures and significant thermal stresses in the samples. Different from directional solidification techniques, some oxide based-eutectics like Al2O3 and ZrO2- based [6-8], exhibiting comparable densification levels, microstructural features and mechanical properties have been produced successfully by Hot Pressing (HP) and Spark Plasma Sintering (SPS). For these pressure-assisted techniques, eutectic powders were generally fabricated by conventional melting processes, such as arc discharge and induction melting. Powders achieved by these techniques exhibit homogeneous dendritic or cellular formations due to large thermal gradients which occur during cooling. However, there is a dearth of literature on the production of boride-based eutectics and their microstructural stability of eutectics at temperatures prepared by these methods.

This paper deals with the production of the SiC-ZrB2 binary and SiC-B4C-ZrB2 ternary eutectics with the spark plasma sintering technique. A binary and ternary eutectic ceramic powders were prepared by vacuum arc melting process without any secondary heat treatment stages. The powders were consolidated by SPS applying different sintering temperatures and dwells in order to investigate feasible sintering conditions and microstructural evolution.

2. Experimental Procedure
2.1. Preparation of Binary and Ternary Eutectic Composites

Commercially available ZrB2 (ABCR GmbH&CO, Grade A), B4C (>99%; Alfa Aesar;) and SiC (Aldrich, -400 mesh) powders were used as starting materials. A eutectic composition of 20 mol% ZrB2, 40 mol% B4C and 40 mol% SiC for ternary composition, 40%mol ZrB2 and 60 mol% SiC for binary composition was selected according to phase diagram calculated by Tu et all. [9]. The powders were planetary ball milled (Pulverisette 6 Fritsch – Germany) in a Si3N4 jar with Si3N4 balls for 90 min in isopropanol at a rotational speed of 450 rpm. The slurry was then dried using a rotary evaporator and the powders were sieved under 100 μm in order to break up agglomerates. The powders were then pelletized by dry pressing. The pellets were then subjected to a controlled arc melting process (Compact Arc Melter MAM-1, Edmund Bühler GmbH) under Ar atmosphere. Pellets were melted for
four times by changing the surfaces subjected to arc directly. After cooling button shaped, eutectic solids were obtained which is illustrated in Fig. 1. These pellets were then crushed and milled in a vibrating cup mill with WC–Co disks and jar in order to produce ternary and binary composite eutectic powders.

Figure 1. Button shaped melts obtained after arc melting

2.2 Spark Plasma Sintering of Arc Melted Powders

Sintering of the eutectic powders was carried out applying 3 min dwell time at 1800°C for ternary composition, 5 min dwell time at 1850°C for binary composition under a uniaxial pressure of 15 MPa and a vacuum atmosphere in a SPS furnace (HPD-50, FCT GmbH, Germany). The powders were put into a 20 mm graphite die and graphite foil was incorporated to prevent reaction between the graphite die and the powders. The heating rate was selected as 100°C/min. The temperature was increased by a controlled electrical current and measured inside the graphite punches by using an optical pyrometer. A maximum sintering temperature was selected as 1850°C and 1800°C, considering the displacement curves achieved during consolidation trials. The specimens were held at the maximum sintering temperature for 5 and 3 min. for binary and ternary composition, respectively. Then, fast (switching power off, ≈600°C) cooling rates were applied.

2.3. Characterization

The polished surfaces of the samples were examined using a scanning electron microscope (Supra 50 VP, Zeiss – Germany) equipped with an EDX detector (Oxford Instruments, UK). For XRD analysis sintered samples were crushed and ground to 63 μm. Qualitative phase analysis was accomplished by using an X-ray diffractometer (Rigaku Rint 2200 series) at a scan speed of 1°/min. The Vickers hardness (Hv10) from the polished surfaces of the sintered samples was measured using an indenter (EMCO-Test, M1C-Germany) with a load of 10kg. The fracture toughness (KIC) of the samples was evaluated from radial cracks formed during the indentation test [10].

3. Results And Discussions

3.1. Phase Analysis of Arc Melted Composites

X-ray diffraction patterns of the arc melted samples are given in Figure 2. ZrB2, B4C and SiC for ternary composition and SiC and ZrB2 for binary compositions were detected as the major crystalline phases, confirming the formation of a desired eutectic composition. Besides these results, several interphases with boron and silicate were observed in binary system. It was considered that; initial materials have an oxide layer their surface and this caused to form an oxide-based interphase (ZrSiO4) during the arc melting process. After all, elemental silicon was observed in ternary system. It was thought that siliconization was occurred because of the high process temperature during arc melting.

3.2. Microstructural Analysis of Arc Melted Composites

The Back-scattered SEM images of obtained from cross section of arc melted composites were shown in Figure 3. In Figure 3a, white contrasted areas represent ZrB2, black contrasted areas represent B4C and grey contrasted areas represents SiC phases. It was observed that ZrB2–SiC directionally solidification was occurred for ternary composition. However, B4C was not involved into the ternary eutectic system which then leads formation of B4C clusters. In Figure 3b, white contrasted areas represents ZrB2 and black contrasted areas represents SiC phases. It was thought that; eutectic composition was observed locally, and porosity and non-melted areas were also observed. Remarkable point is in both microstructure, SiC grains showed elongated morphology. It was thought that, formation of boron during melting have a solubility in SiC. This solubility provides an activation for transport
mechanism in the lattice and it changes the SiC morphology to elongated grains [11].

Figure 3. BSE-SEM images of obtained from cross section of arc melted a) ternary b) binary composition.

3.3. Sintering Conditions and Microstructural Analysis of Sintered Composites

To determine the sintering temperature for the milled arc-melted powders, a sintering trial for ternary composition was carried out. During the trial, the uniaxial pressure was set to 15 MPa. This value is the minimum pressure limit to maintain contact between rams of SPS apparatus to keep the current flowing through the graphite punches and mold. The displacement and punch travel speed curves obtained through this trial was shown in Figure 4.

Figure 4. The displacement and punch speed curves obtained through spark plasma sintering of arc-melted ternary composition powders at 1850°C.

Considering the curves, consolidation of the powders starts at 1725 °C and proceeds up to 1840 °C linearly. Above 1840 °C, the rapid increase in the displacement speed of the graphite punches was observed up to 1850 °C. After rapid cooling, the entire sample was found to have melted and exudate entirely outside of the graphite mold. According to this result the maximum sintering temperature was selected as 1800 °C for ternary composition in order to inhibit melting and achieve densification. For binary composition, sintering temperature was selected 1850 °C because of the binary composition have higher eutectic temperature compared with ternary composition.

BSE-SEM images of SPS’ed samples for ternary and binary compositions were given in Figure 5.

Figure 5. BSE-SEM images of SPS’ed samples for a) ternary b) binary composition.

Similar with arc-melted samples images, white contrasted areas represent ZrB$_2$, black contrasted areas represent B$_4$C and grey contrasted areas represents SiC phases for ternary compositions. In addition to obtained clearly distinguishably phases, homogenous and dense microstructure with elongated whisker like SiC formation was observed. For binary composition, white contrasted areas represent ZrB$_2$ and black contrasted areas represents SiC phases like arc-melted forms. Although porosity was observed on microstructure of arc melted-binary composition, dense microstructure was obtained after SPS. Besides higher densification, homogeneously dispersed fine eutectic colonies were observed, and they are also located in the Chinese script like matrix with an entangled grain formation of ZrB$_2$ and SiC.
3.4. Mechanical Properties of SPS’ed Samples

Hardness and fracture toughness of the samples were determined by Vickers indentation tests (HV10). For comparison, monolithic ZrB2, B4C, SiC ceramics and measured hardness, the indentation fracture toughness and density of the samples were also presented in Table 1. Considering the measured density values, both systems have >95% theoretical density values. (For binary composition 4.64 g/cm³, for ternary composition 3.45 g/cm³).

Table 1. Hardness, Fracture Toughness and Density of samples after SPS process

<table>
<thead>
<tr>
<th></th>
<th>Hardness, HV10 (GPa)</th>
<th>Fracture Toughness (MPa.m½)</th>
<th>Relative Density (%)</th>
</tr>
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<tbody>
<tr>
<td>Binary</td>
<td>11.11 ± 0.5</td>
<td>5.069 ± 0.2</td>
<td>96.11</td>
</tr>
<tr>
<td>Ternary</td>
<td>18.142 ± 2.1</td>
<td>5.048 ± 0.7</td>
<td>97.10</td>
</tr>
<tr>
<td>ZrB2[12]</td>
<td>16.0 ± 1.0</td>
<td>1.8 ± 0.5</td>
<td>93.1</td>
</tr>
<tr>
<td>SiC [13]</td>
<td>24.0 ± 1.2</td>
<td>3.0 ± 0.7</td>
<td>-</td>
</tr>
<tr>
<td>B4C [13]</td>
<td>39 ± 2.0</td>
<td>2.9 ± 0.1</td>
<td>-</td>
</tr>
</tbody>
</table>

Hardness of the ternary system, was higher than the binary system, due to the presence of B4C. However, fracture toughness value was slightly low when compared with binary system due to the not melted boron carbides. Eutectic compositions have lower hardness values compared with monolithic samples. It was thought that the strong bonding was not connected between phases due In terms of the higher residual stress occurred during the fast cooling in arc melting and SPS, decreased the bonding characteristics between phases which than caused defect formation and pull out of grains. This microstructural weakening was thought to be the main reason for the lower hardness values of the samples. However, higher fracture toughness values are obtained for eutectic compositions due to defect formation and pull out grains.

4. Conclusions

SiC-ZrB2 and SiC-B4C-ZrB2 eutectic composites with typically eutectic microstructure without grain boundaries, were successfully fabricated by spark plasma sintering of pulverized arc melted pellets. Different from the relevant literature, powders of eutectic composition were directly subjected to an arc melting process without any pre-heat treatment process, which was suitable for batch production. The eutectic temperatures of the compositions were selected 1850°C for binary composition and 1800°C for ternary composition with using 100/min heating rate under 15 MPa uniaxial pressure. Dwells times for compositions are also 5 min and 3 min for binary and ternary compositions, respectively. Because of the not melted B4C phases in ternary system, B4C agglomeration was observed. For both eutectic system, SiC morphology changed to elongated grains due to the presence of boron. Considering mechanical properties, hardness values are lower compared with monolithic ceramic forms which was related with the weak bonding between phases because of the fast cooling. However, higher fracture toughness values were obtained due to the defect formation during the fast cooling.

5. References