Int. Journal of Refractory Metals and Hard Materials 54 (2016) 127–137

Contents lists available at ScienceDirect

Int. Journal of Refractory Metals and Hard Materials

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

# Effect of $HfB_2$ on microstructure and mechanical properties of $ZrB_2$–SiC-based composites

Z. Balak *, M. Zakeri

*Materials and Energy Research Center (MERC), Tehran, Iran*

ARTICLE INFO

*Article history:*
Received 9 April 2015
Received in revised form 7 July 2015
Accepted 9 July 2015
Available online 26 July 2015

*Keywords:*
$HfB_2$
$MoSi_2$
Microstructure
Densification
Flexural strength
Spark plasma sintering

ABSTRACT

In this work, $ZrB_2$–SiC-based composites with different additives were sintered in different temperature (1600, 1700, 1800 and 1900), time (4, 8, 12 and 16) and pressure (10, 20, 30 and 40 MPa). The effect of $HfB_2$ (0, 5, 10, 15 vol.%) on $ZrB_2$-based ceramics was investigated. Microstructure evaluation and phases were done by SEM and EDAX. Effect of SPS conditions (temperature, time and pressure) on microstructure was investigated. The results showed that Hf and Zr diffuse in each other and (Zr, Hf)$B_2$ solid solution will be formed. In addition, it was concluded that by increasing temperature and time, solid solution formation increases. Pressure has little effect on diffusion. Also, $MoSi_2$ and $ZrB_2$ form (Zr, Mo)$B_2$ solid solution. Finally it is cleared that $HfB_2$ increases open porosity percent slightly. Finally, it was observed that $HfB_2$ has negative effect on densification while improves flexural strength due to (Zr, Hf)$B_2$ solid solution.



## 1. Introduction

IV–V-group transition-metal diborides and carbides possess melting temperatures among the highest known, i.e. above 3000 °C. Among them diborides such as $ZrB_2$ and $HfB_2$ have unique combinations of mechanical and physical properties, including high hardness and elastic modulus, low electrical resistivity, and resistance to chemical attack. As a result, this material has been proposed for a variety of structural applications at room and elevated temperature including armor, cutting tools, molten metal containment, steel processing, and electrodes. Accordingly lower density and cost of ZrB2 rather than HfB2, ZrB2 is considered to be a candidate for use as leading edges and propulsion components in hypersonic aerospace vehicles and advanced reusable atmospheric reentry vehicles [1–3].

To improve mechanical properties of $ZrB_2$ different additives such as metals, Cu, Ni, Fe, Mo, Nb [4], nitrides, AlN, HfN, ZrN [5,6] $Si_3N_4$, carbides, SiC and ZrC [2,7] and disilisides, $MoSi_2$, $ZrSi_2$, and $TaSi_2$ [5,6,8] were applied. SiC reinforcement of ZrB2 is known to increase flexural strength, fracture toughness and oxidation resistance and so was chosen as additive in this study. Although additives, such as Ni, nitrides and disilicides, could reduce the densification temperature of $ZrB_2$, the strength of the resulting composites is also degraded at high temperature, as a result of softening of the inter-granular amorphous phase [2]. As an example, the strength of $ZrB_2$ containing ~3 vol.% Ni has been shown to drop by about 60% between 800 and 1000 [9].

Among the different additives which are mentioned above $HfB_2$ has positive effect on mechanical properties in high temperature as well as low temperature. Until now effect of it on microstructure and densification was not investigated. The aim of this work is to study and discuss it. Also, $MoSi_2$ is used as additives due to its good effect on densification. Effect of $MoSi_2$ on mechanical properties is not expressed clearly.

## 2. Experimental

The aim of this project is to reach composite with the best densification and mechanical properties (such as flexural strength, hardness and fracture toughness). So, all important factors such as SiC, $C_f$, $MoSi_2$, $HfB_2$ and ZrC content, milling time of $C_f$ and SPS parameters such as temperature, time and pressure were chosen according to previous studious [2, 10–18]. Four levels were selected for each of them. The used factors and levels are presented in Table 1.

To investigate all factors and levels, $4^9 = 262{,}144$ samples are needed in which manufacturing of them is impossible due to very high cost and time. So, an optimization strategy is necessary to evaluate all of these factors. Taguchi method is the best opportunity to eliminate variations during the design of experiment. In this study, $L_{32}$ orthogonal array was chosen by Qualitek-4 software. With respect to the $L_{32}$ orthogonal array, conditions in preparing each sample will be as shown in Table 2. The powders corresponding to 32 different compositions,

* Corresponding author.
*E-mail address:* Zbalak1983@gmail.com (Z. Balak).

http://dx.doi.org/10.1016/j.ijrmhm.2015.07.011
0263-4368/

**Table 1**
Process factors and their levels used in the experiments.

| Test | FAC.1 | FAC.2 | FAC.3 | FAC.4 | FAC.5 | FAC.6 | FAC.7 | FAC.8 | FAC.9 |
|---|---|---|---|---|---|---|---|---|---|
| | SiC vol.% | $C_f$ vol.% | Milling time h | $MoSi_2$ vol.% | $HfB_2$ vol.% | ZrC vol.% | Temperature C | Pressure MPa | Time min |
| Lev.1 | 5 | 0 | 0 | 0 | 0 | 0 | 1600 | 10 | 4 |
| Lev.2 | 10 | 2.5 | 2.5 | 2 | 5 | 5 | 1700 | 20 | 8 |
| Lev.3 | 15 | 5 | 5 | 4 | 10 | 10 | 1800 | 30 | 12 |
| Lev.4 | 20 | 7.5 | 7.5 | 6 | 15 | 15 | 1900 | 40 | 16 |

according to Table 2, were mixed by wet ball-milling at 200 rpm for 3 h in a zirconia's bottle, using zirconia's balls and ethanol as media. The mixtures were then dried. The powder mixture was put into graphite die lines with graphite foil which has an inner diameter of 50 mm and sintered using SPS apparatus (SPS-20T-10, China). The sintering was performed at different temperatures (between 1600 °C and 1900 °C), different pressures (between 10 MPa and 40 MPa) and different holding times (between 4 min and 16 min) based on Taguchi design (Table 2) in vacuum. Final sintered specimen size was 50 mm diameter pellets with different thicknesses of 2.8 mm and 6.5 mm related to their compositions and SPS conditions. After removing the surface layer from the obtained disk by grinding, the bulk density was measured according to ASTM C 373-88. Flexural strengths were measured in three-point bending using a fully articulated test fixture according to ASTM Standard C1161 for type-B bars (45 mm by 3 mm by 4 mm). The phase composition was determined by X-ray diffraction (XRD, Siemens, D500) using Cu Ka radiation on polished cross-sectioned composite. Scanning electron microscopy (Sigma/VP, Zeiss) was performed to observe the microstructures of the composites equipped with backscattered electron imaging (BSE).

## 3. Results and discussion

### 3.1. Microstructure

SEM images of some composites are shown in Fig. 1. To identify phases in microstructure EDAX was applied. Fig. 2 shows EDAX analysis of composites 11 and 22. It is clear that the light phases (D, E) which are shown with arrows, have higher Hf content. Also, it can be observed that C and B phases have the most Si and Zr rather than other phases respectively. In composite 22, gray dark phase has the most Zr (spectrum 2) and approximately the light phase has the most Hf (spectrum 1). Since determining accurate content of B and C is impossible, line as well as point analysis was applied. Line analysis of composite 22 is shown in Fig. 3.

With respect to point and line analysis (Figs. 2 and 3), it appears that black grains are SiC due to high Si content. Gray dark grains are pure $ZrB_2$ because of their high Zr content and free of Hf. Totally, by investigating accurately microstructure of all composites, five phases with different color, light, approximately light, gray light, gray dark and black can be distinguished. As explained above, gray dark and black phases

**Table 2**
Conditions preparing for each sample.

| Test | FAC.1 | FAC.2 | FAC.3 | FAC.4 | FAC.5 | FAC.6 | FAC.7 | FAC.8 | FAC.9 |
|---|---|---|---|---|---|---|---|---|---|
| | SiC vol.% | $C_f$ vol.% | M.t (h) | $MoSi_2$ vol.% | $HfB_2$ vol.% | ZrC vol.% | Temperature C | Pressure MPa | Time min |
| 1 | 5 | 0 | 0 | 0 | 0 | 0 | 1600 | 10 | 4 |
| 2 | 5 | 2.5 | 2.5 | 2 | 5 | 5 | 1700 | 20 | 8 |
| 3 | 5 | 5 | 5 | 4 | 10 | 10 | 1800 | 30 | 12 |
| 4 | 5 | 7.5 | 7.5 | 6 | 15 | 15 | 1900 | 40 | 16 |
| 5 | 10 | 0 | 0 | 2 | 5 | 10 | 1800 | 40 | 16 |
| 6 | 10 | 2.5 | 2.5 | 0 | 0 | 15 | 1900 | 30 | 12 |
| 7 | 10 | 5 | 5 | 6 | 15 | 0 | 1600 | 20 | 8 |
| 8 | 10 | 7.5 | 7.5 | 4 | 10 | 5 | 1700 | 10 | 4 |
| 9 | 15 | 0 | 2.5 | 4 | 15 | 0 | 1700 | 30 | 16 |
| 10 | 15 | 2.5 | 0 | 6 | 10 | 5 | 1600 | 40 | 12 |
| 11 | 15 | 5 | 7.5 | 0 | 5 | 10 | 1900 | 10 | 8 |
| 12 | 15 | 7.5 | 5 | 2 | 0 | 15 | 1800 | 20 | 4 |
| 13 | 20 | 0 | 2.5 | 6 | 10 | 10 | 1900 | 20 | 4 |
| 14 | 20 | 2.5 | 0 | 4 | 15 | 15 | 1800 | 10 | 8 |
| 15 | 20 | 5 | 7.5 | 2 | 0 | 0 | 1700 | 40 | 12 |
| 16 | 20 | 7.5 | 5 | 0 | 5 | 5 | 1600 | 30 | 16 |
| 17 | 5 | 0 | 7.5 | 0 | 15 | 5 | 1800 | 20 | 12 |
| 18 | 5 | 2.5 | 5 | 2 | 10 | 0 | 1900 | 10 | 16 |
| 19 | 5 | 5 | 2.5 | 4 | 5 | 15 | 1600 | 40 | 4 |
| 20 | 5 | 7.5 | 0 | 6 | 0 | 10 | 1700 | 30 | 8 |
| 21 | 10 | 0 | 7.5 | 2 | 10 | 15 | 1600 | 30 | 8 |
| 22 | 10 | 2.5 | 5 | 0 | 15 | 10 | 1700 | 40 | 4 |
| 23 | 10 | 5 | 2.5 | 6 | 0 | 5 | 1800 | 10 | 16 |
| 24 | 10 | 7.5 | 0 | 4 | 5 | 0 | 1900 | 20 | 12 |
| 25 | 15 | 0 | 5 | 4 | 0 | 5 | 1900 | 40 | 8 |
| 26 | 15 | 2.5 | 7.5 | 6 | 5 | 0 | 1800 | 30 | 4 |
| 27 | 15 | 5 | 0 | 0 | 10 | 15 | 1700 | 20 | 16 |
| 28 | 15 | 7.5 | 2.5 | 2 | 15 | 10 | 1600 | 10 | 12 |
| 29 | 20 | 0 | 5 | 6 | 5 | 15 | 1700 | 10 | 12 |
| 30 | 20 | 2.5 | 7.5 | 4 | 0 | 10 | 1600 | 20 | 16 |
| 31 | 20 | 5 | 0 | 2 | 15 | 5 | 1900 | 30 | 4 |
| 32 | 20 | 7.5 | 2.5 | 0 | 10 | 0 | 1800 | 40 | 8 |