Synthesis of medium-entropy \((\text{Zr}_{1/3}\text{Hf}_{1/3}\text{Ta}_{1/3})\text{B}_2\) using the spark plasma consolidation of diboride powders

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In this study, we introduce a simple and effective method for producing a ternary solid-solution of diborides, a medium-entropy \((\text{Zr}_{1/3}\text{Hf}_{1/3}\text{Ta}_{1/3})\text{B}_2\). Using commercially available diboride powders with equimolar ratio and performing spark plasma consolidation at 1927 °C we demonstrate that single-phase medium-entropy ceramic can be consolidated using an hour-long procedure. The flexural strength and fracture toughness at room temperature were 318 ± 14 MPa and 2.9 MPa m\(^{1/2}\), respectively.

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1. Introduction

Engineering of material systems capable of functioning at elevated temperatures has increased the industrial importance of transition metal diborides of IVB and VB groups such as HfB\(_2\), TaB\(_2\), ZrB\(_2\), widely known as ultra-high temperature ceramics. The adequate level of high-temperature oxidation resistance of ceramic composites based on these diborides comforts requirement for components of hypersonic aerospace vehicles, thermal protection systems.\(^1,\)\(^2\)

Due to low self-diffusivities, these monolithic diborides require high consolidation temperatures and thus are known to experience spontaneous microcracking after reaching critical grain size, typical above 15 µm.\(^3\) For the HfB\(_2\) or ZrB\(_2\) presence of oxide layers on the surface of initial powders may influence ‘ramp and hold’ strategy for densification, or may result in the formation of the significant amount of oxide grains in bulk specimen.\(^4\) In such case, hardness and strength, elastic moduli and thermal conductivity can be severely affected. To address these issues consolidation with the formation of solid-solution is often used.\(^5,\)\(^6,\)\(^7\)

Recently, more complex, three-, four-, five-component diborides were reported as medium-entropy (number of principle metals <4) or high-entropy (number of principle metals >5) ceramics.\(^8,\)\(^9\) These studies suggest that a new class of ceramics and hence high-performance ceramic composites can emerge. Because of the variety of routes to produce bulk high-entropy diborides, an unconventional relationship between structure and mechanical properties can be anticipated.\(^9,\)\(^10,\)\(^11\)

In the present study to obtain a medium-entropy diboride, the TaB\(_2\), ZrB\(_2\), and HfB\(_2\) were combined at the mixing stage. Formation of a solid solution between diborides was observed during spark plasma consolidation at 1927 °C (2200 K). The present investigation will examine the formation of these ceramics using X-ray diffraction (XRD). In particular, the effect of the processing conditions on the lattice parameters was the main focus of this study.

2. Materials and methods

Commercially available ZrB\(_2\) (Lot # TLN0199, Wako Pure Chemicals, Osaka, Japan), HfB\(_2\) (Lot # T302510, Japan New Metals Co. Ltd., Osaka, Japan), and TaB\(_2\) (Lot # T301160, Japan New Metals Co. Ltd., Osaka, Japan) powders were used as the starting materials.

The raw powders were mixed in equimolar ratios ZrB\(_2\):HfB\(_2\):TaB\(_2\) 1:1:1. Powder mixtures were prepared by wet-chemical mixing in alcohol with low-temperature drying (at ~100 °C) to remove moisture. The resultant powder was screened using a 60-mesh screen.

For simplicity, a ternary equimolar mixture was denoted as ZHT. Dwell time of 1 and 20 min at 1927 °C was used: ZHT–1 and ZHT–20, respectively. Furthermore, to observe phase formation specifics of ternary solid-solution,\(^10\) a ZHT–0 specimen was consolidated at 1800 °C without a dwell.

The SPS experiments were conducted using ‘Dr. Sinter’
1050 (Sumitomo, Japan) unit using a 30 mm die. The schedule for the ZHT specimens prepared in this study had four major steps: (1) heating to 700 °C in four minutes following a five-minute dwell, (2) heating to 1400 °C in 10 min with a five-minute dwell; (3) five-minute ramp to 1927 °C, where dwells of 1 and 20 min were used. The last step included cooling down to 600 °C in 15 min. Steps (1) and (2) were performed in a vacuum; during the dwell at 1400 °C, the SPS chamber was backfilled with argon. At the end of the dwell at stage (2), the pressure was increased from 8 to 12 kN, while reaching 1927 °C the pressure was increased from 12 to 32 kN. The pressure of 32 kN was maintained during the consolidation and cooling stages. Argon gas at the flow rate of 2 L/min was used.

An XRD analysis (D8 Advance, Bruker, Karlsruhe, Germany) was performed on the polished surfaces of the bars before the flexural tests to identify the crystalline phases using the Cu-Kα radiation. The intensity data were collected over the 2θ range of 20–120°, in steps of 0.02–0.05°, using a sampling time of 10 s for each step. The program used for refinement was Topas (TOPAS 4.2, Bruker AXS, Germany). Instrumental broadening was determined using a NIST 660b LaB6 standard is run under the same conditions as each diboride sample.12) The computation of the lattice parameters for the AlB2-type diborides was performed using Topas software or using the analytical method proposed by Cohen.12),13) Lattice parameters were determined with an accuracy of 0.0001 Å.

The structural characteristics of powders and were studied using scanning electron microscopy (SEM, JCM-6000, JEOL) using the backscattered electrons (BSE mode). SEM investigation of the bulk ceramics was undertaken using polished and fractured surfaces.

The three-point flexural strength was determined using rectangular blocks (2 × 2.5 × 20 mm) using strength testing equipment described in depth previously.10) A span of 16 mm was used. Measurements were performed with a loading speed of 0.5 mm/min. Four to six samples were tested at room temperature originated from ceramic tiles that were free of macroscopic cracks. The standard deviation was taken as the measurement accuracy.

The fracture toughness of composites was evaluated using specimens testing in bending which contained a single edge through-thickness notch (2 × 4 × 25 mm, notch width 90 μm, depth 1.2 mm, a/W < 0.275) following ASTM C1421–16. Two tests with loading rates of 0.05 and 0.5 mm/min were performed.

Hardness was determined by an MMT-7 Vickers hardness tester (Matsuzawa MMT-7; Matsuzawa SEIKI Co., Ltd., Tokyo, Japan), using load 9.8 N with a dwell time of 15 s following the standard procedure (ASTM C 1327–15).

3. Results and discussion

Figure 1 shows electron microscopy images of the raw powders with sizes ranging from 0.5 to 4 μm. For the successful synthesis of medium-entropy ceramics, it was suggested in11) that the different diboride powders exhibit different particle morphologies and sizes should be used. Hence within the scope of this study, HfB2 powder had the smallest particle size and irregular shape, whereas the ZrB2 powder had a spherical shape with size up to 5 μm.

Studies on the ternary TaC–ZrC–NbC system10) showed that an intermediate stage for the formation of complex solid-solutions can be observed during the SPS consolidation by adjusting dwell time and pressure application. Likewise in this study, the maximum pressure was applied only at the temperature of consolidation. This step is required to preserve components from the reaction at the lower temperatures.7),14) For instance, Sitler et al.5) reported that solid-solution between ZrB2 and HfB2 can be

![Fig. 1. SEM micrographs of (a) initial powder mixture and (b-d) consolidated ceramics using the spark plasma consolidation method. (b) shows a ZHT bulk after consolidation at 1800 °C without a dwell (ZHT–0). (c) and (d) show ZHT–1 and ZHT–20 bulks after flexural tests following consolidation at 1927 °C after a 1 and 20 min dwell, respectively. All images are taken in BSE mode.](image-url)
obtained at temperatures as low as 1700 °C. We prepared the binary equimolar solid-solution using similar conditions to ZHT–20, to understand the formation of the ZHT diboride (Suppl 1).

The bulk densities of the SPSed ZHT ceramics are 8.51 g/cm³ (ZHT–0), 9.12 g/cm³ (ZHT–1) and 9.36 g/cm³ (ZHT–20). Based on the XRD analyses (Fig. 2), after the SPS consolidation at 2200 K and dwell of 20 min, a single-phase ceramic was formed.

The lattice parameters of the ternary (Zr1/3Hf1/3Ta1/3)B2 (ZHT–20) phase was estimated to be $a = 3.137\,\text{Å}$ and $c = 3.467\,\text{Å}$. These were close to the lattice of the hafnium diboride $a = 3.139\,\text{Å}$ and $c = 3.474\,\text{Å}$.

A theoretical density of the ZHT bulk was assumed to be 9.65 g/cm³ from the XRD data assuming the equatomic contribution of 1/3 of the Zr, Hf and Ta atoms in the AlB2-type unit cell (i.e., two atoms for boron and one atom for metal).

For the (Zr,Hf,Ta)B2 ceramic after a minute dwell at 1927 °C two solid solutions can be observed: solid solution $i$ close to the final ternary phase $a = 3.137\,\text{Å}$ and $c = 3.467\,\text{Å}$ and solid solution $ii$ with lattice parameters $a = 3.107\,\text{Å}$ and $c = 3.415\,\text{Å}$ (see Fig. 2[c]). An explanation of the multistage formation of the ZHT solid–solution would be based on the different diffusivities of the transition metal atoms AlB2-type structure (see Suppl 2).

The SEM micrographs for ceramic bulk after the flexural tests at room temperature (Fig. 1) clearly illustrate the difference in the final composition of ZHT ceramics using different processing conditions: ZHT–1 and ZHT–20 ceramics had a mean grain size between 10 and 20 μm. For the ZHT–1 ceramic presence of two diboride phases was confirmed by observation in the BSE mode. Interestingly, for the ZHT–0 ceramic the grain size comparable with that for initial powders. Due to the relatively low consolidation temperature of 1800 °C, the formation of a binary solid solution could be observed. For clarity, images for Fig. 1 were taken without a change in contrast during a single SEM session.

Due to different diffusivity for transition metal atoms, it is believed that a solid solution between HfB2 and TaB2 would be formed initially, but it is thought that powder particle size may also control a solid-solution reaction.11)

Hardness of bulk ZHT ceramics was within 28.6 ± 1.3 GPa, comparable with that reported in (16,19). In terms of the development of four-component (medium-entropy ceramics) or five-component high-entropy diborides with ZHT atoms, as a structural material for the high-temperature applications, further optimization of the processing may be required.

For the ZHT–20 ceramic, within eight specimens attempted, only two were free of macroscopic cracks.5) Thus it is thought that micro- and macrocracking is the main reason for the wide absence of flexural strength data for these compounds. Further optimization of the consolidation process, especially the dwell and cooling stages is vital to decrease grain size to control the mechanical performance and cracking issue.

For the crack-free specimens, the flexural strength and fracture toughness at room temperature were 318 ± 14 MPa and 2.9 MPa m1/2, respectively (Table 1,15) and Suppl 3). Strength data for the ZHT–20 ceramic agrees favorably with findings for bulk TaB216 or ZrB2.4 For the high-entropy ceramics flexural strength was reported previously for (Ti,Ta,Zr,Hf,Nb)B2 339 ± 17 MPa,15 and (Ti,Ta,Zr,Hf,Nb)C 318 ± 25,17) 332 ± 24.18) One can see that strength in these report remains in the range 320–345 MPa, despite difference in processing, grain size and crystalline lattice. Data in ref19) shows that consolidation of high-entropy carbide with grain size of 0.5 μm allows increasing strength up to 400 ± 27 MPa. This underlines that for high-entropy ceramics or medium-entropy ceramics the effect of grain size can be dominant or modest over solid-solution strengthening. To understand the balance
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high-entropy diboride (Ti,Ta,Zr,Hf,Nb)B₂ with di-

between solid-solution and grain size, it is suggested that

monolithic diboride bulks. There is every reason to believe

size of above 15

research. It is suggested that further systematic research is required.

grain sizes will have strength higher than 350 MPa, but

that medium-entropy and high-entropy diborides with

mechanical performance of monolithic diborides with fi-

Mechanical performance at room temperature for

 Grant the importance of further consolidation kinetics studies on

these ceramics. These studies and high-temperature charac-

terization of bulk diborides ceramics with different grain

sizes are considered as a crucial step in the ongoing

research.

4. Conclusions

Bulk solid-solution or medium-entropy ceramic dibor-

dies been obtained at relatively low consolidation temper-

ature using the spark plasma sintering method. Phase anal-

ysis via lattice parameter measurements by XRD showed

the multi-stage formation of the single-phase medium-

entropy boride with the lattice parameters of \( a = 3.133 \AA \)

and \( c = 3.467 \AA \).

The mechanical performance at room temperature for

\((Zr,Hf,Ta)B₂\) is being controlled by a relatively large grain

size of above 15 \( \mu \text{m} \), and it is on the same level as that for

monolithic diboride bulks. There is every reason to believe

that medium-entropy and high-entropy diborides with finer

grain sizes will have strength higher than 350 MPa, but

further systematic research is required.

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Table 1. Physical and mechanical properties of medium-entropy (Zr,Hf,Ta)B₂ consolidated by SPS

| Designation | Bulk density, \( \text{g/cm}^3 \) | Relative density, \( \% \) | Lattice parameters for solid solution, \( \AA \) | Grain size, \( \mu \text{m} \) | Hardness, GPa | Flexural strength, MPa | Fracture toughness, \( KIC, \text{MPa}m^{1/2} \) |
|-------------|----------------|----------------|-----------------|----------------|----------------|-----------------|---------------------|
| ZHT–0       | 8.51           | 86.48          | 3.1369\(^*\) \( a \) 3.3676\(^*\) \( c \) | 2–8           | \(-17.1\)       | \(-294 \pm 37\)  | \(-\)               |
| ZHT–1       | 9.12           | 93.92          | 3.1373 \( a \) 3.4674 \( c \) | 12 \pm 7       | \(-27.9 \pm 1.5\) | \(-310 \pm 42\)   | \(-3.0\)            |
| ZHT–20      | 9.36           | 96.99          | 3.1374 \( a \) 3.4678 \( c \) | 15 \pm 6       | \(-28.6 \pm 1.3\) | \(-318 \pm 14\)   | \(-2.9\)            |
| \((Ti,Ta,Zr,Hf,Nb)B₂\)\(^{15}\) | 8.29           | 99.8           | 3.1006 \( a \) 3.3604 \( c \) | 4.06          | \(-22.0 \pm 0.9\) | \(-339 \pm 17\)   | \(-3.81 \pm 0.40\)  |

\(^*\) – HfB₂–TaB₂.

\(^{\overset{\circ}{\circ}}\) – Lattice parameters were determined with an accuracy of 0.0001 \( \AA \).

\(^{\overset{\circ}{\circ}}\) – Assuming theoretical density from the XRD data.

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