Stabilizing Softer WB$_2$ and MoB$_2$ Components into High-Entropy Borides via Boron-Metals Reactive Sintering to Attain Higher Hardness

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Abstract:

Five single-phase W- and Mo-containing high-entropy borides (HEBs) have been made via reactive spark plasma sintering of elemental boron and metals. A large reactive driving force enables the full dissolution of 10-20 mol. % WB$_2$ to form dense, single-phase HEBs, including (Ti$_{0.2}$Zr$_{0.2}$Hf$_{0.2}$Mo$_{0.2}$W$_{0.2}$)B$_2$, (Ti$_{0.2}$Ta$_{0.2}$Cr$_{0.2}$Mo$_{0.2}$W$_{0.2}$)B$_2$, (Zr$_{0.2}$Hf$_{0.2}$Nb$_{0.2}$Ta$_{0.2}$W$_{0.2}$)B$_2$, and (Zr$_{0.225}$Hf$_{0.225}$Ta$_{0.225}$Mo$_{0.225}$W$_{0.1}$)B$_2$, for the first time; in contrast, such single-phase W-containing HEBs cannot be made via conventional fabrication routes. In the processing science, this result serves perhaps the best example demonstrating that the phase formation in high-entropy ceramics can strongly depend on the kinetic route. A scientifically interesting finding is that HEBs containing softer WB$_2$ and/or MoB$_2$ components are significantly harder than (Ti$_{0.2}$Zr$_{0.2}$Hf$_{0.2}$Nb$_{0.2}$Ta$_{0.2}$)B$_2$. This exemplifies that high-entropy ceramics can enable unexpected/improved properties beyond the rule of mixture.

Keywords: high-entropy ceramics; high-entropy borides; ultrahigh temperature ceramics; in-situ reactive sintering; hardness

Summary of Novel Conclusions:

A new direct boron-metals reactive sintering route can synthesize W-containing single-phase high-entropy borides that cannot be made before. Interestingly, incorporating softer WB$_2$ and MoB$_2$ components makes single-phase high-entropy borides harder.

Highlights:

- Phase formation in high-entropy borides (HEBs) depends on the fabrication route.
- Conventionally-fabricated W-containing HEBs always have a W-rich secondary phase.
- New direct boron-metals reactive sintering makes single-phase W-containing HEBs.
- Incorporating softer WB$_2$ and MoB$_2$ components makes single-phase HEBs harder.
- High-entropy ceramics enable unexpected properties beyond the rule of mixture.

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1. Introduction

In the physical metallurgy community, high-entropy alloys have received great attentions since their introduction by Yeh et al. [1] and Cantor et al. [2] in 2004. In the ceramics community, high-entropy rocksalt [3], perovskite [4], and fluorite [5] oxides, as well as borides [6], carbides [7-10], silicides [11, 12], and fluorides [13] have been made in the past a few years.

In 2016, Gild et al. [6] first reported the fabrication of single-phase high-entropy borides (HEBs) in the hexagonal AlB$_2$ structure, which represent the first non-oxide high-entropy ceramics fabricated in bulk form and a new class in ultrahigh temperature ceramics (UHTCs). Since then, substantial efforts have been made to fabricate HEBs [14-19]. Notably, Tallarita et al. synthesized (Ti$_{0.2}$Zr$_{0.2}$Hf$_{0.2}$Nb$_{0.2}$Ta$_{0.2}$)B$_2$ [17] and (Ti$_{0.2}$Zr$_{0.2}$Hf$_{0.2}$Nb$_{0.2}$Mo$_{0.2}$)B$_2$ [19] via a two-step processing method, achieving relative densities of ~92.5% for both cases; in their method, elemental metals and boron were first converted to metal diborides via self-propagating high-temperature synthesis (SHS), and subsequently densified by spark plasma sintering (SPS). Tallarita et al. also tried directly reactive SPS (Ti$_{0.2}$Zr$_{0.2}$Hf$_{0.2}$Nb$_{0.2}$Mo$_{0.2}$)B$_2$ from boron and metals in one step (1950 °C, 20 min, 20 MPa), but did not achieve a high density and uniform microstructure due to out-gassing [19]. Moreover, direct reactive SPS from elemental precursors was applied to make high-entropy (Ti$_{0.2}$Zr$_{0.2}$Nb$_{0.2}$Ta$_{0.2}$W$_{0.2}$)C [20] and (Ti$_{0.2}$Zr$_{0.2}$Nb$_{0.2}$Mo$_{0.2}$W$_{0.2}$)Si$_2$ [11].

WB$_2$ of the AlB$_2$ prototype structure is thermodynamically unstable and difficult to synthesize [21, 22]. Instead, a W$_2$B$_{5-x}$ phase (space group P6$_3$/mmc, no.194), a different hexagonal structure of stacking AlB$_2$-type layers separated by defect-rich puckered boron layers of alternating orientations, is the equilibrium phase in the W-B phase diagram. Only a limited number of studies demonstrated the formation of AlB$_2$-type WB$_2$ in nano-scale coating or thin films [23-26] or after extensive ball milling [27]. Notably, an AlB$_2$-type phase can be kinetically stabilized in TiB$_2$-WB$_2$ [28, 29]; yet, a WB secondary phase were found to precipitate out in TiB$_2$-CrB$_2$-WB$_2$ [30]. In recent studies of HEBs, a W-rich secondary phase was reported to form in nominally (Ti$_{0.2}$Zr$_{0.2}$Hf$_{0.2}$Mo$_{0.2}$W$_{0.2}$)B$_2$ specimens made by either SPS of a high energy ball milled (HEBM) mixture of five binary borides [6] or powders synthesized by borocarbothermal reduction [18]. To the best of our knowledge, single-phase HEBs containing 10-20 mol. % WB$_2$ have not been successfully made to date (albeit HEBs containing 20 mol. % MoB$_2$ have been made [6, 15, 19], although AlB$_2$-type MoB$_2$ is also not a stable phase at room temperature).

In this study, we showed that reactive SPS of elemental metal and boron powders enables the
synthesis of three compositions of single-phase HEBs containing 20 mol. % WB₂ (plus another HEB containing 10 mol. % WB₂); in contrast, SPS of milled mixtures of five binary borides always led to the formation of a secondary WB-rich monoboride phase in the same four compositions. Notably, we further made a scientifically interesting discovery: HEBs containing softer WB₂ and/or MoB₂ components [31] are harder than (Ti₀.₂Zr₀.₂Hf₀.₂Nb₀.₂Ta₀.₂)B₂. Thus, this study exemplifies that high-entropy ceramics can enable unexpected properties beyond the rule of mixture.

2. Method

For boron-metals reactive SPS, elemental powders of Ti, Cr, Zr, Nb, Mo, Hf, Ta, and W (>99% purity, ~325 mesh, purchased from Alfa Aesar, MA, USA) and boron (99% purity, 1-2 μm, purchased from US Research Nanomaterials, TX, USA) were utilized for making specimens HEB-A₁ to HEB-F₁ listed in Table 1. For each composition, appropriate amounts of metals and boron (with 10% excess B added to offset the loss due to reaction with native oxide and subsequently evaporation) were weighted out in batches of 5 g. The powders were hand-mixed and subsequently HEBM in a Spex 8000D mill (SpexCertPrep, NJ, USA) in tungsten carbide lined stainless steel jars and 10 mm tungsten carbide milling media, for 50 min with 1 wt. % stearic acid as lubricant. The HEBM was performed in an argon atmosphere (O₂ < 10 ppm) to prevent oxidation.

The milled powders were loaded into 10 mm graphite dies lined with graphite foils in batches of 2 g, and subsequently consolidated into dense pellets via SPS in vacuum (10⁻² Torr) using a Thermal Technologies 3000 series SPS (CA, USA). During the initial temperature ramping at 50 °C/min with uniaxial load of 10 MPa, in-situ reaction of metals and boron likely takes place. Differing from Tallarita et al.’s trial of directly reactive SPS of (Ti₀.₂Zr₀.₂Hf₀.₂Nb₀.₂Mo₀.₂)B₂ in one step (1950 °C, 20 min, 20 MPa) that did not achieve a high density [19], our specimen was first held in SPS at 1400 °C and 1600 °C, successively, for 40 min each, to allow out-gassing and reduction of native oxides with excess boron [32]. After that, the temperature was raised to 2000 °C at a lower heating rate of 30 °C/min and sintered isothermally for 10 min for final densification; at the same time, the load was increased to 50 MPa at a rate of 5 MPa/min. Finally, the sintered specimen was cooled in the SPS machine to room temperature.

For a comparison study, specimens of the four W-containing compositions were also synthesized via conventional HEBM and SPS of five binary metal borides (following the route in Ref. [6]), and these benchmark specimens are labelled as HEB-C₂ to HEB-F₂. It should be noted
that Mo$_2$B$_{5.3}$ and W$_2$B$_{5.3}$ powders were used as the starting binary borides of Mo and W since the AlB$_2$-structured MoB$_2$ and WB$_2$ are unstable and not commercially available.

Densities for specimen HEB-A1 to HEB-F1 were measured via the Archimedes method after grinding and polishing; their relative densities were calculated based on theoretical densities calculated from the ideal stoichiometry and the lattice parameters measured by X-ray diffraction (XRD) and listed in Suppl. Table S1. XRD characterizations were carried out on all specimens using a Rigaku Miniflex diffractometer with Cu Kα radiation at 30 kV and 15 mA. Scanning electron microscopy (SEM), electron dispersive X-ray spectroscopy (EDS), and electron backscatter diffraction (EBSD) data were collected with a FEI Apreo microscope equipped with an Oxford N-Max$^N$ EDX detector and an Oxford Symmetry EBSD detector. Vickers’ microhardness tests were carried out on a diamond indenter with loading force of 1.96 N (200 gf) and holding time of 15 seconds abiding by the ASTM standard C1327. Multiple measurements were conducted at different locations to ensure statistical validity.

3. Results and Discussion

XRD showed that all six specimens HEB-A1 to HEB-F1 synthesized via boron-metals reactive SPS have virtually single AlB$_2$-structured HEB phases without any detectable secondary phase (Fig. 1(a)). Additional XRD patterns of the as-milled metal and boron powders are shown in Suppl. Fig. S2, which shows that the HEB phase formed during the reactive SPS. SEM further showed that these specimens are dense with <3 vol. % of total porosity and/or extra boron (Fig. 2), which is consistent with measured relative densities (95.5% for HEB-D1 and >97% for all other five specimens as shown in Table 1). EDS elemental maps shown in Fig. 2(a-1) to (f-1) confirm the formation of homogeneous HEB solid solutions for all six compositions.

In a critical comparison, XRD patterns in Fig. 1(b) show that the four W-containing specimens...
HEB-C2 to HEB-F2 synthesized by conventional HEBM and SPS of five binary borides all exhibit a primary AlB$_2$-structured HEB phase with a secondary phase of orthorhombic (CrB prototype, space group Cmcm, no. 63) monoboride. Small amounts of (Zr, Hf)O$_2$ native oxides were also detected in HEB-C2, HEB-E2, and HEB-F2 where ZrB$_2$ and HfB$_2$ were utilized as precursors (while the specimens HEB-C1, HEB-E1, and HEB-F1 of the same compositions made by reactive SPS of elemental boron and metals are essentially oxide-free, as shown in Fig. 1(a)). EDS elemental maps in Fig. 2(c-2) to (f-2) further showed that the secondary monoboride phases are W-rich. Furthermore, the compositions of these monoboride phases were measured by EDS point analyses to be (W$_{0.78}$Mo$_{0.19}$Ti$_{0.02}$Hf$_{0.01}$)B in HEB-C2, (W$_{0.41}$Mo$_{0.28}$Cr$_{0.18}$Ta$_{0.09}$Ti$_{0.04}$)B in HEB-D2, (W$_{0.54}$Ta$_{0.15}$Hf$_{0.13}$Nb$_{0.11}$Zr$_{0.07}$)B in HEB-E2, and (W$_{0.55}$Mo$_{0.36}$Ta$_{0.09}$Hf$_{0.01}$)B in HEB-F2, respectively (Suppl. Fig. S4). Noticeably, the IVB elements Ti, Zr and Hf all have low fractions in these monoboride phases, because their corresponding monoborides not stable [33]. The higher concentrations of VIB elements Cr, Mo, and W than the VB elements Nb and Ta can be justified by the differences in their formation enthalpies between CrB-type and AlB$_2$-type structures. The differences in formation enthalpies ($H_{MB}^M - H_{MB_2}^M$) are -0.277, -0.211, -0.186, -0.163, and -0.07 in eV/atom, respectively for $M = W, Mo, Cr, Ta, and Nb$, respectively, based on the Material Project Database [34]. This order largely confirms the relative fractions of these metals in the secondary monoboride phase, where the most negative $H_{WB}^W - H_{WB_2}^W$ corresponds to the highest W concentrations in the monoboride phase (followed by Mo, Cr, and Ta).

The combination of XRD, SEM, EDS and density measurements showed that four dense, W-containing, single-phase specimens HEB-C1 to HEB-F1 have been successfully synthesized via this new reactive SPS of elemental boron and metals route, which could not be fabricated by conventional HEBM and SPS of mixtures of five binary borides (HEB-C2 to HEB-F2). While one may argue that the use of nonstoichiometric W$_2$B$_{5-x}$ powder might cause a difference here, we note that a W-rich monoboride secondary phase was also observed in a (Ti$_{0.2}$Zr$_{0.2}$Hf$_{0.2}$Mo$_{0.2}$W$_{0.2}$)B$_2$ (i.e. composition HEB-C) specimen synthesized via borocarbothermal reduction of mixed oxides and B$_4$C and subsequent SPS in a most recent study [18] (while the compositions HEB-A and HEB-B were also made into single-phase HEBs via that borocarbothermal reduction route [18]).

The stabilization of 20 mol. % WB$_2$ into the three compositions (plus 10 mol. % WB$_2$ into another composition) of single-phase HEBs represents an achievement of the current work, which have not been achieved in any prior study. This can be explained by the large reactive
thermodynamic driving forces with elemental boron and metals as the starting powders. It is yet unknown whether these W-containing single-phase HEBs are truly thermodynamic stable, or metastable, phases. Nonetheless, this work serves as perhaps the best demonstration to date that the phase formation in HEBs can strongly depend on the kinetic (synthesis and processing) route.

EBSD inverse pole figure orientation maps and their grain size distributions are shown in Fig. 3 for all six specimens synthesized via boron-metals reactive SPS. The averaged grain size varies from 8.6 ± 4.8 μm (for HEB-B1) to 20.7 ± 14.8 μm (for HEB-F1). Notably, all specimens contain some small grains, which is due to the reactive process (as seen in prior studies of reactive sintering of Ti + B [35] and TiH₂ + B [36]). Moreover, preferred grain orientation of (001) plane normal to the direction of the applied pressure is observed, as shown in the inverse pole figure in Suppl. Fig. S5. This texture was further confirmed by comparing the experimental XRD pattern with the calculated XRD pattern (Suppl. Fig. S6). To quantify the degree of this texture, Lotgering orientation factor [37] \( f \) was calculated to be from ~0.08 (for HEB-E1 with the least texture) to ~0.15 (for HEB-C1 with the most texture), which represent moderate textures. For comparison, a prior study showed a significant texture in \( f \sim 0.6 - 0.7 \) in TiB₂ made by a similar in-situ reactive SPS from TiH₂ [36]. We find that the formation of this texture in our HEBs is related to the applied pressure. To demonstrate this, an HEB-B specimen was fabricated at a reduced initial loading of <1 MPa via the same routine to achieve minimal texture \( (f < 0.01) \) (Suppl. Fig. S7 and S8).

Vickers’ microhardness was measured for all six specimens made by reactive SPS of elemental boron and metals and the results are summarized in Table 1. The measured hardness of HEB-A1 (20.9 ± 1.1 GPa) is consistent with those previously-reported dense specimens of the same compositions \((\text{Ti}_{0.2}\text{Zr}_{0.2}\text{Hf}_{0.2}\text{Nb}_{0.2}\text{Ta}_{0.2})\text{B}_2\) synthesized via different routines [15, 18]. Note that single-phase specimens HEB-A1 and HEB-B1 sintered in this study are harder than those less dense (91-93%) specimens first reported in 2016, where the differences can be well explained by the porosity as well as oxide inclusions in those earlier specimens [6].

Most interestingly, the five Mo- and W-containing single-phase specimens HEB-B1 to HEB-F1 are harder than the Mo- and W-free reference specimen HEB-A1: \((\text{Ti}_{0.2}\text{Zr}_{0.2}\text{Hf}_{0.2}\text{Nb}_{0.2}\text{Ta}_{0.2})\text{B}_2\) (Vickers hardness 20.9 ± 1.1 GPa). In comparison, the Vickers hardness of the Mo-containing specimen HEB-B1: \((\text{Ti}_{0.2}\text{Zr}_{0.2}\text{Nb}_{0.2}\text{Ta}_{0.2}\text{Mo}_{0.2})\text{B}_2\) is increased to 24.9 ± 1.1 GPa. This is consistent with two prior studies [6, 18]. More interestingly, four W-containing specimens HEB-C1 to HEB-F1 have been made into single HEB phase for the first time. Three of them (HEB-C1, HEB-E1,
and HEB-F1) have even greater Vickers hardness of 26-27.5 GPa, while the relatively lower hardness of HEB-D1 (23.7 ± 1.3 GPa) may be explained from its lower relative density (95.5%).

This observation (that W- and Mo-containing HEBs are harder) is somewhat surprising and highly interesting since prior DFT calculations predicted WB₂ (along with MoB₂ and CrB₂) to have significantly lower hardness (and more ductile) than other diborides (TiB₂, ZrB₂, HfB₂, NbB₂, and TaB₂) [31]. It is possible that this enhanced hardness is due to a “cocktail” effect of introducing different elements that can enhance different mechanical properties (e.g., ductility vs. modulus) [31] as well as higher valence electron concentrations from introducing VIB elements to contribute more p electrons to form p-d hybridization with boron [38]. Further modeling study is needed to uncover the exact underlying mechanism. Nonetheless, this clearly demonstrates that high-entropy ceramics can exhibit unexpected/improved properties beyond the rule of mixture.

4. Conclusions

In summary, this study has demonstrated the synthesis of single-phase HEBs that contains 20 mol. % WB₂ for the first time via reactive SPS of elemental boron and metals, whereas they are not attainable by conventional HEBM and SPS of five binary borides (or borocarbothermal reduction synthesis shown in a separate study [18]). These single-phase HEB specimens have achieved high relative density with virtually no native oxides. This serves as perhaps the best example to date demonstrating that the phase formation in HEBs depends on the kinetic route and suggests that reactive sintering of elements with large reactive driving forces may represent a new route to synthesize single-phase high-entropy ceramics to allow alloying of certain elements that are otherwise difficult to dissolve in significant amounts.

Mostly interestingly, this study further demonstrates that the incorporation of softer WB₂ and/or MoB₂ components in HEBs can make them harder, thereby suggesting that high-entropy ceramics can enable unexpected properties beyond the rule of mixture.

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Appendix A. Supplementary Data

Supplementary Table S1 and S2 and Supplementary Figures S1-S8 related to this article can be found, in the online version, at doi: xxxxxxxx. (The Supplementary Data are included as “Electronic Annex” for review).
Table 1. Summary of the six specimens synthesized via reactive sintering of elemental boron and metals. See Suppl. Table S1 for additional data of lattice parameters and theoretical densities.

| Specimen | Compositions                  | Density (g/cm$^3$) | Vickers’ Hardness (GPa) |
|----------|-------------------------------|--------------------|-------------------------|
| HEB-A1   | (Ti$_{0.2}$Zr$_{0.2}$Hf$_{0.2}$Nb$_{0.2}$Ta$_{0.2}$)B$_2$ | 8.13 (98.1%)       | 20.9 ± 1.1              |
| HEB-B1   | (Ti$_{0.2}$Zr$_{0.2}$Nb$_{0.2}$Ta$_{0.2}$Mo$_{0.2}$)B$_2$ | 7.46 (99.2%)       | 24.9 ± 1.3              |
| HEB-C1   | (Ti$_{0.2}$Zr$_{0.2}$Hf$_{0.2}$Mo$_{0.2}$W$_{0.2}$)B$_2$  | 8.35 (97.5%)       | 26.0 ± 1.5              |
| HEB-D1   | (Ti$_{0.2}$Ta$_{0.2}$Cr$_{0.2}$Mo$_{0.2}$W$_{0.2}$)B$_2$  | 8.37 (95.5%)       | 23.7 ± 1.3              |
| HEB-E1   | (Zr$_{0.2}$Hf$_{0.2}$Nb$_{0.2}$Ta$_{0.2}$W$_{0.2}$)B$_2$  | 9.78 (98.1%)       | 26.7 ± 1.1              |
| HEB-F1   | (Zr$_{0.225}$Hf$_{0.225}$Ta$_{0.225}$Mo$_{0.225}$W$_{0.1}$)B$_2$ | 9.56 (98.8%)       | 27.5 ± 1.1              |
Fig. 1. XRD patterns of specimens of different compositions, synthesized via (a) reactive SPS of elemental boron and metals and (b) conventional SPS of mixtures of binary borides. On the one hand, specimens HEB-A1 to HEB-F1 fabricated via reactive SPS of elemental boron and metals all demonstrate a single AlB$_2$-structured hexagonal phase without detectable secondary phase by XRD. On the other hand, the four W-containing specimens fabricated from mixed binary borides all show noticeable amounts of a WB-rich (as revealed the EDS analysis) secondary monoboride phase, as well as minor (Zr, Hf)O$_2$ native oxides (except HEB-D2). Note that a similar XRD pattern for HEB-C2 was reported in Ref. [6] and included here for comparison purpose.
Fig. 2. SEM micrographs and EDS elemental maps of specimens synthesized (a-1 to f-1) via reactive SPS of elemental boron and metals and (c-2 to f-2) conventional SPS of mixtures of binary borides. On the one hand, all six specimens fabricated by reactive SPS of elemental boron and metals show homogenous elemental distributions. On the other hand, the four W-containing specimens HEB-C2 to HEB-F2 fabricated from SPS of mixtures of binary borides exhibit W-rich secondary phase particles, as well as high porosity. Note that similar EDS elemental maps for HEB-C2 was reported in the Suppl. Data for Ref. [6] and included here for comparison purpose.
Fig. 3. EBSD normal direction inverse pole figure orientation maps for specimens (a) HEB-A1, (b) HEB-B1, (c) HEB-C1, (d) HEB-D1, (e) HEB-E1, and (f) HEB-F1, synthesized via reactive SPS of elemental boron and metals. Insets are grain size distributions.
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