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Synthesis of Ultra-Refractory Transition Metal Diboride Compounds

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Abstract

This paper critically evaluates methods used to synthesize boride compounds with emphasis on diborides of the early transition metals. The earliest reports of the synthesis of boride ceramics used impure elemental powders to produce multi-phase reaction products; phase-pure borides were only synthesized after processes were established to purify elemental boron. Carbothermal reduction of the corresponding transition metal oxides emerged as a viable production route and continues to be the primary method for synthesis of commercial transition metal diboride powders. Even though reaction-based processes and chemical synthesis methods are mainly used for research studies, they are powerful tools for producing diborides because they provide the ability to tailor purity and particle size. The choice of synthesis method requires balancing factors that include cost, purity, and particle size with the performance needed in expected applications.

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Synthesis of Ultra-Refractory Transition Metal Diboride Compounds

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Abstract

This paper critically evaluates methods used to synthesize boride compounds with emphasis on diborides of the early transition metals. The earliest reports of the synthesis of boride ceramics used impure elemental powders to produce multi-phase reaction products; phase-pure borides were only synthesized after processes were established to purify elemental boron. Carbothermal reduction of the corresponding transition metal oxides emerged as a viable production route and continues to be the primary method for synthesis of commercial transition metal diboride powders. Even though reaction-based processes and chemical synthesis methods are mainly used for research studies, they are powerful tools for producing diborides because they provide the ability to tailor purity and particle size. The choice of synthesis method requires balancing factors that include cost, purity, and particle size with the performance needed in expected applications.

I. Introduction

Transition metals (TMs) form a tremendous variety of boride compounds ranging from boron-rich dodecahedron or icosahedral structures such as ScB_{12} and YB_{25} to metal-rich close-packed compounds such as W_2B_5 and TiB. From the larger family of boride compounds, the early transition metals all form metal-rich refractory borides TMs, Table I,[121] although synthesis methods described herein are applicable to other boride compounds with different stoichiometries and structures, including ternary borides. From the larger family of metal-rich

TM borides, the paper focuses on methods to produce Ti, Zr, and Hf diborides, which share the AlB_2 structure with other TM diborides including CrB_2, TaB_2, and NbB_2. The TM diborides have a complex mix of bond types resulting in a remarkable combination of metal-like and ceramic-like properties.[22-25] The AlB_2 structure consists of layers of close-packed metal atoms that alternate with boron in graphite-like sheets. Metallic bonding in the TM layers leads to high electrical (10^7 S/m for ZrB_2)[26,27] and thermal (~130 W/m•K for ZrB_2)[27-29] conductivities, while strong covalent bonding in the B layers gives high hardness (~33 GPa for TiB_2)[30] and elastic modulus (~560 GPa for TiB_2)[31] values. Strong cohesion between TM and B layers is the result of complex bonding that includes ionic, hybridized covalent, and metallic character.[32,33] The same characteristics (high melting temperature, strong covalent bonds) that give TM boride compounds attractive properties also result in challenges related to producing high purity ceramics with high relative density.[34] Based on their inherent properties, TM diboride compounds have the potential to withstand extreme environments such as those associated with hypersonic aerospace vehicles, rocket motors, scramjet engines, lightweight armor, high speed cutting tools, refractories for molten metal contact applications, plasma-facing materials for nuclear fusion reactors, and fuel forms for advanced nuclear fission reactors.[35-46] These applications involve temperatures, heat fluxes, radiation levels, strain rates, and/or chemical reactivities that are beyond the capabilities of existing structural materials.[47] For example, the sharp leading edges of hypersonic aerospace vehicles are expected to experience temperatures of 2000°C or higher and heat fluxes of more than 300 W/cm^2,[48-50] which are well beyond the capabilities of the current generations of Si-based structural ceramics and Ni-based superalloys. Realization of improved boron-based ceramics could enable revolutionary advances in these and other technologies leading to broad improvements in performance, operating lifetime, and/or efficiency.

Existing and future boron-based ceramics will find application in forms ranging from thin films to bulk structures.[51] Accordingly, different synthesis methods will best suit the different structures. For example, hard boride coatings for high speed cutting tools might best be synthesized and deposited by vapor phase methods,[52] whereas liquid precursors would be preferred to produce ceramic matrices for continuous-fiber reinforced composites.[53] Other high temperature structural applications will require fabrication of bulk ceramics, which might be best accomplished by processes that combine reactive synthesis with densification.[54] Hence, a variety of methods are needed, some of which will only be capable of producing milligrams of material per day whereas others could produce kilograms of high purity ceramic powders.

The purpose of this paper is to review and evaluate methods used to synthesize TM diboride compounds. The focus is on refractory diborides of early transition metals, but the same methods can be used to produce new boron-based ceramics with compositions, microstructures, and/or properties tailored for future applications.

II. Historic Reports

Synthesis processes for TM diborides trace back to the late 1800s and early 1900s. Henri Moissan identified a number of boride compounds,[55,56] including mentioning titanium boride in a study of the purification of titanium metal reported in 1895,[57] as part of his pioneering work using the electric arc furnace to produce compounds by fusion processes. In 1901, Tucker and Moody described the synthesis of zirconium boride by reaction of elements, although they assigned the formula Zr_3B_4 to their impure material.[58,59] Likewise, Wedekind prepared impure borides by vacuum melting.[60] One of the first reports of carbothermal reduction, Reaction 1 shown in Table II, to produce diborides was by McKenna who produced TiB_2 and ZrB_2 in 1936.[61] In contrast to the earlier papers on most other TM diborides, the first report of the synthesis of HfB_2 was in 1931.[62] Hafnium itself was not isolated until 1923,[63] which accounts for the delay in describing synthesis of HfB_2 compared to other TM borides. While TM boride compounds were reported in this era, none of the materials were phase pure.

Preparation of phase pure diborides was enabled by Kiessling's production of high purity boron in the late 1940s.[64] This breakthrough led to the synthesis of a number of nominally pure TM diboride compounds,[65-67] including zirconium diboride,[68] by reaction of boron with elemental metals, Reaction 2, as well as later work on borothermal reduction of oxides, Reaction 3.[69-73] Other methods such as reactions with boron carbide, Reactions 4 and 5,[74-76] metallothermic reduction, Reactions 6 and 7,[77,78] electrolysis of fused salts, Reaction 8,[79,80] and vapor phase methods, Reaction 9[81-83] were also used to produce boride compounds. Through the 1950s and 1960s, research on diborides, particularly those of Ti, Zr and Hf, typically utilized commercially available powders.[84-86] Some of the exceptions were the phase equilibria studies by Rudy[87] and the examination of borides of alkali,[88] alkaline earth,[89] rare-earth,[90] or less-common transition metals[91] as well as studies of ternary and higher borides.[92,93] This trend continues to hold true to the present time whereby the majority of studies of the more common diborides (e.g., TiB_2, ZrB_2, and HfB_2) use commercial powders whereas self-synthesis is mainly used for other borides.

III. Reduction Processes

Commercially available TM diboride powders are predominantly synthesized by carbothermal reduction of the corresponding TM oxides, Reaction 1.[94-98] The resulting powders typically contain oxygen and excess carbon as impurities along with any metallic impurities present in the starting raw materials. For example, commercial ZrB_2 is produced from naturally-occurring zircon ores, which contain Hf as an impurity. Therefore, most commercial ZrB_2 powders contain Hf. A recent analysis showed that a widely used commercial powder (H.C. Starck, Grade B) contained ~1.7 wt.% Hf,[99] although the natural abundance of Hf in Zr-bearing minerals generally ranges from 1 to 5 wt% depending on the deposit.[100] While the Hf impurities do not appear to have an affect on most properties, recent reports have shown that the presence of Hf has a strong, negative impact on thermal transport with thermal conductivity decreasing from ~140 W/m•K for ZrB_2 with a Hf content of 0.01 at% to ~100 W/m•K for ZrB_2 with the natural abundance of Hf (0.33 at%).[101] Likewise, the natural Hf content of ZrB_2 reduces its heat capacity by about 15% compared to powders synthesized from Zr with lower Hf contents.[102]

Carbothermal reduction of transition metal oxides by Reaction 1 only becomes thermodynamically favorable at elevated temperatures. For example, the standard state change in Gibbs' free energy (ΔG^o_{rxn}) for the formation of ZrB_2 by carbothermal reduction, Reaction 10, is given by Equation 11, which shows that the reaction becomes favorable (i.e., ΔG^o_{rxn} is less than zero) above ~1500°C. In addition, carbothermal reduction reactions are highly endothermic (ΔH^o_{rxn}= 1475 kJ at 298 K). As a result of these factors, carbothermal reduction reactions are carried out at elevated temperatures.

$$ZrO_{2\,(s)} + B_2O_{3\,(l)} + 5C_{(s)} \rightarrow ZrB_{2\,(s)} + 5CO_{(g)} \qquad (10)$$

$$\Delta G^o_{rxn} = 1,430,600 - 803.25T \text{ (J)} \qquad (11)$$

Similarly, other reactions that form transition metal borides from oxide precursors, Reactions 4 and 5, also become favorable at elevated temperature and are highly endothermic. Comparison of the values of ΔG^o_{rxn} for Reactions 1, 4, and 5 normalized to formation of one mole of ZrB_2

shows that each becomes favorable between 1300°C and 1500°C, Figure 1.[103] Hence, selecting different precursors does not necessarily affect the temperature required for formation, but can impact the resulting particle morphology or reaction efficiency.

An interesting variation of carbothermal synthesis of borides has been utilized densify TM diborides. Baik and Becher were the first to observe that densification of TiB_2 was enhanced by decreasing the oxygen content of the starting powder.[104] Subsequently, Chamberlain observed that ZrB_2 containing WC impurities could be densified by pressureless sintering and attributed the enhanced densification to the removal of surface oxide impurities by reaction with WC.[105] In addition, carbon,[106] carbides,[107-108109] nitrides,[110,111] and combinations of these additives[112,113] have all been identified as sintering aids for TM diborides based on their ability to react with and remove oxide impurities from the surface of diboride powder particles. The mechanism for oxygen removal from ZrB_2 was studied by Zhu et al.[106] and is summarized by the schematic in Figure 2. Hence, carbothermal reduction reactions can not only be used to form boride or carbide phases, but can also be harnessed to enhance densification of pre-reacted TM diborides by removing surface oxide impurities that promote preferential coarsening rather than densification.

Both borothermal and boro/carbothermal reduction reactions can also be used to produce boride powders. The former involves a pure source of boron, which is usually more expensive than carbon and requires a higher reaction temperature. The main advantage of borothermal reduction is the purity of the final powders and the potential for achieving a fine particle size.[114] For example, borothermal reduction of HfO_2 at 1100°C, followed by washing with hot water and the removal of residual B_2O_3 at 1550°C yielded powders with ~0.56 wt% O_2 and a particle size in the range of 0.5 to 1 μm.[114] Addition of excess B, whilst keeping the synthesis conditions the same, resulted in lowering of the O content to just 0.51 wt%. Other work on the densification of ZrB_2-SiC ceramics with additional B also showed that the latter can reduce oxygen impurities and enhance the densification process.[115] High-purity ZrB_2 powders with submicron particle size have also been synthesized by borothermal reduction of nanometric ZrO_2 powders in vacuum.[116] The ZrO_2 completely converted to ZrB_2 at 1000°C, but removal of residual boron species required temperatures above 1500°C. In addition, powders obtained at 1000-1200°C were ~150 nm and showed a faceted morphology, whereas those prepared above 1500°C were coarser, typically ~0.66 µm, with a nearly spherical morphology. The oxygen content of the ZrB_2 powders synthesized at 1650°C was as low as 0.43 wt%.

Carbo/borothermal reduction uses the combination of B_4C and C as reducing agents. The temperature at which such reductions are initiated can be quite low, e.g. 1200°C for ZrB_2,[117] though to yield high-purity powders a higher heat treatment temperature was needed. The carbo/borothermal reduction reaction has also been exploited to promote densification of ZrB_2 due to the ability of excess B_4C to react with oxides and thereby reduce the amount of oxide impurities in the non-oxide ceramics.[107]

IV. Reactive Processes

Direct synthesis and displacement reactions are also widely employed to produce boride ceramics. Compared to oxides, starting from pure metals or metal compounds provides the ability to control impurity levels in the resulting ceramics. For example, a series of ZrB_2 ceramics with Hf contents ranging from ~0.01 at% to 0.33 at% were produced by reactive hot pressing.[101] Reactive processes can be used to design boride ceramics, particularly on the laboratory scale. Furthermore, reactive synthesis is routinely combined with densification into a single, *in-situ* process to produce dense ceramics[118-121] or fiber reinforced composites.[122]

Ceramics could be densified at a relative lower temperature by reactive sintering, as a result of the newly formed fine powder with a higher sinterability and a lower oxygen content, which was generated from these *in-situ* reactions.

A. Direct Reaction of Elements, Hydrides, or Chlorides

The formation of transition metal boride compounds from elemental precursors (Reaction 2) is highly favorable. For example, the reaction of zirconium and boron to produce ZrB_2 is thermodynamically favorable at room temperature (ΔG^{o}_{rxn} = -319 kJ at 298 K) and the process is highly exothermic (ΔH^{o}_{rxn} = -323 kJ at 298 K). Because they are highly exothermic, these reactions also have extremely high adiabatic temperatures, T_{ad}. For the reaction of Zr and B to form ZrB_2, T_{ad} is ~3100 K. Previous empirical analysis has concluded that self-propagating high-temperature synthesis (SHS) can initiate for reactions when $T_{ad} > 1800$ K, indicating that an SHS reaction is likely for the reaction of TMs and B by Reaction 2. Although the latter is highly favorable at room temperature, kinetic limitations require elevated temperatures for the reaction to proceed. No ZrB_2 was detected after attrition milling of Zr and B powders at a speed of 600 rpm up to 4h when the milling container remained at room temperature.[123] In this case, reaction required further heat treatment of milled powders at temperatures above 600°C, but the reaction occurred over a broad range of temperatures. In contrast to the attrition milling studies, mechanical alloying using planetary milling at 250 rpm for 20 hr in argon resulted in ZrB_2 formation during milling.[124] However, the temperature inside the chamber was not monitored during milling. Together, these studies revealed that reducing the size of the elemental precursors reduced the onset temperature for reaction, as expected.

The reaction between TMs and B proceeds by diffusion of B atoms through the TMB_2 reaction layer to react with the TM. Figure 3.[123] The preferred diffusion path for B atoms is octahedral site (Oct)-basal bond center (Bc)-Oct, which was identified using nudged elastic band simulations.[125] The latter also revealed that the Oc-Bc-Oct mechanism had a lower energy by a factor of ~20 compared to the next most favorable process. Building on these findings, the morphology of TMB_2 produced by Reaction 2 is strongly influenced by the shape and size of starting TM powder particles. As shown in Figure 4a and b, ZrB_2 with spherical morphology was synthesized directly from elements using precursors with sizes in the range of 200 nm to 1μm.[123,124,126] Anisotropic grain growth can be promoted through additions to the starting powder mixture. For example, ZrB_2 grains showing preferred growth along the a- and/or b-axes was achieved by adding Si and a TM such as Mo, Nb, Ti, or W into the initial Zr and B powder mixture, Figure 4c.[127]. Not only can reactive methods help control the shape of the particles, but they also provide control over particle size.

Because they are brittle, the size of B particles can be reduced by conventional milling processes.[128] In contrast, milling of ductile TM particles typically results in the formation of thin platelets or flakes due to the strong shearing forces during attrition or planetary milling.[123,129] Extended milling times can result in the incorporation of impurities from the milling media, which can affect the reactions, densification behavior, and properties of the resulting ceramics. To reduce milling times and, therefore, limit impurity incorporation, brittle compounds such as TM chlorides, Reaction 9, or hydrides, Reaction 13, can be used as precursors for synthesis reactions.[130-132]

$$TMH_{2\,(s)} + 2B_{(s)} \rightarrow TMB_{2\,(s)} + H_{2\,(g)} \qquad (13)$$

Thermodynamically, ZrH_2 can be spontaneously dehydrogenated to metallic Zr during heating. In the standard state (assuming unit activity for condensed phases and a partial pressure of 101 kPa for H_2), the decomposition of ZrH_2 is favorable above ~975°C. Because the partial pressure of hydrogen is typically drastically lower than 101 kPa, the reaction can become favorable at much lower temperatures. For example, the Gibbs change for dehydrongenation becomes negative at ~510°C under 10 Pa of H_2 gas. In the presence of B, Reaction 13, the formation of ZrB_2 is favorable across a broad range of temperatures regardless of the partial pressure of H_2, indicating that ZrB_2 formation should occur simultaneously with ZrH_2 decomposition as compared to a sequential process in which ZrH_2 decomposes at one temperature followed by ZrB_2 formation at a second higher temperature. Ran[131] and Guo[130] separately observed that ZrH_2 dissociation occurred between 600°C and 1300°C, depending on the particle size of ZrH_2 and the decomposition conditions. Kinetically, dehydrogenation of ZrH_2 follows occurs in steps (e.g., $ZrH_2 \rightarrow ZrH_m$ ($m<2$) $\rightarrow$ Zr), which results in separate endothermic peaks at 700°C and 1300°C in differential scanning calorimetry.[130] Guo's conclusion was that ZrB_2 formation occurred in steps whereas Ran hypothesized that dehydrogenation and reaction occurred in a single step at a fixed temperature. Heating rate may also have an effect on reaction. Heating ZrH_2-B mixtures at 100°C/min to 900°C resulted in the formation of ZrB_2 with a primary crystallite size of ~100 nm, Figure 4d and 4e.[131] Together, previous studies show that TMB_2 with high purity can be formed by synthesis from metals or hydrides and that these processes provide control over particle size and shape.

Unlike TMH_2 compounds, $TMCl_4$ sublimes prior to decomposition. For $ZrCl_4$, sublimation is favorable above ~340°C for standard state conditions. In typical synthesis processes, powder mixtures will be heated in vacuum or inert atmosphere, which will shift sublimation to even lower temperatures. Although thermodynamic calculation show that reaction between solid $ZrCl_4$ and B is favorable below 300°C, TMB_2 powders have not been reported to be produced by direct reaction of solid chlorides with B. In addition to the vapor phase routes, $TMCl_4$ compounds can readily hydrolyze to oxides (TMO_2) or oxychlorides ($TMOCl_2$), which can then react with B in the solid state. For example, Guo produced ZrB_2 powders consisting of plate-like particles and whiskers by reaction of hydrolyzed $ZrCl_4$ at 1200°C.[132]

Chemical exchange (metathesis) reactions have also been used to produce borides from transition metal halides. Operating in a similar manner to SHS reactions discussed above, the basic form of the reaction is: $AB + CD \rightarrow AC + BD$. Borides have been produced, for example, by reaction a transition metal chloride with MgB_2.[133-135] In general, such metathesis reactions can yield rapid, highly exothermic reactions with temperatures >1000°C on very short time scales of <1 s. The products are often crystalline and single phase with crystallite sizes varying from tens of angstroms to a few microns, depending on the refractory nature of the material and the reaction conditions (i.e., scale and the use of inert additives). For the reaction between $TMCl_4$ and MgB_2, it has been reported to occur above 650°C in an evacuated silica tube. However, apart from TMB_2 and $MgCl_2$, boron was also detected in addition to the TMB_2 and $MgCl_2$ so these routes can struggle to yield phase pure products.[133]

To summarize this section, direct synthesis reactions have been widely used to produce TM boride ceramics. Precursors can include metals, TM hydrides, or TM compounds. These routes are highly advantageous on the laboratory scale due to the ability to control the purity of the resulting ceramic powders in addition to providing compositional flexibility and reduced particle sizes. These reactions tend to be highly exothermic, but SHS type-reactions can be inhibited by adding inert diluents or using slow heating rates. Further development of appropriate precursors and control of process parameters would be necessary to extend these methods to practical powder production routes on larger scales.

B. Displacement Reactions

Displacement reactions are another common method used for *in-situ* synthesis of ceramics and composites.[121] These reactions offer the same advantages as direct synthesis reactions (e.g., low temperatures, high purity, control of particle morphology), but often using less costly or more stable precursors. The section below separately considers reactions involving TM metals and TM compounds such as carbides or nitrides.

Pure TMs can react with B-containing inorganic compounds. Some examples of reactions, thermodynamic favorability, and reaction conditions for the production of ZrB_2-containing materials are summarized as Reactions 14-22 in Table III.[136144] Reaction 14 has been widely investigated to produce ZrB_2-SiC ceramics.[118,145-147] When batched according to the reaction stoichiometry, the reaction produces 74.9 vol% ZrB_2 and 25.1 vol% SiC, although the ratio can be adjusted by adding either ZrB_2 or SiC into the precursors.[118] Furthermore, the ratio of the precursors can be altered as described by Reaction 15 to introduce ZrC as a reaction product.[148] Likewise, HfB_2 ceramics containing 22 vol% SiC and 5 vol% ZrC can be synthesized below 1200°C from a mixture of Hf, Si, and B_4C.[149]

Overall, Reaction 14 leads to the formation of ZrB_2 and SiC. However, analysis of the reaction path revealed that ZrC formed prior to ZrB_2 as an intermediate product at temperatures as low as 800°C.[148] The preferential formation of ZrC at moderate temperatures was attributed to the lower activation energy for diffusion of C in Zr (~75 kJ/mole) compared to diffusion of B in Zr (~145 kJ/mole).[144] Qu et al. suggested that the intermediate carbide was carbon-deficient (e.g., ZrC_x with $x < 1$) due to diffusion limitations during reaction.[144] Similarly, ZrC_x was also formed by incorporating excess Zr into ZrC.[142] Above 1100°C, XRD analysis suggested that the amount of ZrC decreased gradually with increasing temperature, indicating that ZrC reacted with residual B_4C and Si to form ZrB_2 and SiC, Reaction 22. By 1500°C, ZrB_2 formation was complete, but ZrC could be retained in the final powder mixture depending upon the Zr to B_4C ratio, Reaction 15.

$$2ZrC + B_4C + 3Si \rightarrow 2ZrB_2 + 3SiC \qquad (22)$$

The kinetics of Reaction 14 and 15 can be manipulated by controlling the processing conditions.[144150,151] During SHS reactions ignited by rapid heating of Zr-Si-B_4C mixtures, Reaction 14 appeared to proceed in one step.[151] Particle size also had an effect on reaction as demonstrated by Wu et.al who observed an increase in gas pressure at ~900°C during heating of fine Zr and B_4C, while no pressure change on vacuum was monitored for coarse powders.[150] Interestingly, densification behavior also benefited from the lower reaction temperature as dense ZrB_2-SiC-ZrC ceramics were produced at 1600°C for fine powders compared to temperatures at least 200°C higher for reaction of coarse powders.[150]

In a variation of SHS, Reaction 15 has been ignited using an infrared lamp as a heat source.[151] Combustion could be ignited when the Zr-B_4C-Si mixture was heated in air, but not in argon. Interestingly, the powders produced by combustion in air had a lower oxygen content (0.4 wt%) than typical commercial powders, which contain 1 wt% oxygen or more. Analysis showed that the infrared lamp only heated the powder surface to ~100°C in air or in argon, so ignition of the SHS reaction was attributed to the exothermic oxidation of Zr when powders were heated in air.[151] Similarly, ZrB_2-ZrC powders were synthesized by SHS that was ignited by exposing finely ground Zr-B-C powder mixture to air at room temperature.[152,153] After SHS, the powders are typically agglomerated, although deagglomeration can be achieved by ball milling. In additions, powders produced by SHS can exhibit better sinterability compared to conventional powders due to finer particle size or increased defect concentrations.[144]

In another variation, replacing the Si in Reaction 14 with Si_3N_4 results in production of ZrB_2-SiC ceramics that also contained BN, Reaction 18.[154] These ceramics had an excellent combination of high strength (>600 MPa) and machinability. Additional variations in precursor chemistry and the resulting phases are summarized in Reactions 23-25. Similarly, TMC and TMN can also be used are precursors for the preparation of TMB_2-based ceramics. Thermodynamic analysis indicates that neither TM carbides nor TM nitrides are stable in contact with boron compounds at elevated temperatures. Reactions 22-24 are representative displacement reactions for synthesis of ZrB_2-based ceramics from carbide and nitride precursors.

$$TMC + 6B \rightarrow TMB_2 + B_4C \tag{23}$$

$$TMN + B \rightarrow TMB_2 + BN \tag{24}$$

$$4TMN + 3B_4C + 3Si \rightarrow 4TMB_2 + 3SiC + 4BN \tag{25}$$

Rapid heating of the precursors for Reactions 23-25 can result in ignition of SHS reactions between 1300°C and 1400°C.[155,156] In general, an SHS reaction produces local extreme temperatures (e.g., approaching T_{melt} for one or more of the product phases) for a short duration (e.g., a few seconds). As a result, fine powders produced by SHS can be partially sintered, which produces hard agglomerates and decreasing sinterability. Reactions 23-25 are classified as "mild" SHS reactions because T_{ad} is below 1800°C.[150] As a consequence, the resulting ZrB_2-B_4C powder mixtures can be densified below 1800°C.[150] Not only can displacement reactions be used to produce sinterable powders, but the reactions can also provide increased control over the morphology of the resulting powders, Figure 5.[156] Although the mechanisms have not been confirmed, the authors speculated that nucleation of the product phases at defects in the coarse precursor particles resulted in a substantial reduction in the size of the resulting powders compared to the size of the precursors.[156] Similar reductions in grain size were observed for synthesis of TiB_2-B_4C ceramics. For example, Reaction 23 was used to synthesize particles with an average size of ~50 nm at 1200°C and to produce ceramics in the Ti-B-C system.[157,158]

Both TiB_2 and ZrB_2 have also been formed at room temperature via the mechanical milling of a mixture of Mg, B_2O_3 and the corresponding TM oxide under vacuum and argon respectively for up to 15 h in a laboratory scale ball mill.[159,160] X-ray diffraction analysis showed increasing conversion with milling time, eventually leading to phase-pure borides as detected by XRD. For ZrB_2, differential thermal analysis revealed multiple overlapping reactions, all of which seemed to be related to TM boride formation. After milling, separation of the boride from the MgO co-product was achieved by a mild acid leaching, leaving essentially pure boride powders with crystallite sizes of <100 nm. Similar results were obtained for TiB_2 by Ricceri et al. using high-energy ball milling for ~1 hr.[161]. They hypothesized that two nearly simultaneous thermite reactions occurred, one between TiO_2 and Mg and the other between B_2O_3 and Mg; the first provided sufficient heat to ignite the second. These reactions were immediately followed by reaction between elemental Ti and B to provide TiB_2. XRD revealed a gradual decrease in crystallite size of the reactant TiO_2, with formation of intermediate reaction products followed by a near-instantaneous reaction that produced mainly MgO and TiB_2 as final products. Intermediate reaction products, such as less stable borides, were retained for shorter milling times, but TiB_2 and MgO were the only products for milling times of 2 h. After removal of MgO by leaching in dilute HCl, pure TiB_2 was obtained with a typical molar yield of 81%. The powders were impact-welded aggregates composed of 50–100 nm particles. It is possible that a similar approach could also lead to the self-propagation formation of ZrB_2.

Overall, displacement reactions are a highly attractive synthesis route for multiphase ceramics. Displacement reactions afford the ability to produce TM boride-based ceramics containing additional hard phases such as SiC, ZrC, or B_4C that limit grain growth and improve physical and/or mechanical properties. In addition, precursors can also be designed to produce phases such as BN that improve fracture toughness or machinability. Hence, displacement reaction-based processes can be used to tailor the composition, microstructure, and properties of TM boride ceramics.

V. Chemical Synthesis

A broad range of chemical synthesis methods have been used to produce boride powders on the laboratory scale when highly pure and/or extremely fine particles are needed. For comparison to the methods discussed in previous sections, reduction-based processes, which are predominantly used for commercial synthesis of boride powders due to simplicity and low cost, yield coarse particles with low sinterability.[162] Considerable grinding is required for particle size reduction, which can result in the incorporation of impurities. Likewise, the size of the end product for reaction-based processes depends on the size of the precursors; thus they are usually milled before reaction. Hence, research that aims to produce highly pure and/or extremely fine powders typically utilizes chemical synthesis routes. In addition to synthesis solely involving chemical processes, this section discusses hybrid processes that combine chemical (typically solution) routes with other processes such as direct reactions or carbothermal reduction.

Figure 6[163] summarizes the broad range of reactions for synthesis of HfB_2, several of which are possible below 1500°C. Various reactions other than borothermal and carbothermal reduction reactions, using elemental Hf or its carbide or nitride, lead to successful synthesis. These reactions allow for use of combinations of polymeric precursors and reactive powders to synthesize group IV metal borides. All of the reactions need to be considered during design and development of practical precursor processing as intermediate reactions and their products may play a key role in obtaining the desired phases and microstructures.

Most chemical routes involve reactions between TM-containing and B-containing precursors. For example, a principle synthesis route for TiB_2 involves reduction of titanium tetrachloride and a boron halide at ~1500°C, Reaction 26, although the solid diboride product requires grinding.[162]

$$TiCl_{4\,(g)} + 2BCl_{3\,(g)} + 5H_{2\,(g)} \rightarrow TiB_{2\,(s)} + 10HCl_{(g)} \qquad (26)$$

Boride powders can also be formed by decomposition of borohydrides. $Ti(BH_4)_3$ was first synthesized as long ago as 1949 by passing $TiCl_4$ vapor over lithium borohydride, Reaction 27,[164] whilst nearly a decade later $Ti(BH_4)_3$ was prepared by bubbling diborane, B_2H_6, through a titanium butoxide solution in tetrahydrofuran.[165] Interestingly, $Ti(BH_4)_3$ decomposes at ~140°C when dissolved in xylene, Reaction 28.[166] Whilst the resulting powder was agglomerated, it had a high chemical purity and a particle size in the range of 100 to 200 nm.

$$2TiCl_4 + 8LiBH_4 \rightarrow 2Ti(BH_4)_3 + 8LiCl + B_2H_6 + H_2 \qquad (27)$$

$$2Ti(BH_4)_3 \rightarrow 2TiB_2 + B_2H_6 + 9H_2 \qquad (28)$$

Nano-crystalline ZrB_2 and HfB_2 have been synthesized by Reaction 29 at temperatures of 500-700°C and 600°C, respectively, using a hydrothermal reaction in an autoclave.[167,168] These studies make no mention of the purity of the final powder, which is a concern because sodium-bearing compounds are usually not ideal for producing engineering ceramics since the presence of alkali metals is detrimental to the subsequent properties. Nevertheless, these are amongst the lowest synthesis temperatures reported for these borides via an elevated temperature reaction. The particle sizes were reported to be as fine as 10-25 nm in both cases.[167-168]

$$TMCl_{4\,(g)} + NaBH_{4\,(g)} \rightarrow TMB_{2\,(s)} + 2NaCl_{(s)} + 3H_{2\,(g)} \qquad (29)$$

Boride powders have also been synthesized via sol-gel processing followed by carbothermal reduction. Molecular level mixing in the liquid form allows transformation to the final product at lower temperatures than by many other routes with improved homogeneity of the final product. Yan et al. prepared high-purity ZrB_2 with particle sizes from 100 – 200 nm, Figure 7, using inorganic–organic hybrid precursors of zirconium oxychloride ($ZrOCl_2 \bullet 8H_2O$), boric acid and phenolic resin as sources of zirconia, boron oxide and carbon, respectively.[169] The reactions were substantially completed at the relatively low temperature of ~1500°C. The synthesized powders had a smaller average crystallite size (<200 nm), larger specific surface area (~32 m^2g^{-1}) and lower oxygen content (<1.0 wt%) than for many commercially available ZrB_2 powders. Ultra-fine TiB_2 powders have also been prepared by sol-gel processing with tetrabutyl titanate, boric acid and phenolic resin as the solution precursors.[170] The carbothermal reduction reactions were substantially completed below 1400°C. At temperatures below 1100°C, titanium carbide was the predominant phase and the resulting products consequently had a fine average crystallite size of <200 nm. A sol-gel mixture of $HfCl_4$, H_3BO_3 and phenolic resin was used to obtain intimately mixed, yet unreacted, HfO_2, B_2O_3 and C, which was calcined to produce HfB_2.[171] Usually this approach results in minor impurities such as HfO_2, HfC and B_4C in the final product; in this study the ratios of the different precursors were optimized to obtain HfB_2 powder with negligible impurities. Calcination at temperatures as low as 1300°C produced HfB_2, but required 25 h to form pure phase HfB_2. The long dwell time gave rise to a significant fraction of rod shaped particles, with screw dislocation driven growth occurring along the c-axis.[172] The use of a higher calcination temperature avoided this problem.

Carbon sources with different structures were studied to produce HfB_2 particles with different size and morphology using $HfCl_4$ and H_3BO_3 as precursors. The carbon sources included liquid phenolic resin, phenolic resin powder, pitch, sucrose, graphite, carbon black, and carbon nanotubes.[173] In general, the structure and level of agglomeration of the carbon source influenced the particle size of HfB_2 powder, Figure 8. For example, carbon black and carbon nanotube precursors produced HfB_2 particles whose size directly depended on the level of agglomeration of carbon sources whilst, on pyrolysis, the liquid phenolic resin, sucrose, graphite and powder phenolic resin all resulted in sheet-like carbon that engulfed the ceramic particles. Finer and more dispersed sheets produced finer and less agglomerated HfB_2 particles. The finest HfB_2 powder was obtained when using phenolic resin powder as the carbon source, which resulted in a final particle size between 30 and 150 nm with a surface area of 21.8 m^2/g.

Duplex submicron ZrB_2-SiC powders have been synthesized *in-situ* via a combined sol-gel and microwave boro/carbothermal reduction route, Figure 9.[174] Additives such as SiC, $MoSi_2$, LaB_6, WC, TaC, $TaSi_2$, and TaB_2 are commonly used to improve the performance of TM borides in high temperature applications,[175-178] although they are typically added as a second phase during powder processing.[179-182] The most widely studied additive is SiC, which reduces the oxidation rate of TM borides by forming a borosilicate layer on the surface during oxidation at temperatures below 1600°C.[183- 185] Using chemical methods, the optimum molar ratios were determined to be $n(B)/n(Zr) = 2.5$ and $n(C)/n(Zr+Si) = 8$. Chemical synthesis reduced the calcination temperature to only 1300°C, which was ~200°C lower than conventional methods. Examination of microstructures and phase morphologies revealed a mixture of particles with three different chemistries, morphologies, and sizes. A sizeable fraction of 1-2 μm columnar ZrB_2 grains were in a matrix consisting of ~500 nm granular particles mixed in with numerous

<100 nm particles. Both of the latter contained Zr, B, Si and C, which was interpreted to be a ZrB_2-SiC composite powder in which SiC grains were distributed evenly amongst ZrB_2 grains. ZrB_2-SiC duplex powders with different morphologies have also been synthesized from amorphous hydrous ZrO_2-SiO_2 produced by precipitation and sol-gel processing.[186] Calcining at 1500°C resulted in formation of the desired phases. The powder derived from the precipitation route consisted of rod-like ZrB_2 with smaller, irregular SiC particles adhering to them while the sol-gel route yielded equiaxed particles in which both ZrB_2 and SiC were evenly distributed.

Chemical synthesis routes have also been used to produce TM borides doped with group IV and V metals. Dopants have been shown to modify the morphology of the crystalline phase in the oxide scale and reduce the oxygen permeation rate.[187-189] Dopants such as Ti, Nb, and Ta, form continuous solid solutions with ZrB_2,[190,191] with solid solution formation limited by diffusion of TM atoms. Hence, activation energies for metal diffusion correlate to the ease of forming a solid solution. Activation energies are 112 kJ/mole for ZrB_2-TiB_2, 175 kJ/mole for TiB_2-NbB_2 and 400 kJ/mole NbB_2-CrB_2, which have atomic radii differences of 1% for Ti and Nb; 9% for Zr and Ti; and 13% for Nb and Cr.[192] Note that the latter does not form a continuous solid solution. Uniform distribution of the dopants is desired and chemical synthesis routes are more successful for introducing dopants than solid state mixing techniques. For example, when milling was used to mix commercially available ZrB_2 and TaB_2 powders, samples required hot pressing at 1900-2000°C[178]. In contrast, Xie used tantalum ethoxide and zirconium n-propoxide dissolved into solution in 2,4-pentanedioneas to produce precursors that converted to solid solution (Zr,Ta)B_2 powders at only 1600°C due to the homogeneous distribution of the metal cations.[175] Co-precipitation is another approach that promotes distribution of dopants in boride powders, though this requires precise control of the pH values to precipitate the dopant and matrix simultaneously. Jiang[193] used this route to synthesize ZrO_2-WO_3 precursors that were subsequently reacted with amorphous boron at 1550°C to produce W-doped ZrB_2 powders with a mean particle size of ~400 nm. Besides borides and W, chemical synthesis has also been used to dope other Group IV and V refractory metal compounds, such as $TaSi_2$, TaC and WC, into HfB_2 and ZrB_2 [194-198]. These carbide and silicide dopants can be partially reduced by boron and become mutually soluble with the host matrices, hence modifying the crystalline phase in the oxide scale as for the additions of one boride to another.

Chemical synthesis routes are attractive due to the ability to control the purity and particle size of the resulting TM boride powders. In addition, these methods can be used to uniformly distribute second phases or dopants at temperatures significantly lower than conventional powder process. Although these methods are only used at the laboratory scale presently, they have the potential for widespread use in applications that demand uniform, highly sinterable powders with controlled compositions.

VI. Summary and Outlook

Synthesis methods for boride ceramics have been reviewed. While these methods can be generally used for many different boride compounds, this review emphasized methods applicable to TM diboride ceramics. Initial reports of the discovery of TM diboride compounds describe the formation of impure multiphase materials. Purification of boron enabled the isolation of phase-pure TM diborides, although present-day commercial production typically utilizes carbothermal reduction of TM oxides and boric acid based on cost considerations. Laboratory scale syntheses by reactive methods or chemical routes allows for precise control of particle size and purity for fundamental studies, although these methods have not proved commercially viable to date. The choice of methods for synthesis can be made based on a balance of cost with the properties of the resulting powders with the most important properties being starting particle size, purity, and oxygen content.

In the future, continued research into synthesis methods will be driven by the need for materials that exhibit improved performance in extreme environments, higher purity for improved properties, or smaller particle size for enhanced densification and control of final microstructure. As such, interest in the all of the synthesis methods discussed in this review should continue to increase. At the same time, continual increases in operating temperatures in applications that strive for increased energy efficiency or revolutionary changes in performance will continue provide motivation to synthesize boride compounds with improved properties. Hence, future research will likely increasingly focus on existing and emerging methods that produce ceramic powders with sub-micron particle sizes, metallic impurity contents in the part-per-million range, and oxygen impurity contents below one weight percent.

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List of Tables

Tables

Table I. Summary of composition, crystal structure, and properties of selected transition metal boride compounds.

Metal	Boride Compounds	Melting Temperature (°C)[1]	Structure Type	Space Group[2]	Density (g/cm^3)[2]	Hardness (GPa)/ Load (N)	Elastic Modulus (GPa)
Ti	TiB Ti_3B_4 TiB_2	~2200 ~2200 3225	FeB - AlB_2	Pnma Immm P6/mmm	4.58 4.56 4.51	18.6/9.8[3] 33.1/*[4] 35/9.8[31]	427[5] 554[4] 560[31]
Zr	ZrB_2	3250	AlB_2	P6/mmm	6.09	23/9.8[6]	526[7]
Hf	HfB[1] HfB_2	2100 3380	FeB AlB_2	Pnma P6/mmm	12.19 11.212	- 28/*[25]	- 480[35]
Nb	NbB_2	2990	AlB_2	P6/mmm	6.97	18.0/9.8[10]	505[23]
Mo	Mo_2B MoB $M.oB_2$ Mo_2B_5	2290 2600 2375 2140	Al_2Cu - AlB_2 -	I4/mcm $I4_1$/amd P6/mmm $R\bar{3}m$	9.23 8.67 7.87 6.80	18.9/*[11] 21.3/*[11] 24.4/*[11] 22.8/*[11]	389[11] 496[11] 569[11] 554[11]
Ta	TaB TaB_2	3090 3037	NiAs AlB_2	$P6_3$/mmc P6/mmm	14.20 12.6	28.6/*[12] 25.6/9.8[13]	420[14] 555[13]
W	W_2B WB WB_2 W_2B_5	2670[15] 2665[15] - 2365[15]	Al_2Cu - ReB_2 ReB_2	I4/mcm $I4_1$/amd $P6_3$/mmc $P6_3$/mmc	17.09 15.74 12.76 11.19	- 28.9/??[16] - -	441[17] 489[18] - 37[17]
Re	ReB_2	2400	ReB_2	$P6_3$/mmc	12.7	18/4.9[19]	382[19]
Os	OsB_2	1870[20]	RuB_2	Pmmn	12.83	20/2.0[21]	410[21]

* Calculated value and ?? indicates not stated in the reference

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[1] HfB is shown on phase diagrams including those by Rogl [8] and Rudy [9], but no property data or reports of synthesis were found for this compound.

Table II. Example synthesis reactions for transition metal (TM) diborides.

Reaction	
$TMO_{2\,(s)} + B_2O_{3\,(l)} + 5C_{(s)} \rightarrow TMB_{2\,(s)} + 5CO_{(g)}$	1
$TM_{(s)} + 2B_{(s)} \rightarrow TMB_{2\,(s)}$	2
$3TMO_{2\,(s)} + 10B_{(s)} \rightarrow 3TMB_{2\,(s)} + 2B_2O_{3\,(l)}$	3
$2TMO_{2\,(s)} + B_4C_{(s)} + 3C_{(s)} \rightarrow 2TMB_{2\,(s)} + 4CO_{(g)}$	4
$7TMO_{2\,(s)} + 5B_4C_{(s)} \rightarrow 7ZrB_{2\,(s)} + 3B_2O_{3\,(l)} + 5CO_{(g)}$	5
$3TMO_{2\,(s)} + 10Al_{(l)} + 3B_2O_{3\,(l)} \rightarrow 3TMB_{2\,(s)} + 5Al_2O_{3\,(s)}$	6
$TMO_{2\,(s)} + 5Mg_{(l)} + B_2O_{3\,(l)} \rightarrow TMB_{2\,(s)} + 5MgO_{(s)}$	7
$TMO_{2\,(s)} + B_2O_{3\,(s)} \xrightarrow{CaO+CaF_2} TMB_{2(s)} + \frac{5}{2}O_{2\,(g)}$	8
$TMCl_{4\,(g)} + 2BCl_{2\,(g)} + 5H_{2\,(g)} \rightarrow TMB_{2\,(s)} + 10HCl_{(g)}$	9

Table III. Synthesis reactions, ΔG^{o}_{rxn} at 300 K, and reaction conditions for the formation of ZrB_2-containing ceramics by displacement reactions using Zr as a precursor.

	Reaction	$\Delta G^{o}_{rxn,300K}$ (kJ)	Reaction Conditions	References
14	$2Zr + Si + B_4C \rightarrow 2ZrB_2 + SiC$	-644	<1500°C in Ar	[118,145]
15	$(2+x)Zr + (1-x)Si + B_4C \rightarrow ZrB_2 + (1-x)SiC + xZrC$	-657 at x = 0.1	<1500°C in Ar	[148,144]
16	$8Zr + 1.5Si + 2B_4C + 3.5C \rightarrow 4ZrB_2 + 1.5SiC + 4ZrC$	-2027	SHS	[136]
17	$Zr + 2Si + Mo + 2B \rightarrow ZrB_2 + MoSi_2$	-437	~1000°C in Ar	[137,138]
18	$3Zr + 2BN \rightarrow ZrB_2 + 2ZrN\ (ZrN_{1-x}\ \text{with}\ 0 < x < 1)$	-542	~1600°C in Ar	[139,140]
19	$4Zr + Si_3N_4 + 3B_4C \rightarrow 4ZrB_2 + 3SiC + 4BN$	-1478	1200°C, vacuum	[141]
20	$3Zr + B_4C \rightarrow 2ZrB_2 + ZrC\ (ZrC_{1-x}\ \text{with}\ 0 < x < 1)$	-768	<800°C	[148,142]
21	$10Zr + Si_3N_4 + 3B_4C \rightarrow 6ZrB_2 + 3SiC + 4ZrN$	-2562	<1800°C	[143]

List of Figures

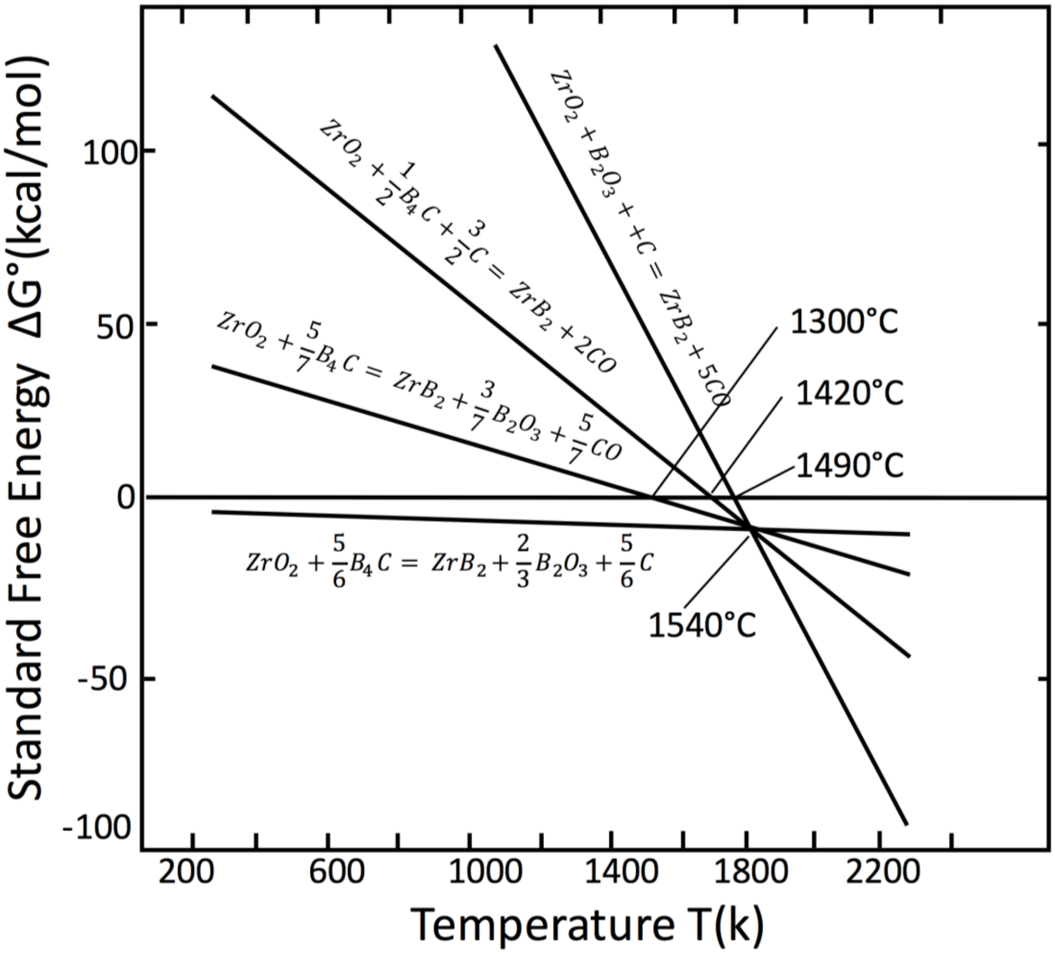


Figure 1

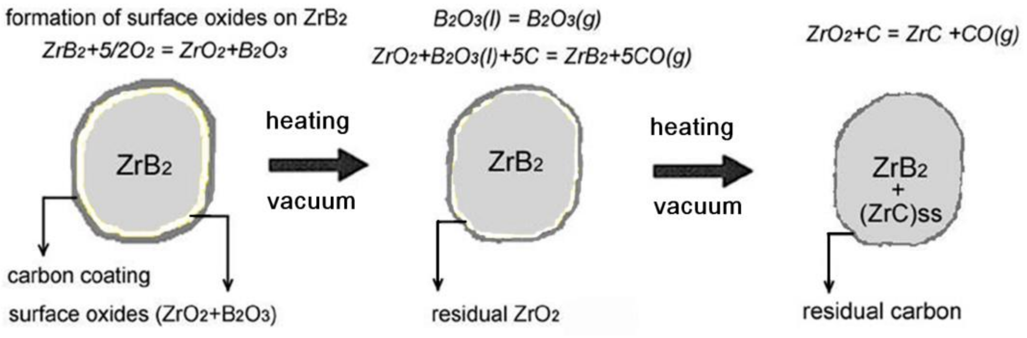
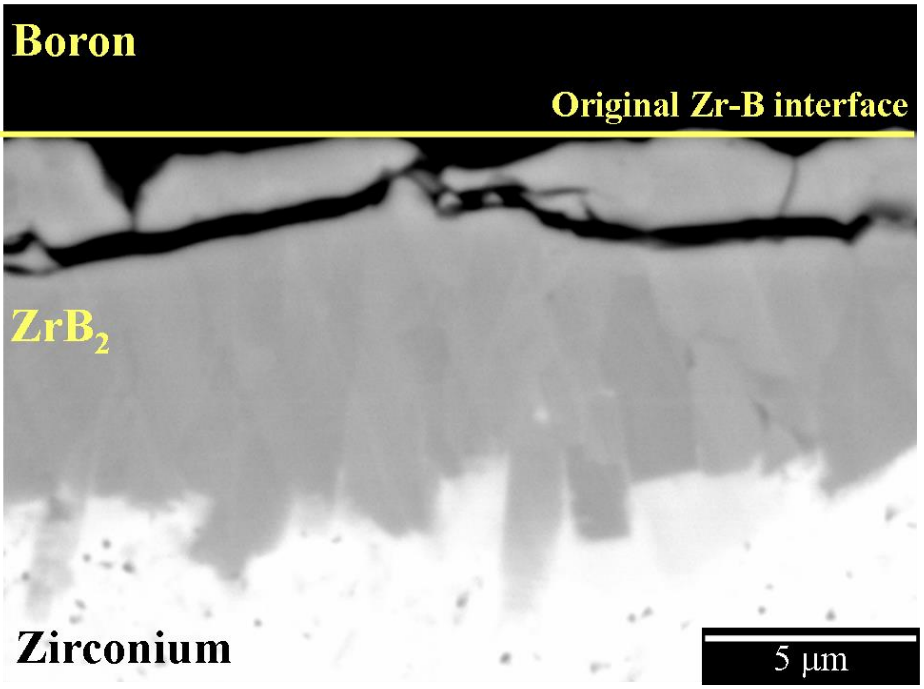


Figure 2



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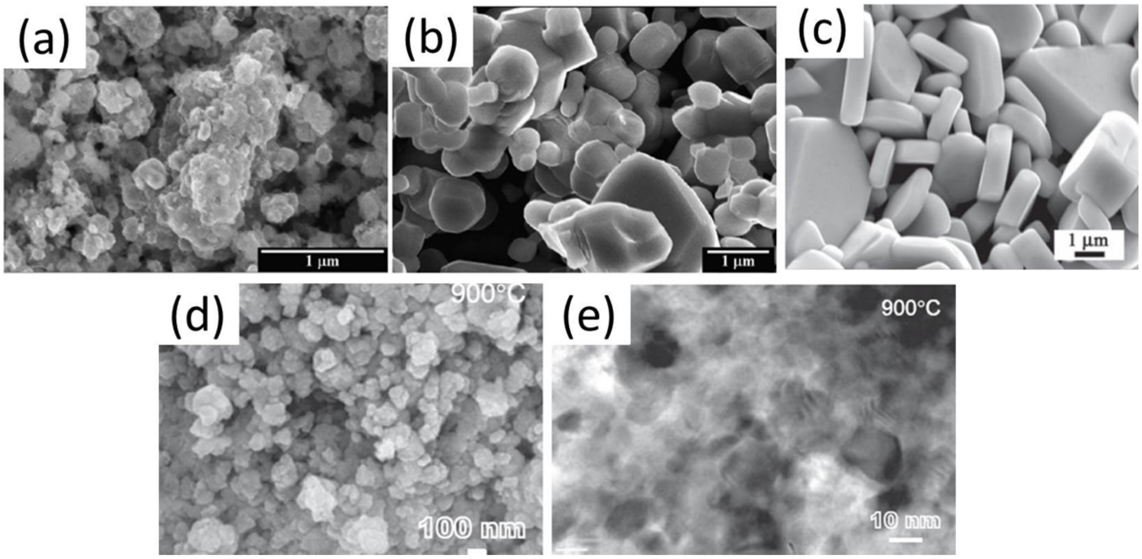

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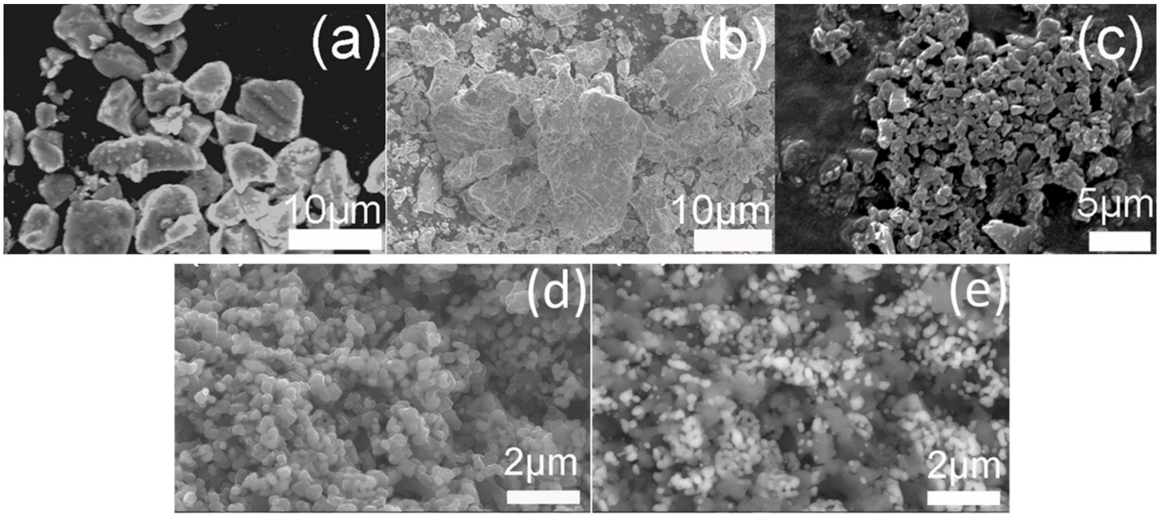

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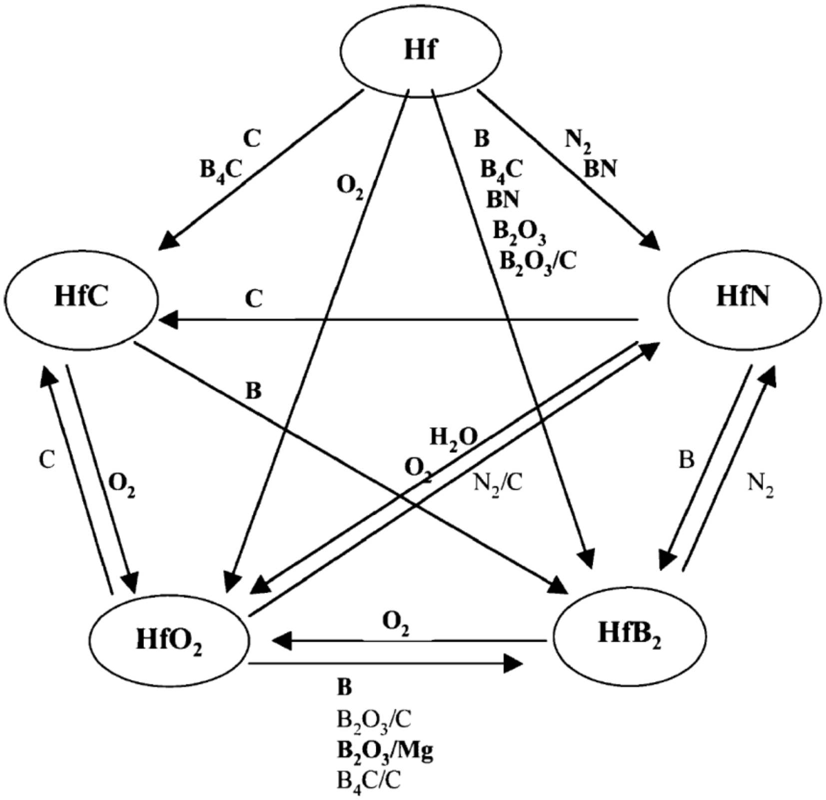

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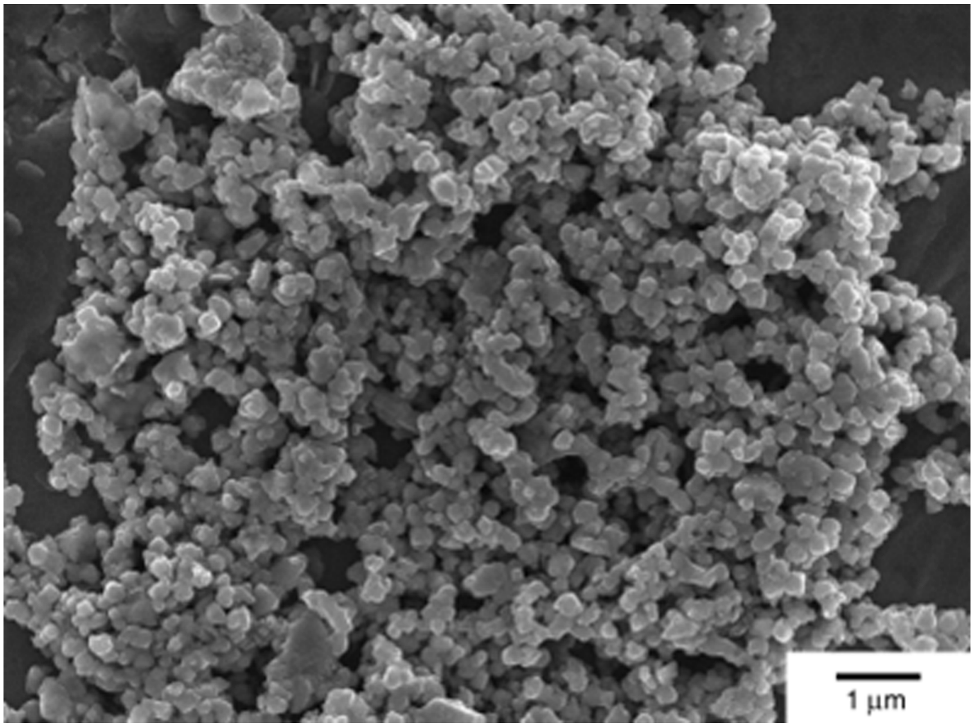

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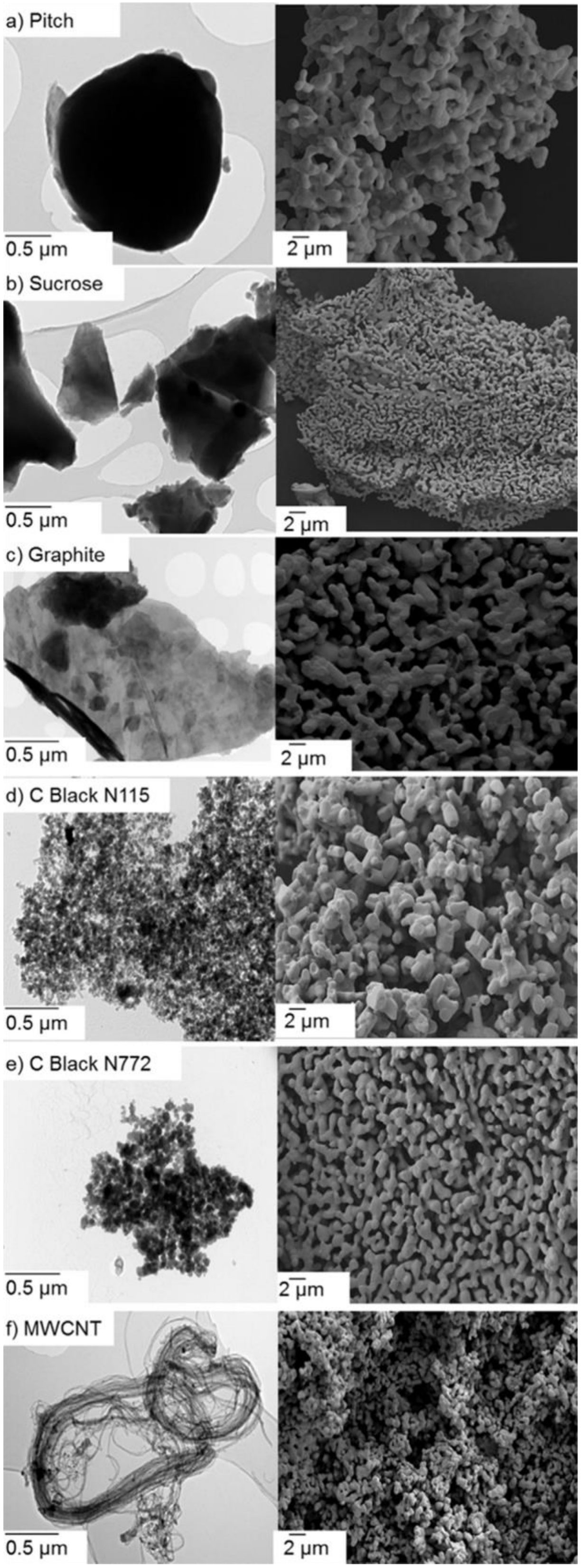
a) Pitch
0.5 µm
2 µm
b) Sucrose
0.5 µm
2 µm
c) Graphite
0.5 µm
2 µm
d) C Black N115
0.5 µm
2 µm
e) C Black N772
0.5 µm
2 µm
f) MWCNT
0.5 µm
2 µm

Figure 8