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Polymeric precursors to refractory metal borides

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Polymeric precursors to zirconium and hafnium diboride are described. Initial studies concentrated on carbothermal/borothermal reduction of metal alkoxides; however, improved results were obtained from oxide free-precursors prepared from the metal borohydride and borazine. The metal borides are obtained in good chemical and ceramic yield upon pyrolysis, and the polymeric precursors obtained through the reaction of borazine with the metal borohydride exhibit viscosities amenable to use as preceramic binders in powder processing.

1. Introduction

The rocket propulsion environment is exceedingly hostile to all materials that are available currently. The erosion that occurs in a rocket motor nozzle during operation limits the performance of current missile systems. Exotic metals, such as rhenium, have been used to limit erosion, but rhenium is costly and difficult to work. In addition to the metal itself being very expensive, the performance of rhenium components is highly susceptible to small changes in their fabrication procedure.

Much effort has gone into the identification and development of high temperature materials and designs to replace rhenium in rockets and missiles [1, 2]. Thermodynamic calculations have been used to identify thrust chamber material candidates, and indicate that refractory metal ceramics (RMCs) based on hafnium and/or zirconium have the potential to serve as non-eroding materials with a wide range of non-aluminized propellants [3].

Because of their exceptional thermochemical stability, hafnium-based RMCs have been examined as candidates for rocket propulsion applications by the Navy [4–6]. NASA has funded the development of similar RMCs, known as Ultra-High Temperature Ceramics (UTHCs), which are composed of hafnium diboride (HfB_2) or zirconium diboride (ZrB_2), with varying amounts of silicon carbide (SiC) [7]. Formulations with approximately 20% by volume SiC have exhibited good oxidation resistance [8]. Although hafnium-based materials have received the majority of attention, similar zirconium-based compounds may yield nearly equal performance at significantly lower density. Hafnium and zirconium diboride-based UHTCs have densities of roughly 12 and 6 g/cm^3 and melting points of approximately 3250 and 3040°C, respectively [9]. These properties compare very favorably with those of the current nozzle materials rhenium and tungsten, which have densities of approximately 21 and 19 g/cm^3 with melting points of 3180 and 3410°C, respectively. If effective processing methods can be developed that are capable of producing nozzles, RMCs will have the potential to serve as lightweight, low-cost alternatives to rhenium and tungsten.

While the properties of RMCs indicate a great promise for rocket propulsions, they are currently produced by hot-pressing and related methods that are not amenable to scale-up and net-shape production. The availability of polymeric precursors to RMCs would facilitate the development of alternative processing methods, such as preceramic binder and infiltration/pyrolysis processing. This paper describes our initial efforts to develop polymeric precursors to zirconium diboride (ZrB_2) and hafnium diboride (HfB_2).

2. Experimental procedures

Unless otherwise stated, all manipulations of chemical reagents and preceramics were carried out under anhydrous and anaerobic conditions using an inert atmosphere/vacuum manifold or a nitrogen-filled glovebox (Vacuum Atmospheres). Reagents were purchased from Alfa Aesar or Aldrich and used as received. Solvents were dried by reflux over sodium or potassium/

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benzophenone under nitrogen [10]. Decaborane-dicyanopentane was prepared using the literature method [11]. Borazine and polyborazylene were prepared using the method of Sneddon *et al.* [12]. Heavy-walled glass pressure vessels were obtained from Andrews Glass Company, Vineland, New Jersey, USA. Nuclear Magnetic Reasonance (NMR) spectra were obtained with the aid of a Brucker AC250 spectrometer, operating at (nominally) 250.13 MHz (^{1}H) and 80.25 MHz (^{11}B). The ^{1}H chemical shifts are reported relative to tetramethylsilane (TMS), while ^{11}B chemical shifts are reported relative to boron trifluoride diethyl etherate.

The method of Opeka *et al.* [8] was used to hot-press zirconium diboride powder compacts. Zirconium diboride powder (−325 mesh) was purchased from Cerac and used as-received. Powder molding mixtures were prepared with the aid of a SPEX high-energy shaker mill. High-temperature pyrolysis (ca. 1750°C) was carried out in the hot-press at Naval Surface Warfare Center (NSWC) under an atmosphere of dry helium.

2.1. Carbothermal/borothermal reduction of zirconium isopropoxide

In the glovebox, decaborane-dicyanopentane polymer (3.6 g) was combined with tetrahydrofuran (11.6 g), and zirconium tetrakis(isopropoxide) (19.0 g) in isopropanol was added dropwise. The mixture was allowed to stir at room temperature overnight. Volatiles were removed from the resulting clear, golden yellow solution under vacuum, first at ambient temperature, and then with the flask heated to ca. 85°C, to yield a dark yellow wax. The material was heated in a quartz crucible in a tube furnace under flowing nitrogen to ca. 1150°C, yielding a dark solid in 46% yield (by weight). A portion of this dark, solid material was sent to NSWC, where it was heated to ca. 1750°C under helium.

2.2. Reaction of metal borohydrides with borazine

Borazine (7.7 g) was placed in a 3oz. heavy walled, glass pressure vessel fitted with a pressure gauge and cooled to ca. −78°C under nitrogen. Zirconium borohydride (4.11 g) and 2,2′-azo-bis-isobutyronitrile (AIBN, 0.1 g) were added to the chilled borazine, and the mixture allowed to warm to room temperature while stirring. The mixture was heated over the course of 90 min to 80°C, and maintained at that temperature for approximately 36 h. Periodically during this time, the mixture was cooled to −78°C and the reaction vessel was vented to return the internal pressure to ambient. The resulting black, tarry material was dissolved in toluene and transferred to a Schlenk flask, where the volatiles were removed under vacuum to yield a black, brittle material. The ^{11}B NMR spectrum (d_6-benzene, 25°C) consists of a broad doublet centered at 30 ppm ($J_{BH} = 137$ Hz) and a pentuplet centered at −8 ppm ($J_{BH} = 90$ Hz). The ^{1}H spectrum consists of a broad multiplet centered at ca. 4.5 ppm and a quadruplet centered at 1.5 ppm.

The material was heated in a zirconium crucible in a tube furnace under flowing nitrogen to ca. 1150°C, yielding a black solid in 86% yield (by weight). A portion of this pyrolyzed material was sent to the NSWC, where it was heated to ca. 1750°C under helium. Repeating the reaction without the AIBN and maintaining the mixture at 80°C for ca. 12 h yielded a soft, waxy material.

The hafnium analogue was prepared using the same basic procedure, without AIBN. Hafnium borohydride (12.1 g) was combined with borazine (8.1 mL) in a 3oz. heavy walled, glass pressure vessel at ca. −78°C. The mixture was allowed to warm while stirring to room temperature, and then heated to 80°C. The mixture was maintained at that temperature, with periodic venting as before, for a period of eight days to yield a black solid that was insoluble in hexane, toluene, and ether. The reaction was repeated, maintaining the temperature at 80°C for ca. 96 h to yield a dark red solid, from which NMR spectra were obtained. The ^{11}B NMR spectrum (d_6-benzene, 25°C) of this red material consists of a broad doublet centered at 30.5 ppm ($J_{BH} = 137$ Hz) and a pentuplet centered at −11 ppm ($J_{BH} = 89$ Hz). The 1H spectrum consists of a broad multiplet centered at ca. 4.75 ppm and a quadruplet centered at 2.7 ppm.

The product obtained from the eight-day reaction was heated in a zirconium crucible in a tube furnace under flowing nitrogen to ca. 1150°C, yielding a black solid in 93% yield (by weight). A portion of the pyrolyzed material was sent to the NSWC, where it was heated to ca. 1750°C under helium.

3. Results and discussion

3.1. Carbothermal/borothermal reduction of zirconium alkoxide

Sneddon *et al.* have reported the preparation of zirconium diboride through the borothermal/carbothermal reduction of ZrO_2 with polymers at 1400°C (Reactions A and B) [13]. Although the viscosity of the copolymer can be controlled via the use of the appropriate $\alpha-\omega$-dicyanoalkyl group [11], it was considered difficult to obtain a uniform microstructure using ZrO_2 particulate. Exploration of single-phase precursors to ZrB_2 began with the substitution of the ZrO_2 particulate with zirconium isopropoxide (Reaction C).

$$B_{10}H_{14} + NC(CH_2)_5CN \longrightarrow \left[(H_{12}B_{10}) - NC(CH_2)_5CN \right]_x \tag{A}$$

$$\left[(H_{12}B_{10}) - NC(CH_2)_5CN \right]_x + MO_2 \longrightarrow MB_2 + CO \tag{B}$$

$$\left[(H_{12}B_{10}) - NC(CH_2)_5CN \right]_x + Zr(OPr)_4 \longrightarrow ZrB_2 + CO \tag{C}$$

The solvents were removed under vacuum, resulting in a dark yellow, waxy polymer. This zirconium propoxide decaborane polymer had the consistency of petroleum wax and appeared to be stable in air, providing the potential for use as a preceramic binder.

A char yield of 45% by weight was obtained under flowing nitrogen at 1150°C. The X-ray diffraction pattern (Fig. 1) confirms the production of ZrB_2; however,

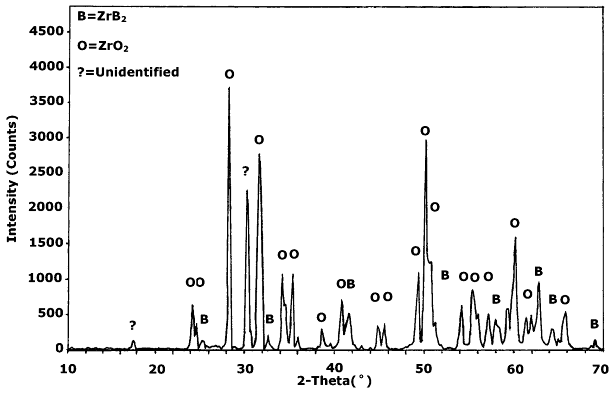

Figure 1 XRD pattern obtained from zirconium isopropoxide/decaborane-dicyanopentane polymer char pyrolyzed to 1150°C under flowing nitrogen.

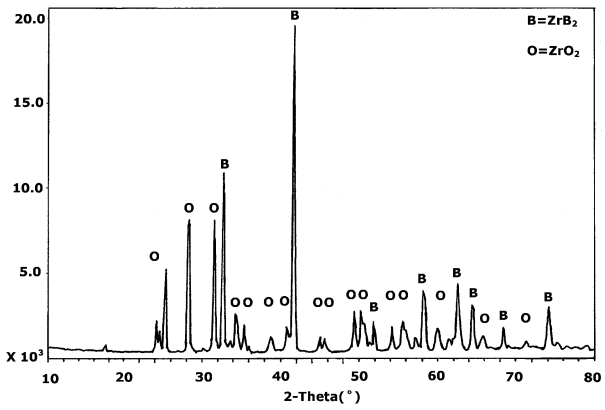

Figure 2 XRD pattern obtained from the polymer char of Fig. 1 following pyrolysis under helium at 1750°C.

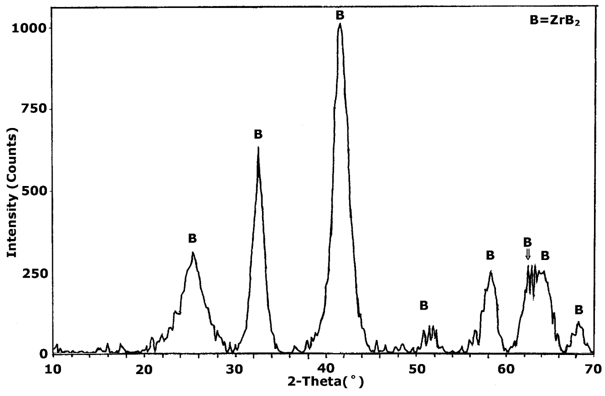

Figure 3 XRD pattern obtained from zirconium borohydride/polyborazylene polymer char pyrolyzed to 1150°C under flowing nitrogen.

zirconium oxide appears to be the dominant phase, and other, unidentified phases are present as well. Although no longer the dominant phase, zirconium oxide is still observed in the XRD pattern after firing to 1750°C (Fig. 2). Although it may be possible to obtain oxide-free ZrB_2 by this route, extended firing times may be required.

3.2. Borazine-derived ZrB_2 precursors

Alternate chemistries, based on borazine and zirconium borohydride $\{Zr(BH_4)_4\}$ have formed the basis for development of precursors to oxide-free ZrB_2. Metal borohydrides have been shown to be useful small molecule precursors for the production of thin metal boride films through chemical vapor deposition and related techniques [14–16]. Reaction of $Zr(BH_4)_4$ with borazine (Reaction D) yields a red, waxy material with viscoelastic properties that appear adequate for use as a powder binder. Initially, 2,2′-azo-diisobutyronitrile (AIBN) was included in the synthesis procedure to facilitate reaction of the borohydride with the growing borazylene polymer. Subsequent studies have shown, however, that the AIBN is unnecessary. The reaction can be carried out with differing ratios of zirconium to borazene; however, at higher zirconium contents, the resulting polymers are intractable. The maximum amount of zirconium that can be incorporated into the polymer while maintaining tractability has not been determined.

$$\begin{tikzcd}
B_3N_3H_6 + Zr(BH_4)_4 + 2{,}2'\text{-azo-diisobutyronitrile} \arrow[rr, "", "\substack{80\text{ deg C}\\ 25\text{hrs}}"'] & & \text{dark red viscous paste} \arrow[d] \\
\underset{75\%\text{ ceramic yield}}{ZrB_2} & \arrow[l, "", "\text{fired at1700 deg C}"'] & \arrow[l, "", "\substack{\text{fired at, 1150 deg C}\\ 86\%\text{ cermaic yield}}"'] \text{glossy, hard black material}
\end{tikzcd} \qquad (D)$$

A grey solid was obtained in 86% yield (by weight) when the product of Reaction D was fired to 1150°C under flowing nitrogen in a zirconium crucible. Zirconium diboride is the only phase detected by XRD in the 1150°C char product (Fig. 3). Although not confirmed by analysis, the width of the lines in this XRD pattern suggest that the polymer-derived material is nanostructured at this temperature. A sample of the 1150°C char product was fired to 1750°C in a graphite furnace under a helium atmosphere. A ceramic yield of 75% overall was obtained when the product of Reaction D was fired to 1750°C, and ZrB_2 was the only phase detected by XRD, although significant grain growth appears to have taken place (Fig. 4), as suggested by the decrease in line width in the XRD pattern. The 1750°C char product was subjected to elemental analysis (Galbraith Laboratories), the results of which are presented in Table I. Nitrogen was found to be a significant constituent of the char product. The phase containing the nitrogen has not been identified.

To investigate the potential for the polymer-derived ceramic to facilitate densification, a brief study was conducted in which the polymer-derived zirconium diboride was employed as a additive in ZrB_2 powder compacts. The red zirconium borohydride/polyborazylene material was pyrolyzed under nitrogen in a zirconium crucible at 1150°C, and combined with commercial

TABLE I Elemental analysis of 1750°C char material

Element	Found (%)	Theory for ZrB_2 (%)
Zr	83.34	80.84
B	6.82	19.16
N	6.74	
C	<0.5	
H	<0.5	

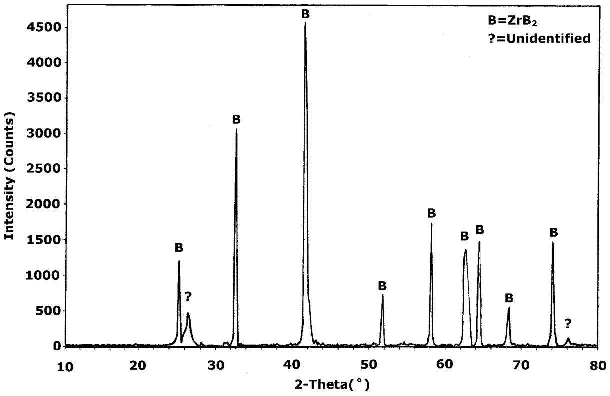

Figure 4 XRD pattern obtained from the polymer char of Fig. 4 following pyrolysis under helium at 1750°C.

(Cerac) ZrB_2 powder to form a mixture containing 15% by weight polymer-derived material. This mixture was shaken for 60 min in the Spex mill.

The resulting powder mixture was packaged under nitrogen and sent to Los Alamos National Laboratory, where it was hot-pressed using the method of Opeka *et al.* [8], but without the other, reactive additives specified in that procedure. In addition, the temperature was limited to 1750°C, rather than 2100°C as employed in that procedure. While powder compacts made with commercial ZrB_2 powder and processed under the same conditions, but without additives, exhibit little strength and crumble readily, the compact obtained the polymer-derived ceramic additive appeared to be quire dense and was handled easily, although it did fracture, presumably as it cooled in the press (Fig. 5).

3.3. Hafnium diboride

Although they are twice as dense, HfB_2-based RMCs exhibit greater thermochemical stability than their zirconium analogues. This increase may be significant enough to enable certain applications for which ZrB_2-based RMCs are inadequate. The chemistries of zirconium and hafnium are sufficiently similar that substitution of the hafnium borohydride for zirconium borohydride in Reaction D was expected to yield a useful precursor to HfB_2.

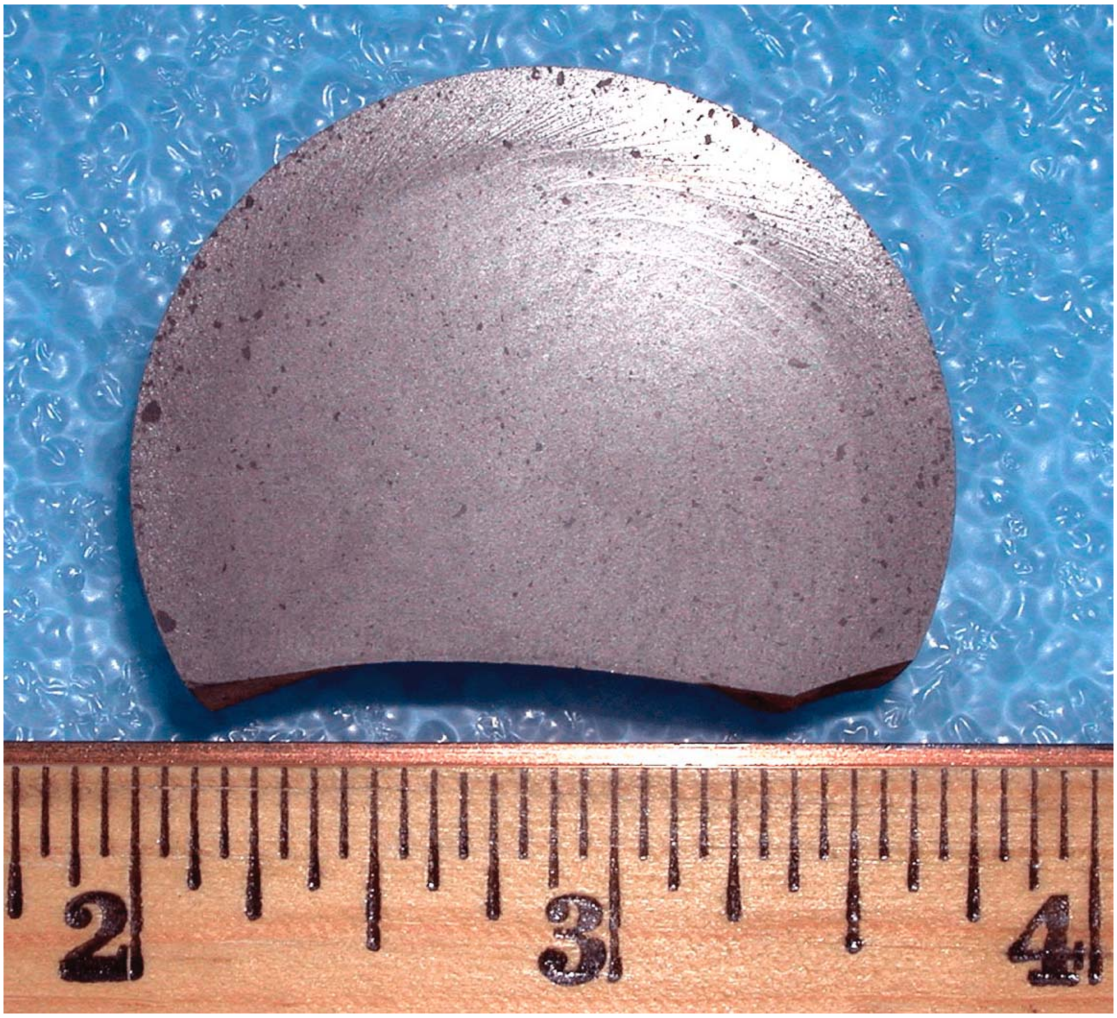

Figure 5 ZrB_2 billet hot-pressed with 15 wt% polymer—derived ZrB_2. (scale is in inches)

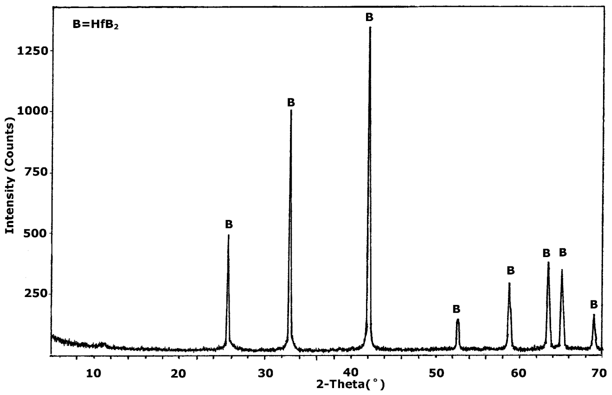

Figure 6 XRD pattern obtained from hafnium borohydride/polyborazylene polymer char pyrolyzed to first 1150°C under flowing nitrogen and then to 1750°C under helium.

Reaction D was carried out using $Hf(BH_4)_4$ in place of the zirconium analogue, yielding a dark red solid similar to the zirconium borohydride/polyborazylene material; however, the hafnium borohydride/polyborazylene exhibited significantly lower degree of solubility in common organic solvents, such as hexane and ether. The reaction was repeated with a significantly shorter reaction time (ca. 96 h), yielding a dark red solid that proved to be sufficiently soluble d_6-benzene for spectroscopic analysis.

A portion of the intractable material prepared through reaction over 96 h was fired to 1150°C under nitrogen, and was found to exhibit a ceramic yield in excess of 90% by weight. The very high ceramic yield and poor solubility is consistent with the material being highly a cross-linked organometallic polymer. Except for the width of the lines, the XRD pattern obtained from the char material produced at 1150°C was very similar to that obtained from the char material produced at 1750°C (Fig. 6). As seen in the figure, only HfB_2 is detected; however, as suggested by the zirconium system, nitrogen is likely to be present in significant amounts.

4. Conclusion

Polymeric precursors to zirconium and hafnium diboride ceramics were prepared by inserting zirconium and hafnium borohydride functions into the polymerization of borazene. Oxide-free, ZrB_2 was obtained from the precursor at 1150°C, and exhibited a very fine grain size, as evidenced by the line width of the XRD pattern. Although a substantial amount of nitride material was also found to be present through elemental analysis, ZrB_2 was the only phase detected by XRD after 1750°C pyrolysis. Using $Hf(BH_4)_4$ in place of the zirconium analogue during polymerization yields a precursor to HfB_2. The utility of these materials as preceramic binders or additives in powder processing is under investigation.

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