JOURNAL OF MATERIALS SCIENCE **39** (2004) 6043–6049

Precursor routes to Group 4 metal borides, and metal boride/carbide and metal boride/nitride composites

K. FORSTHOEFEL, L. G. SNEDDON
Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323, USA
E-mail: lsneddon@sas.upenn.edu

Precursor routes to Group 4 metal borides, as well as metal-boride/carbide and metal-boride/nitride composites, that employ metal-oxide/polymer and metal/polymer dispersions are described. The metal boride precursors were initially obtained by dispersing metal oxides in a decaborane-dicyanopentane polymer, but better results have now been achieved using a newly developed polyhexenyldecaborane polymer. Subsequent pyrolyses of the metal-oxide/polymer dispersions afford metal borides, including TiB_2, ZrB_2, and HfB_2 in high chemical and ceramic yields. On the other hand, pyrolyses of hafnium/polyhexenyldecaborane dispersions provide an efficient route to hafnium-boride/carbide composites. Metal-boride/nitride composites, including TiB_2/TiN and HfB_2/HfN materials, are also readily obtained by pyrolyses of metal dispersions in the boron-nitrogen polymer polyborazylene, $(B_3N_3H_4)_X$. The high ceramic yields of the metal-boride/nitride systems (~98%), enable their use for the controlled formation of shaped monolithic TiB_2/TiN or HfB_2/HfN materials by pyrolysis of pressed precursor green bodies. © *2004 Kluwer Academic Publishers*

1. Introduction

Group 4 Metal (Ti, Zr, Hf) borides, carbides and nitrides are high-melting, extremely hard solids with high thermal stabilities and chemical inertness [1–7]. As a result, they are important high heat- and wear-resistant materials that may be used in various hostile environments, such as nose and leading edge materials in aerospace vehicles [8], engines, cutting tools, high temperature shielding, and plasma arc electrodes [9]. Many of these materials also have metallic like conductivity and/or unusual magnetic properties. Traditionally these materials have been prepared by high temperature powder techniques that are limited in their ability to generate homogeneous materials with controlled compositions and macroscopic properties. In this paper, we review some of our work that has resulted in the development of new precursor systems for the efficient syntheses of Group 4 metal borides, as well as metal-boride/carbide and metal-boride/nitride composites.

2. Precursor routes to metal borides

Metal borides have classically been synthesized by a number of high temperature techniques, with one of the most common being the carbothermal reduction of metal oxides with boron carbide and carbon [1, 5, 10–12]. This method has been successfully applied to the large-scale preparation of, for example, selected metal hexaborides and tetraborides, and to the diborides of most transition metals.

$$MO_2 + 1/2B_4C + 3/2C \xrightarrow{\Delta} MB_2 + 2CO \qquad (1)$$

Although efficient, the carbothermal reduction can only be used to generate metal borides in powder form, since neither metal oxides nor boron carbide are easily processed into complex forms.

The development of several polymeric precursors to boron carbide [13–16] suggested that a processable metal boride precursor might be obtained by dispersing a metal source, such as a metal oxide, in a boron carbide polymeric precursor. Subsequent heating could then result in either *in situ* generation of a boron-carbon material followed by reduction to produce the boride, or direct reaction of the polymer with the metal oxide to give the final boride product.

$$MO_2 \quad \text{or} \quad M_2O_5 + \text{polymer} \xrightarrow{\Delta} B_4C + C + MO_2$$

or

$$M_2O_5 \xrightarrow{\Delta} MB_2 + CO \qquad (2)$$

In our initial studies [17, 18], a decaborane-dicyanopentane polymer [19] was employed as a boron carbide precursor. The metal-oxide/polymer dispersions were prepared by adding a metal oxide to a THF solution of the polymer, followed by solvent evaporation under vacuum. The metal/boron/carbon ratios in

0022–2461 © *2004 Kluwer Academic Publishers*

the dispersions were adjusted by varying the metal-oxide/polymer ratios in the mixtures.

Pyrolyses of the metal-oxide/decaborane-dicyanopentane polymer dispersions, under argon or in vacuo, produced metal diborides in excellent chemical and ceramic yields. According to their X-ray powder diffraction spectra, dispersions employing TiO_2, ZrO_2, HfO_2, Nb_2O_5 and Ta_2O_5 gave the metal diborides, TiB_2, ZrB_2, HfB_2, NbB_2 and TaB_2, respectively, as the only crystalline products.

$$[B_{10}H_{12}N{\equiv}C(CH_2)_5C{\equiv}N]_X + MO_2$$
$$\text{or}\quad M_2O_5 \xrightarrow{\Delta} MB_2 \tag{3}$$
$$M = Ti, Zr, Hf, Nb, Ta$$

The elemental analyses of all samples exhibited near 1:2 metal:boron ratios. Nitrogen and carbon contents were low at temperatures $\geq$1450°C. The oxygen contents also decreased with elevated reaction temperatures, for example—the oxygen contents for the ZrB_2 samples prepared at 1450° (21 h), 1650° (7 h) and 2000°C (3 h) were 4.97, 1.53 and 0.2%, respectively.

Studies of the reaction processes for the metal-oxide/polymer dispersions showed that the reduction of the metal oxides to metal diborides proceeded differently depending upon the metal. The analytical and XRD (Fig. 1) data for the TiO_2/polymer system suggested that, following initial polymer decomposition (Equation 4), titanium borate, titanium carbide and boron oxide form in the reaction of TiO_2 with the BCN material by one or more of the reactions shown in Equations 5–7. At higher temperatures further reaction (Equations 8–9) to produce the final titanium diboride product occurs.

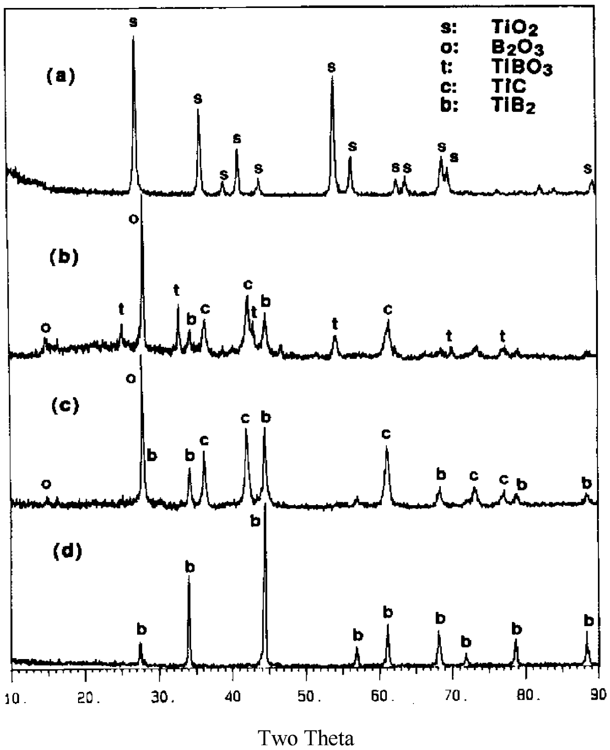


Figure 1 X-ray diffraction patterns of TiO_2/polymer dispersions heated for 2 h at (a) 580°C, (b) 1000°C, (c) 1100°C, (d) 1450°C. Reproduced with permission from *Chem. Mater.* **5**(1993), 1659–1668. Copyright 1993 Am. Chem. Soc.

$$TiO_2/\text{polymer} \rightarrow TiO_2/\text{“BCN”} + H_2 \tag{4}$$
$$3TiO_2 + 3B + 2C \rightarrow TiBO_3 + 2TiC + B_2O_3 \tag{5}$$
$$3TiO_2 + 10B \rightarrow 3TiB_2 + 2B_2O_3 \tag{6}$$
$$TiO_2 + 3C \rightarrow TiC + 2CO \tag{7}$$
$$2TiBO_3 + 5C \rightarrow 2TiC + B_2O_3 + 3CO \tag{8}$$
$$TiC + B_2O_3 + 2C \rightarrow TiB_2 + 3CO \tag{9}$$

Thus, as shown in Fig. 1b, when the TiO_2 dispersion was heated at 1000°C for 2 h, the TiO_2 completely disappeared and the material was found to be composed of $TiBO_3$, TiC, B_2O_3 and a small amount of TiB_2. The XRD pattern (Fig. 1c) of the material annealed at 1100°C showed only diffraction peaks corresponding to TiC, TiB_2 and B_2O_3. The complete disappearance of $TiBO_3$ indicates that the borate is formed at the initial stage of the reaction, and that its further reaction (Equation 8) with the amorphous carbon present in the material results in TiC and B_2O_3. Since no weight loss occurred over the 580–1250°C range, the loss of nitrogen (as N_2, NO etc.) does not seem likely. Although the formation of crystalline TiN by carbothermal reduction of TiO_2 under nitrogen at 1100°C has been reported [20, 21], no evidence of crystalline metal nitride or carbonitride was found in the XRD spectra of dispersions pyrolyzed above 1100°C. Therefore, the nitrogen must be present in the amorphous phase, presumably, as boron nitride. The absence of TiN is not surprising, since it is unstable in the presence of excess boron at $\geq$1100°C [22]. At 1300°C, TiB_2 was formed as the major crystalline phase. The reduction of TiO_2 was complete when the sample was annealed at 1450°C for 1 h (Fig. 1d).

In contrast to the above observations, no intermediate species were observed in the ZrO_2 and HfO_2/polymer systems. The XRD patterns of the materials obtained before completion of the reactions showed only the unreacted metal oxides and the diborides. For example, no reaction was observed between the ZrO_2 and the BCN material at 1000°, but the 1450°C material contained ~90% crystalline ZrB_2, together with unreacted ZrO_2. The reaction was complete when the sample was pyrolyzed at 1450°C for 21 h. Similar results were observed in the HfO_2/polymer system (Fig. 2), except that a higher reaction temperature (1900°C) was necessary to drive the reaction to completion. These observations suggest that ZrO_2 and HfO_2 react with the BCN material in one-step, as shown in Equation 10, or that alternately, the initial formation of carbides and boron oxide is followed by a fast reaction to produce the borides (Equations 11 and 12).

$$MO_2(M = Zr \text{ or } Hf) + 2B + 2C \rightarrow MB_2 + 2CO \tag{10}$$

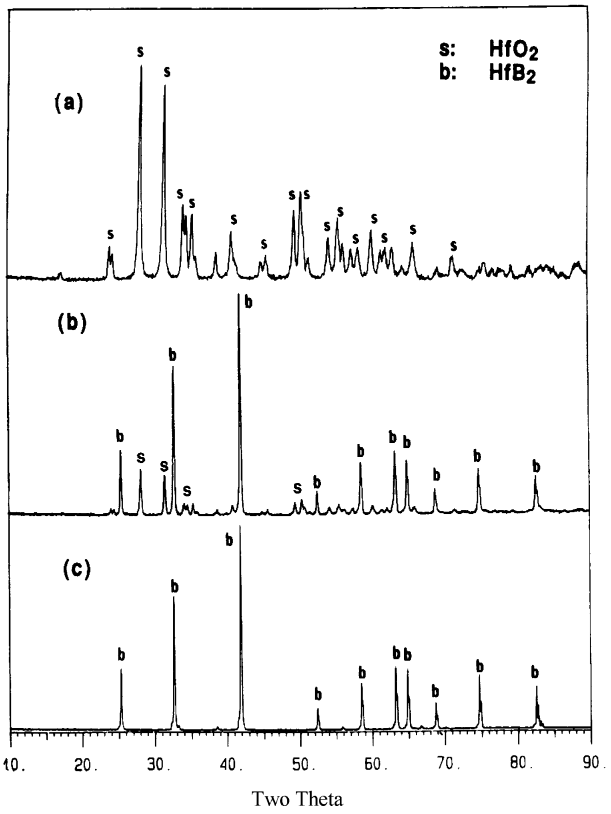


Figure 2 X-ray diffraction patterns of (a) HfO_2, (b) HfO_2/polymer dispersion heated at 1450°C (2.5 h), and (c) HfO_2/polymer dispersion heated at 1900°C (2.5 h). Reproduced with permission from *Chem. Mater.* **5**(1993), 1659–1668. Copyright 1993 Am. Chem. Soc.

or

$$3MO_2 + 3C + 4B \rightarrow 3MC + 2B_2O_3 \qquad (11)$$

$$MC + B_2O_3 + 2C \rightarrow MB_2 + 3CO \qquad (12)$$

The latter explanation would imply that the ZrC and HfC are much more reactive than TiC and react with boron oxide to give diborides immediately after their formation.

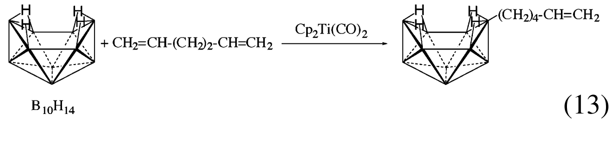
The grain sizes and microstructure of the metal boride powders were found to depend upon the metal and the reaction conditions. Scanning electron microscopy (SEM) studies of the TiB_2 and ZrB_2 powder samples showed particle sizes of 2–5 μm at 2000°C, but submicron crystallites at lower temperatures. Transmission electron microscopy (TEM) showed nanometer-sized TiB_2 and ZrB_2 particles in the 1300°C (2 h) samples, but significant grain growth upon high temperature annealing (1450°C, 21 h).

We have also shown [17] that the metal-oxide/polymer dispersions can be used to prepare coatings. In order to obtain a homogeneous dispersion, an organic polymeric surfactant, DuPont AB dispersant, was used to enhance the suspension of submicron TiO_2 particles in a decaborane-dicyanopentane polymer/THF solution. The precursor coatings were obtained by either dipping the substrate into the emulsion or by dispersing the emulsion on the carbon plates with the thickness of TiB_2 coating adjusted by either multiple coatings or by increasing the viscosity of the precursor solution. Subsequent pyrolysis of the coated carbon plates under argon or in vacuo above 1450°C produced TiB_2 coatings.

Auger analysis of coatings annealed at 2000°C showed a 1:2 titanium:boron ratio, in agreement with XRD which showed only crystalline TiB_2. SEM studies of a coated graphite plate pyrolyzed at 1450°C showed that a homogeneous, porous TiB_2 coating is formed on the surface. The coatings prepared at 1450°C were composed of submicron TiB_2 crystals. When the coatings were heated at 2000°C, larger crystals (2–4 μm) were formed. These preliminary results on TiB_2 coatings suggest that submicron-metal-oxide/polymer dispersions employing suitable surfactants should be useful for the generation of a variety of metal boride coatings of potential technological importance.

The key requirements for the polymer component of the metal-oxide/polymer dispersions are that the polymer should be stable and soluble. In addition, the polymer must be readily synthesized and have high char yields at reasonably low temperatures. Ideally, the polymer reagent should also not contain other ceramic forming elements, such as nitrogen or phosphorus. The studies described above demonstrated that while the decaborane-dicyanopentane polymer could be employed to produce metal borides, new polymers with higher stabilities and controllable properties were needed. Several investigators have shown that boron carbide ceramics are formed upon the pyrolysis of other organoboron-based polymers, but these polymers also contain other elements [14–16, 23] or are too reactive [13] to allow handling and processing, and are likewise unsuitable for use.

We have recently developed methods for synthesizing several new types of poly(organodecaborane) polymers that better satisfy the above criteria and these polymers are now proving to be useful as reagents for the synthesis of both metal boride and metal-boride/carbide materials. The new polymers contain a polyolefin backbone with pendant carborane and decaborane fragments. An important example of these new processable polymers is the new decaborane-based polyolefin polymer, polyhexenyldecaborane [24]. The monomeric building block for the polymer, 6-hexenyl-decaborane, is synthesized (Equation 13) by the $Cp_2Ti(CO)_2$ catalyzed reaction of hexadiene with decaborane and is obtained in over 90% isolated yields [25].



(13)

The 6-hexenyl-decaborane is then readily polymerized (Equation 14) by the $Cp_2ZrMe_2/B(C_6F_5)_3$ catalyst system to yield a polyolefin backbone with pendant decaboranes [24]. Typical molecular weights obtained using 1 mol% catalyst and are $M_n = 3950$ and

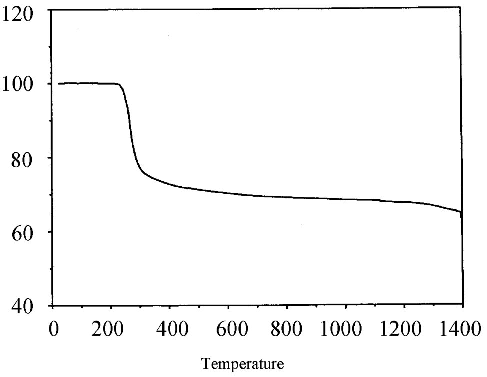
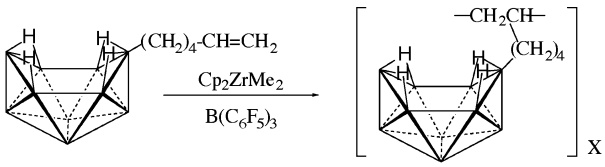


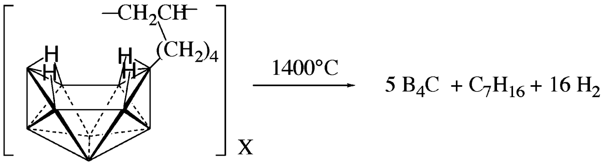
Figure 3 TGA analysis of polyhexenyldecaborane under flowing argon with a heating rate of 10°C/min. (The apparent drop at 1400°C is an instrumental effect). Reproduced with permission from *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **41**(2000), 551–552. Copyright 2000 Am. Chem. Soc.

$M_w = 5860$ (determined using viscometry).



(14)

The polyhexyldecaborane polymers are air stable for extended periods and are highly soluble in organic solvents. As shown in the Fig. 3, TGA studies of their ceramic conversion reaction (Equation 15) show that polymer decomposition does not begin until around 225°C and that weight loss is essentially complete by 600°C. The observed TGA (65%) and bulk (60%) ceramic yields are close to the theoretical ceramic yield of 68%.



(15)

Elemental analyses of bulk samples heated to 1250, 1450 and 1850°C are consistent with $B_{3.6}C$ to $B_{3.8}C$ stoichiometries. As shown in the Fig. 4, XRD studies show that the onset of boron carbide crystallization is ∼1250°C, with highly crystalline materials being obtained at 1850°C.

It is also significant that the Tgs (T_g = 50–60°C) [24] of the polyhexenyldecaboranes are considerably below their initial decomposition temperatures. Dispersion of metals into the neat polymer melts should yield a precursor system that should be useful to form metal boride films or coatings, by simply dipping or painting the metal/polymer-melt on the substrate followed by pyrolysis.

As indicated in Equation 16, our initial studies have now shown that hafnium-oxide/polyhexenyldecaborane dispersions readily yield hafnium boride.

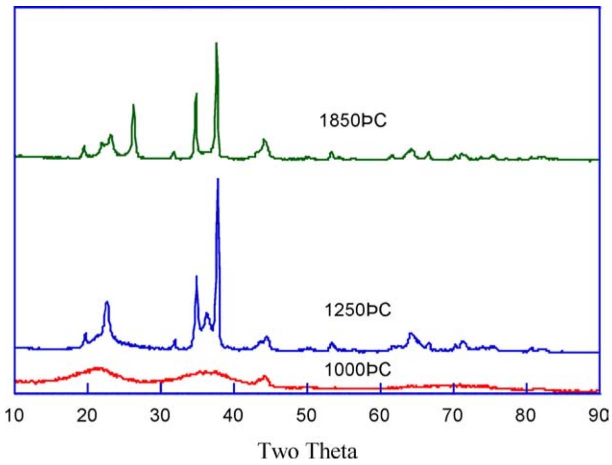


Figure 4 X-ray diffraction patterns of polyhexenyldecaborane pyrolyzed to different temperatures.

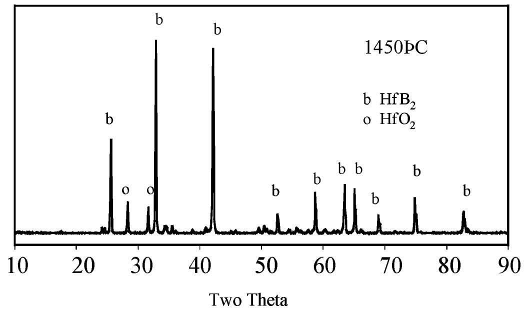
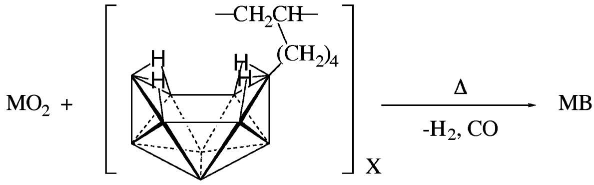


Figure 5 X-ray diffraction pattern of HfO_2/polyhexenyldecaborane pyrolyzed at 1450°C (2 h).

In a typical procedure, 2.58 g of hafnium oxide (-325 mesh, Alfa-Aesar) was added to a dry benzene solution containing 0.65 g of the polyhexenyldecaborane polymer. The solution was then ultrasonically agitated while the solvent was vacuum evaporated. Pyrolysis to 1450°C of a 0.87 g sample of the solid HfO_2/polyhexenyldecaborane polymer dispersion under argon produced 0.54 g of product. The observed ceramic yield of 62.1% is in somewhat lower than the theoretical 75.9% ceramic yield predicted by Equation 16. As indicated in Fig. 5, XRD analysis of this sample showed that while HfB_2 was the only crystalline product, a small amount of unreacted HfO_2 remained. We are now optimizing both the reaction conditions and the polymer to metal ratios in these dispersions to produce pure HfB_2.

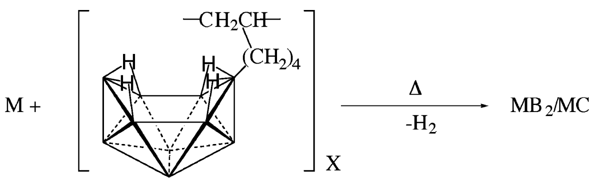


(16)

3. Precursor routes to metal boride/carbide composites

Although much of the past work on ultra high temperature materials has focused on pure metal borides, the properties of composite metal-boride/carbide, as well as the metal-boride/nitride composites discussed in the next section, have been largely unexplored. This absence of attention has probably been the result of the inability to make such composites in a controlled and systematic fashion.

As illustrated in Equation 17, our recent work has shown that metal/polyhexenyldecaborane dispersions can provide efficient synthetic routes to metal-boride/carbide composites. In a typical procedure, a hafnium/polymer dispersion was prepared by adding 3.50 g of hafnium metal (−325 mesh, Strem) to a dry benzene solution of 0.40 g of polyhexenyldecaborane. The solution was then ultrasonically agitated while the solvent was evaporated under vacuum.



(17)

Pyrolysis of a 0.68 g sample to 1650°C (2 h) of the solid Hf/polyhexenyldecaborane polymer dispersion under argon produced 0.66 g of product for a ceramic yield of 96.2% (theoretical ceramic yield 98.0%).

XRD studies of the ceramic conversion reaction (Fig. 6) showed there was little apparent reaction between the hafnium and polymer when the sample was heated at 800°C for 2 h, but that upon heating at 1100°C for 2 h hafnium carbide formed. Further formation of hafnium carbide and initial crystallization of hafnium boride was observed when the sample was heated at 1450°C for 2 h. It was not until the sample was treated at 1650°C for 2 h that all of the hafnium metal was consumed. The stoichiometry of the hafnium/polyhexenyldecaborane dispersion used in this experiment should lead to a ceramic composite with a 5:6 HfB_2:HfC ceramic ratio. However, XRD analysis of the sample heated at 1650°C for 2 h showed much greater intensity for the HfC diffraction peaks indicating that HfB_2 crystallization was incomplete at this temperature.

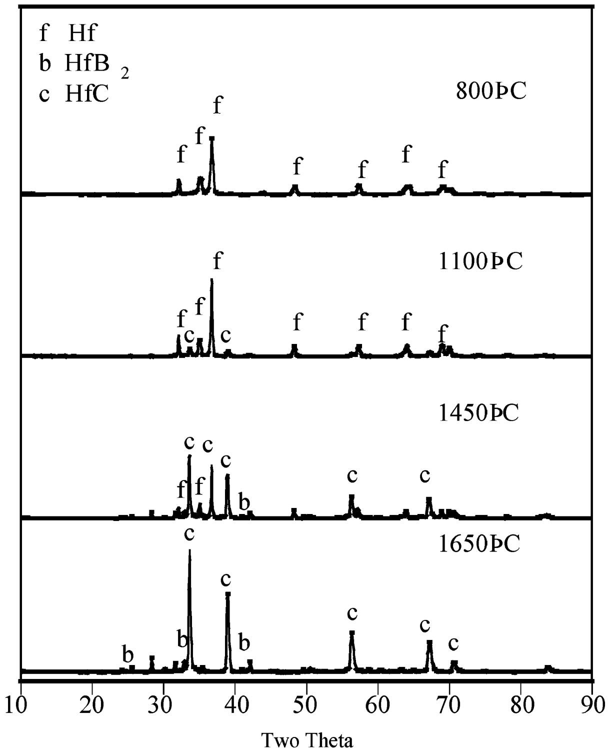
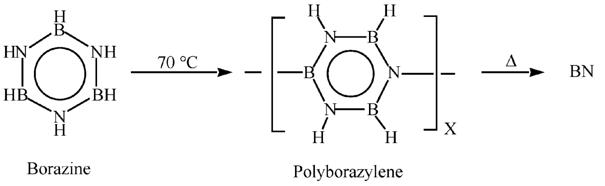


Figure 6 X-ray diffraction patterns of Hf/polyhexenyldecaborane dispersions pyrolyzed at different temperatures.

4. Precursor routes to metal boride/nitride composites

The results presented in the previous sections demonstrated general routes to metal borides and metal-boride/carbide composites based on the reaction of a metal oxide or metal with a boron-carbon based polymer. The success of this approach suggested that a wider range of solid-state materials could be generated by employing the reactions of metal (or metal reagents) with polymers containing other elements.

As shown in Equation 18, we have previously shown that borazine can be readily dehydropolymerized to produce the new boron-nitrogen polymer, polyborazylene, $(B_3N_3H_4)_x$ [26, 27]. The polymer has a complex structure, related to those of the organic polyphenylenes, having linear, chain-branched and fused-cyclic segments. Pyrolysis studies have demonstrated that polyborazylene converts via a two-dimensional crosslinking reaction to turbostratic boron nitride in excellent chemical (89 to 99%) and ceramic yields (84 to 93%) at temperatures as low as 800°C.



(18)

We then showed that TiB_2/TiN composites could be made from this polymer in both high chemical and ceramic yields by pyrolysis of titanium/polyborazylene dispersions under an inert atmosphere (Equation 19) [28–30].

$$(B_3N_3H_4)_X + Ti \xrightarrow{\Delta} TiN/TiB_2 + H_2 \qquad (19)$$

In this system, both the polymer boron and nitrogen atoms react with the metal to produce the new composite metal-nitride/metal-boride material. Ceramic powders prepared at 800 and 1450°C had compositions of $Ti_{1.0}B_{0.66}N_{0.64}H_{0.51}O_{0.39}C_{0.04}$ and $Ti_{1.0}B_{0.50}N_{0.57}H_{0\cdot06}O_{0.1}C_{0.14}$,respectively. The composition of the 1450°C material is consistent with a $(TiN)_{0.57}(TiB_2)_{0.25}Ti_{0.18}O_{0.1}C_{0.14}$ mixture.

XRD and TEM studies of the ceramic conversion reaction (Equation 19) showed changes in composition and crystallinity as the processing temperature is increased. As can be seen in the XRD spectra in the Fig. 7, there appears to be little reaction between the polymer and the titanium metal when the sample was heated at 800°C for 9.5 h. Consistent with this conclusion, elemental analyses of a sample at this point showed that

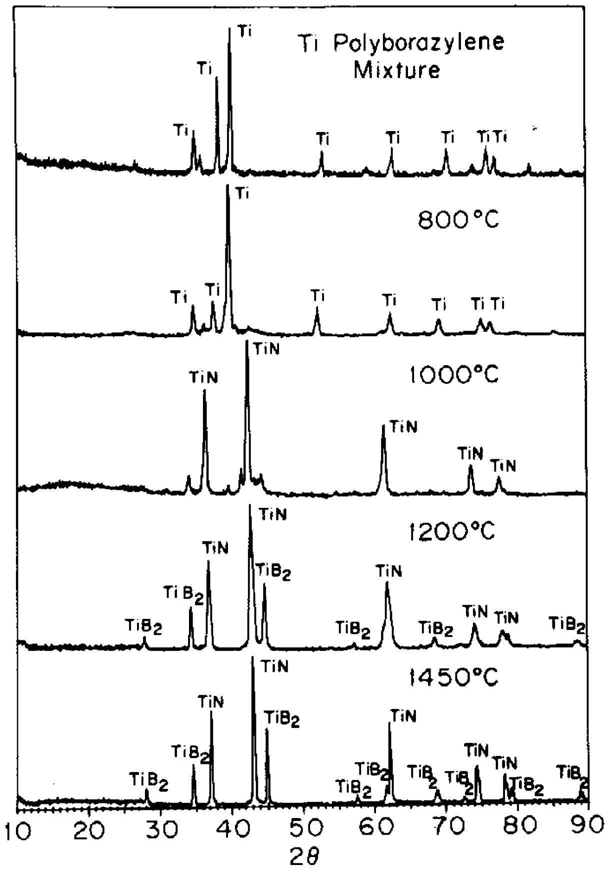


Figure 7 X-ray diffraction studies of Ti/polyborazylene dispersions pyrolyzed at different temperatures. Reproduced with permission from *Chem. Mater.* **4** (1992), 1139–1141. Copyright 1992 Am. Chem. Soc.

the material still had a significant hydrogen content with the observed $B_{1.03}:N_{1.0}:H_{0.79}$ ratio suggesting that polymer crosslinking was still occurring. When the sample was heated at 1000°C for 2 h, the titanium metal was completely consumed by reaction with the polymer and crystalline titanium nitride was initially observed to form. The XRD pattern obtained from the 1200°C sample clearly indicated the presence of both crystalline TiB_2 and TiN. The decrease in linewidths from the 1450 and 2000°C samples suggests that some grain coarsening occurred at high temperature. Although not detected in the XRD, TEM imaging provides evidence that some BN crystallized during the reaction.

Similar investigations utilizing hafnium provide a new route to hafnium-boride/nitride composites (Equation 20). In a typical process, 3.73 g of hafnium metal was added to a dry glyme (ethylene glycol dimethyl ether) solution of 0.40 g of polyborazylene. The solution was then ultrasonically agitated while the solvent was evaporated under vacuum.

$$(B_3N_3H_4)_X + Hf \xrightarrow{\Delta} HfN/HfB_2 + H_2 \qquad (20)$$

Pyrolysis of a 0.87 g sample to 1450°C (2 h) of the solid Hf/polyborazylene dispersion under argon produced 0.85 g of product for a ceramic yield of 98.2%. The stoichiometry of the hafnium/polyborazylene dispersion used in this experiment should ideally yield a ceramic composite with a 1:2 HfB_2:HfN ceramic ratio in a theoretical 98.6% ceramic yield. In this system, both the polymer boron and nitrogen atoms react with the metal to produce the new composite metal-nitride/metal-boride material.

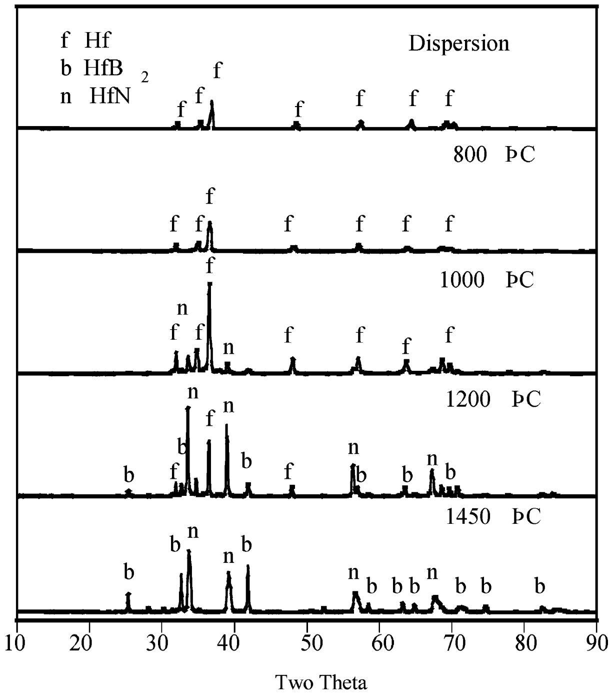


Figure 8 X-ray diffraction studies of Hf/polyborazylene dispersions pyrolyzed at different temperatures.

A TGA study of the ceramic conversion reaction showed initial weight loss of only (ca. 2%) between 50–200°C. This is consistent with a loss of hydrogen indicative of further dehydropolymerization and crosslinking of the polyborazylene polymer. XRD analysis (Fig. 8) showed, in fact, that there appears to be little or no reaction between the polymer and the hafnium metal when the sample was heated at 800°C for 2 h. When the sample was heated at 1000°C for 2 h, hafnium nitride is initially observed along with small amounts of crystalline hafnium boride. Hafnium metal is still present after the sample was heated at 1200°C for 2 h and it is not until the sample was heated at 1450°C for 2 h that the hafnium metal was completely consumed.

Since polyborazylene functions as both a reactant and binder in these systems, monolithic green bodies were also readily achieved by isostatic pressing of 1–5 g samples of titanium/polyborazylene or hafnium/polyborazylene dispersions at room temperature at 75000 psi. The titanium/polyborazylene bodies were then heated [30] under argon separately at 1000, 1200, and 1450°C, resulting in the production of ceramic bodies with ceramic yields of 96.0, 95.5, and 94.9%, respectively. The final ceramic bars showed excellent shape retention. The ceramic monolith prepared at 1000°C had a linear shrinkage of about 6%. The densities of the ceramic bodies increased from 3.0 (1000°C) to 3.9 g/cm^3 (1450°C) with the increasing reaction temperatures which can be compared with the density of pure $TiB_2 = 4.5$ g/cm^3 and TiN $= 5.22$ g/cm^3. The hafnium/polyborazylene green bodies were likewise heated under argon at 1000 and 1450°C to produce hafnium-boride/nitride ceramic bars in ceramic yields of 98–99%. The final ceramic bars again showed excellent shape retention.

The preparations of TiB_2/TiN, TiB_2/Ti(CN), HfB_2/HfN composite materials by sintering TiB_2 and TiN, TiCN and HfB_2 and HfN powders at high temperatures have previously been reported [31–33]. Seyferth has also reported that a crystalline TiB_2/TiN powder composite can be made by the pyrolysis of $[B_{10}H_{12}\cdot\text{diamine}]_x$ polymer Ti under NH_3 atmospheres [34]. TiB_2/TiN composite coatings have also been achieved by CVD methods [35]. The polyborazylene-based route discussed herein is unique, however, as it is the only reported direct chemical method which can be used to produce monolithic titanium and hafnium boride/nitride composites, consisting of intimately mixed polycrystals with grain sizes on the order of nanometers, in high ceramic and chemical yields. We are currently investigating the microstructure evolution and properties of these and related composite materials.

Acknowledgements

We thank the Air Force Office of Scientific Research, USAF, under grant number F49620-03-1-0242 and the NSF-MRSEC program at the University of Pennsylvania for support of this work.

References

1. N. N. GREENWOOD, R. V. PARISH and P. THORNTON, *Q. Rev.* **20** (1966) 441.
2. V. I. MATKOVICH, "Boron and Refractory Borides" (Springer-Verlag, New York, 1977).
3. B. POST, "Refractory Binary Borides" in "Boron, Metallo-Boron Compounds and Boranes," edited by R. M. Adams (Interscience, New York, 1964) p. 301.
4. N. N. GREENWOOD and A. EARNSHAW, "The Chemistry of Boron" (Butterworth-Heinemann, Oxford, 1997) p. 139.
5. R. THOMPSON, "Progress in Boron Chemistry" (Pergamon, New York, 1970) p. 173.
6. J. L. HOARD and R. E. HUGHES, "The Chemistry of Boron and Its Compounds," edited by E. L. Muetterties (Wiley, New York, 1967) p. 25.
7. A. M. WEIMER (ed.), "Carbide, Nitride, and Boride Materials: Synthesis and Processing" (Chapman & Hall, New York, 1997).
8. C. BARTULI, T. VALENTE and M. TULUI, *Surf. Coat. Tech.* **155** (2002) 260.
9. M. M. OPEKA, I. G. TALMY, E. J. WUCHINA, J. A. ZAYKOSKI and S. J. CAUSEY, *J. Eur. Cer. Soc.* **19** (1999) 2405.
10. P. PESHEV, L. LEYAROVSKA and G. BLIZNAKOV, *J. Less-Comm. Met.* **5** (1968) 259.
11. P. PESHEV and G. BLIZNAKOV, *ibid.* **14** (1968) 23.
12. J. K. WALKER, *Adv. Ceram. Mater.* **3** (1988) 602.
13. M. G. L. MIRABELLI and L. G. SNEDDON, *J. Amer. Chem. Soc.* **110** (1988) 3305.
14. W. S. REES, Jr., *J. Amer. Ceram. Soc.* **71** (1988) C194.
15. W. S. REES, Jr., and D. SEYFERTH, *Chem. Mater.* **3** (1991) 1106.
16. D. SEYFERTH, W. S. REES, Jr. J. S. HAGGERTY and A. LIGHTFOOT, *ibid.* **1** (1989) 45.
17. K. SU and L. G. SNEDDON, *ibid.* **3** (1991) 10.
18. *Idem.*, *ibid.* **5** (1993) 1659.
19. J. GREEN, M. M. FEIN, N. MAYES, G. DONOVAN, M. ISRAEL and M. S. COHEN, *Polym. Lett.* **2** (1964) 987.
20. G. V. WHITE, K. J. D. MACKENZIE and J. H. JOHNSTON, *J. Mater. Sci.* **27** (1992) 4287.
21. G. V. WHITE, K. J. D. MACKENZIE, W. M. BROWN, M. E. BOWDEN and J. H. JOHNSTON, *ibid.* **27** (1992) 4294.
22. T. MATSUDAIRA, H. ITOH, S. NAKA, H. HAMAMOTO and M. OBAYASHI, *J. Mater. Sci.* **23** (1988) 288.
23. W. S. REES, Jr. and D. SEYFERTH, *Ceram. Eng. Sci. Proc.* **10** (1989) 837.
24. M. PENDER and L. G. SNEDDON, *Polym. Prepr.* (*Amer. Chem. Soc., Div. Polym. Chem.*) **41** (2000) 551.
25. M. J. PENDER, P. J. CARROLL and L. G. SNEDDON, *J. Amer. Chem. Soc.* **123** (2001) 12222.
26. P. J. FAZEN, J. S. BECK, A. T. LYNCH, E. E. REMSEN and L. G. SNEDDON, *Chem. Mater.* **2** (1990) 9697.
27. P. J. FAZEN and L. G. SNEDDON, *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **32** (1991) 544.
28. K. SU, M. NOWAKOWSKI, D. BONNELL and L. G. SNEDDON, *Chem. Mater.* **4** (1992) 1139.
29. M. NOWAKOWSKI, K. SU, L. G. SNEDDON and D. BONNELL, *Mater. Res. Soc. Proc.* **286** (1993) 425.
30. The green bodies were first annealed at 800°C for 9.5 h, then heated (5°C/min) separately to 1000, 1200, or 1450°C and held at temperature for 2 h.
31. O. A. MEDVEDEVA, *Mater. Izdeliya, Poluchamye Metodom Poroshk. Metall.* (1974) 154.
32. K. SHOBU, T. WATANABE, Y. ENOMOTO, K. UMEDA and Y. TSUYA, *J. Amer. Ceram. Soc.* **70** (1987) C103.
33. T. WATANABE, H. YAMAMOTO, K. SHOBU and T. SAKAMOTO, *ibid.* **71** (1988) C202.
34. D. SEYFERTH, N. BRYSON, D. P. WORKMAN and C. A. SOBON, *ibid.* **74** (1991) 2687.
35. J. G. M. BECHT, P. J. VAN DER PUT and J. SCHOONMAN, *J. Solid State Ion.* **32** (1989) 789.

Received 22 December 2003
and accepted 15 March 2004