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Zirconium Borohydride as a Zirconium Boride Precursor

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Synthesis of zirconium boride, ZrB_2, from zirconium borohydride, $Zr(BH_4)_4$, has been explored by a variety of methods, including chemical vapor deposition (CVD) in a hot tube, laser CVD with both continuous-wave (cw) and pulsed lasers, and cw-laser synthesis of fine powders. In all cases, ZrB_2 was the only crystalline product identified. Products made at high temperature contained excess boron, while those made at low temperature were boron-deficient.

Metal borides tend to be hard, refractory materials with substantial chemical inertness. The materials form a wide range of compositions, from M_5B to MB_{12},[1,2] with quite varied structures.[2,3] Syntheses of bulk borides have been accomplished by direct combination of the elements, reduction of metal oxides with B or B_4C, and coreduction of mixed metal and boron oxides with carbon. Such preparations have typically been conducted at >1000°C.[1]

There are several reports in the literature on the preparation of thin coatings of metal diborides, MB_2, through chemical vapor deposition (CVD) by H_2 reduction of mixed BCl_3 and MCl_x gases.[4–10] Group IV (Ti, Zr, and Hf) diboride films were initially made at 1400°C.[10] Subsequent depositions of TiB_2 on graphite have been accomplished at temperatures as low as 800°C,[8,9] and $(Ti,Zr)B_2$ solid solutions were reported to form on graphite at 900° to 1400°C from mixtures of $TiCl_4$, $ZrCl_4$, BCl_3, and H_2.[8] However, Randich found that coatings formed on graphite at 900°C from such mixtures contained no zirconium, while at 1100°C the Zr/Ti ratio in the coating was only one-tenth of that in the gas.[4] The result is consistent with the relative ease of reduction of titanium(IV) versus zirconium(IV).[11]

Chemical vapor deposition of metal boride coatings from the chlorides limits the choice of substrate. Pierson and Randich pointed out that preparing good CVD coatings of TiB_2 from the chlorides requires that the substrate withstand both the high deposition temperature employed and the HCl byproduct.[5,6]

The highly volatile group IV borohydrides—$Ti(BH_4)_3$, $Zr(BH_4)_4$, and $Hf(BH_4)_4$—are attractive molecular precursors to the borides. When first prepared by Hoekstra and Katz, they were reported to decompose at very slow (Zr and Hf) to moderate (Ti) rates to nonvolatile solids of indefinite composition.[12] Although pyrolysis of the $Th(BH_4)_4$ analogue was reported to yield $ThB_{3.83}$,[12] pyrolysis of $Zr(BH_4)_4$ has been claimed to give "zirconium in a mixture of zirconium boride" as a coating on graphite.[13] There is also a recent patent reporting use of $Zr(BH_4)_4$ to deposit boron-containing material as a "consumable poison" on uranium dioxide nuclear fuel.[14] A recent paper by Gallagher *et al.* on preparation of the group IV diborides from the borohydrides[15] prompts us to report our experiments with $Zr(BH_4)_4$. We have conducted $Zr(BH_4)_4$ pyrolysis by a variety of methods at different temperatures and find that it can be decomposed either to a coating or to a high-surface-area powder.

EXPERIMENTAL PROCEDURE

Zirconium tetrachloride, $LiBH_4$, and $LiBD_4$ were purchased[†] and used as received. All reactions were conducted under dry nitrogen in a glove box[‡] or in Schlenk-type glassware.[16] Synthesis of $Zr(BH_4)_4$ has been reported by several methods, including reaction of $NaZrF_5$ with liquid $Al(BH_4)_3$,[12] reaction of $ZrCl_4$ and $LiBH_4$ in ether,[17] and reaction of $ZrCl_4$ and $LiBH_4$ by "intensive grinding" of the dry solids in a vacuum ball mill at 100°C.[18] Since the purchased materials were fine powders, good yields were obtained in the laboratory by magnetic stirring of the dry solids in a flask above the melting point (29°C[12]) of the product. After a fairly long induction time, the liquid $Zr(BH_4)_4$ produced seemed to act as a flux for further reaction. The product was separated from residues by vacuum sublimation into a chilled flask. The deuterated analogue, $Zr(BD_4)_4$, was similarly produced using $LiBD_4$ and $ZrCl_4$ reactants. **Caution:** $Zr(BH_4)_4$ and residues from its synthesis react violently with air or protic solvents.

Conventional CVD experiments employed iron-foil substrates in a 25-mm-diameter glass tube in a small tube furnace. The $Zr(BH_4)_4$ was held at 0°C, where its reported vapor pressure is 240 Pa (1.8 torr[12]), and continuously pumped past the substrates with a roughing pump capable of an ultimate pressure of 10 Pa. The (unmeasured) pressure in this dynamic system was estimated to be 100 Pa. This vapor was admitted to the hot-walled reaction tube via a room-temperature, 8-mm tube terminating near the iron substrates. Experiments in the same reactor, but using atmospheric-pressure argon as a carrier for $Zr(BH_4)_4$ (22°C source, 1.6 kPa, 1.6% $Zr(BH_4)_4$), produced fine powders in addition to coatings. While fine powders are themselves of interest, conditions that yield powders are unsuitable for coating deposition.

Laser CVD was attempted by several methods. In all cases, the irradiation cells contained only $Zr(BH_4)_4$, with its pressure controlled over a range of 240 Pa to 2 kPa by maintaining the source between 0° and 25°C. With CO_2 infrared lasers, operating at 10.6 μm, no coatings were produced on reflective metallic substrates (continuous-wave (cw): 20 W; pulsed: 2 J/pulse, 110-ns full width at half-maximum (FWHM), 2 J/cm^2), but coatings could be formed on absorbing quartz surfaces (cw: 4 W). Deposition on metallic substrates was achieved with a pulsed Nd:YAG near-infrared laser operating at 1.06 μm (200 mJ/pulse, 25-ns FWHM, 6-Hz repetition rate, 5 J/cm^2). Absorption of laser radiation by $Zr(BH_4)_4$ is small at both 10.6 and 1.06 μm, and all reactions are due to laser-induced surface heating.

Powder synthesis was attempted using laser-pyrolysis methods that have been described previously.[19,20] Zirconium borohydride has no strong absorptions in the spectral region accessible with CO_2 lasers, so pyrolysis experiments used either $Zr(BH_4)_4$ with SF_6 sensitizer and the 10 P(20) laser line at 944 cm^{-1}, or the deuterated analogue $Zr(BD_4)_4$ with no sensitizer and the 10 P(22) laser line at 942 cm^{-1}. Laser power was 20 W in both cases.

RESULTS

Conventional CVD

Conventional CVD on iron substrates was examined at three temperatures. At 182°C, no deposition occurred. At 265° and 398°C, however, the pyrolysis appeared to go to completion because coatings on the hot-walled reaction tube were localized near the reactant inlet. The results of a series of Auger electron spectroscopic analyses, made while sputtering away the coating produced at 265°C, are shown in Fig. 1.[§] It shows that a 2-min deposition produced a coating ≈150 nm thick, with a 3- to 5-nm oxide surface layer. The boride layer's composition was $ZrB_{1.6}$. This presumably corresponds to the previous report of zirconium–zirconium boride mixtures formed by pyrolysis of the borohydride.[13] Corresponding analysis of a coating produced on iron at 398°C revealed at 450-nm boride layer with the composition $ZrB_{3.1}$, and a 1- to 3-nm oxide surface layer. Elemental analysis[¶] of flakes scraped from the

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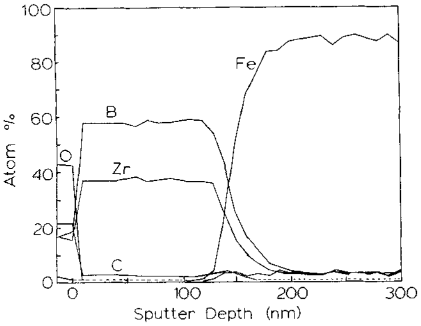

Fig. 1. Auger sputtering depth profile of a zirconium boride coating on iron produced at 265°C.

reactor wall in the same run gave the composition $ZrB_{3.3}$, in substantial agreement with the Auger result. X-ray diffraction on the $ZrB_{3.3}$ flakes indicated that ZrB_2 was the only crystalline phase present. Diffraction peaks were very broad (3° to 5°). These sharpened to 1° after vacuum annealing at 900°C for 16 h, but no new phases — such as ZrB_{12} or B — were observed that would account for the excess boron.

The different coating compositions obtained at 265° and 398°C imply an intermediate, optimum temperature for forming stoichiometric ZrB_2. Since the excess boron in $Zr(BH_4)_4$ must be transported away from the coated surface as volatile boranes, which themselves decompose by hydrogen loss at relatively low temperature,[21] coating composition may be affected by conditions such as gas-flow velocities and pressure of added hydrogen as well as substrate temperature. The following section shows that transient heating also permits removal of the borane byproducts.

Laser CVD

Laser CVD was attempted under conditions intended to produce coatings by localized heating of substrates. Laser CVD on metal substrates with a 20-W cw CO_2 laser was unsuccessful because of the high reflectivity of the substrates. Deposition on absorbing quartz substrates was achieved with only 4 W of incident power. The coatings were smooth when very thin but spalled off as deposition continued. Thin coatings were adherent, whereas thicker ones could be wiped away easily. It was also noted that reducing the $Zr(BH_4)_4$ pressure from 1500 to 400 Pa substantially increased coating adherence and resistance to dissolution by aqua regia.

Laser-CVD coatings on iron substrates were obtained with 1.06-μm radiation, where iron is less reflective than at 10.6 μm. A near-infrared laser CVD (10 min of irradiation, 3600 pulses) was compared with two conventional CVD experiments (398°C for 3 min, 265°C for 11 min). Auger analysis of the pulsed-laser CVD coating showed that it was nearly stoichiometric, with a composition of $ZrB_{2.1}$. Measured at the depths where sputtering exposed equal amounts of coating and substrate, the laser-produced coating was much thinner (10 nm) than the conventional coatings (160 and 510 nm for the 398° and 265°C coatings, respectively.) These thicknesses and deposition times yield calculated deposition rates of 1 nm/s for the laser-CVD coating, 9 nm/s for the 398°C conventional coating, and 8 nm/s for the 265°C conventional coating. However, the laser pulse width was only 25 ns, so the exposure time in the laser-CVD experiment was only 90 μs for 3600 pulses. This gives a deposition rate of 110000 nm/s during exposure of the substrate to laser radiation. The high deposition rate with laser CVD suggests high transient surface temperatures, and the stoichiometric ZrB_2 composition indicates that borane byproducts are able to diffuse away from the reaction zone between pulses, thereby avoiding incorporation of excess boron into the coating.

Powder Synthesis

The laser-driven powder-synthesis experiments are more aptly described as informative rather than successful. Zirconium borohydride has only one very weak absorption band, centered at 1033 cm^{-1}, in the spectral range accessible with CO_2 lasers. No solid product was obtained by irradiation at 1045 cm^{-1} on the wing of this band. Upon deuteration, a stronger absorption band that occurs at 1222 cm^{-1} in $Zr(BH_4)_4$ shifts down to 917 cm^{-1} (shoulder at 935 cm^{-1}) in $Zr(BD_4)_4$, and powder was obtained by irradiation at 933 cm^{-1}. These powders were black and free-flowing, with very broad X-ray diffraction peaks for ZrB_2, but their analytical compositions ranged from $ZrB_{3.3}$ to $ZrB_{3.7}$. Brunauer–Emmett–Teller surface areas were 40 to 125 m^2/g for different runs. The powders were remarkably air-sensitive. Although bulk ZrB_2 is quite oxidation-resistant,[22,23] with potential short-term use to 1500°C,[24–26] laser-synthesized powders exposed to air immediately became red hot and changed to white oxides. Air sensitivity is undoubtedly due to the high surface area.

Pyrolysis of $Zr(BH_4)_4/SF_6$ mixtures was attempted because SF_6 absorbs strongly at 944 cm^{-1} and is often used as a sensitizer in laser-chemistry experiments.[27] In this case, it was not a sensitizer but a reactant. X-ray diffraction clearly showed that both ZrB_2 and ZrF_4 were present in the product, and ZrS_2 lines were tentatively identified as well. Elemental analysis of the powder gave the empirical formula $ZrS_{0.6}F_{1.3}B_{1.7}$.

DISCUSSION

This work was undertaken to determine whether $Zr(BH_4)_4$ had any potential as a ZrB_2 precursor. The results show that it does. Laser synthesis of the diboride powder from the borohydride, however, is less attractive than other powder-synthesis methods recently reported. These include conventional pyrolysis of group IV borohydrides by Gallagher *et al.*,[15] as well as synthesis of TiB_2 from $TiCl_4$ and BCl_3 via laser pyrolysis of the gases[28] and sodium reduction in solution.[29] The CVD and laser-CVD techniques are much more promising.

The availability of borohydride precursors for other metals is, unfortunately, rather limited. Titanium, zirconium, and hafnium are the only transition metals reported to form volatile borohydrides that can be isolated without additional ligands.[2] Volatile nontransition-metal borohydrides are few, including those of beryllium, aluminum, thorium, and uranium.[12] The laser-CVD work with $Zr(BH_4)_4$ is highly predictive of the behavior of $Hf(BH_4)_4$, because "the chemistries of zirconium and hafnium are more nearly identical than for any other two cogeneric elements."[30] The $Zr(BH_4)_4$ work is less predictive of $Ti(BH_4)_3$ behavior, but laser CVD of TiB_2 coatings from $Ti(BH_4)_3$ should also be possible.

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High-Temperature Behavior of Chemically Treated Silicon Nitride Powders

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The mechanical properties of chemically treated, then sintered, Si_3N_4 was studied. Raw materials consisted of two types of Si_3N_4 produced by the nitridation of silicon. The chemical treatment involved leaching in different acids (HCl, HNO_3, HF, and combinations thereof). The powders were sintered by hot isostatic pressing with 2.5% yttria, and the high-temperature properties of the resultant materials were evaluated by the stepped-temperature stress rupture (STSR) method (24-h hold time at 150-MPa stress at 1000°, 1100°, 1200°, 1300°, and 1400°C). A significant decrease in high-temperature performance was observed for acid-leached powders, especially when HF-containing acids were used.

THE successful application of advanced structural ceramics presupposes precise knowledge of the relations between the chemical and physical attributes of the presintered materials (ceramic powders+powder systems), forming processes, etc., and the relevant material properties. Also, the relations between the material properties and performance of the final component in its particular environment/application are obviously required to be thoroughly understood if technical success is to be guaranteed.

Alternative routes for the synthesis of Si_3N_4 powders include the conventional nitridation of silicon, decomposition of metallorganic precursors (CVD and laser-driven reactions), the imide process, and the carbothermic reduction of silica in nitrogen. The various methods yield Si_3N_4 powders with specific characteristics that must be considered during subsequent forming and sintering. These powder characteristics can also profoundly influence material properties.

In the present work, attention was focused on alternative acid-leaching treatment of Si_3N_4 powders produced by nitriding silicon powders. Acid leaching is often used to eliminate undesirable contaminants and/or remaining elemental silicon in the "raw nitride" that may adversely affect subsequent material properties.[1] The leaching treatment may also affect the sinterability of the nitride itself by modification of morphology, surface chemistry, and/or the chemical composition of the glass phase in the sintered component.

Basically, in the conventional nitridation of elemental Si, two routes can be used. Impure silicon is partially or totally nitrided and the resultant raw nitride purified. Alternatively, purified silicon is nitrided totally and the product reduced to a sinterable state with a minimum of contamination.

The original Si_3N_4 powders* (Siconide P95) were produced by nitriding pure silicon powder (Sicomill IV D)* according to standard procedure for production, including computer-governed reaction control. After the Si_3N_4 was nitrided, it was milled either in an iron-free environment (P95-1) or with equipment containing iron (P95-2) (Table I). The powders were leached for 6 h at 50°C with three different acids while stirring: 2*M* HNO_3, 1*M* HF+1*M* HNO_3, and 1*M* HF+1*M* HCl. After the powder was leached, it was washed thoroughly with distilled water. Leaching and washing were performed in polypropylene equipment. Drying was conducted for 24 h at 100°C in air; the resultant chemical compositions are shown in Table I.

Table I. Chemical Analyses of the Powders P95-1 and P95-2 Before and After Leaching

Element (wt%)	Untreated		Leaching in			
			HNO_3		HNO_3+HF	HCl+HF
	P95-1	P95-2	P95-1	P95-2	P95-1	P95-1
Fe	0.027	0.07	0.025	0.06	0.022	0.025
Al	0.044	0.04	0.036	0.04	0.034	0.035
Ca	0.003	<0.01	0.005	<0.01	0.005	0.004
C	0.44	0.31	0.53	0.78	0.40	0.48
O	1.0	1.0	1.2	1.2	1.5	0.83
F	<0.01	<0.01	0.01	<0.01	0.02	0.02
Cl	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

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