

Solution-Based Synthesis of Submicrometer ZrB₂ and ZrB₂-TaB₂

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Zirconium diboride and a zirconium diboride/tantalum diboride mixture were synthesized by solution-based processing. Zirconium *n*-propoxide was refluxed with 2,4-pentanedione to form zirconium diketonate. This compound hydrolyzed in a controllable fashion to form a zirconia precursor. Boria and carbon precursors were formed via solution additions of phenol-formaldehyde and boric acid, respectively. Tantalum oxide precursors were formed similarly as zirconia precursors, in which tantalum ethoxide was used. Solutions were concentrated, dried, pyrolyzed (800° -1100°C, 2 h, flowing argon), and exposed to carbothermal reduction heat treatments (1150° -1800°C, 2 h, flowing argon). Spherical particles of 200–600 nm for pure ZrB₂ and ZrB₂-TaB₂ mixtures were formed.

I. Introduction

N recent years, a renewed interest has developed in borides of groups IV and V transition metals (e.g., ZrB_2 , HfB_2 , and TaB_2), referred to as ultrahigh temperature ceramics. The thermal and chemical stability of these compounds makes them candidates for use in the extreme environments associated with hypersonic flight (1400°C and above in air), atmospheric reentry (2000°C and above), and rocket propulsion (3000°C and above).¹⁻³ These materials have melting temperatures above 3000°C, retain their strength at temperatures above 1200°C, and exhibit good thermal shock resistance. They can be modified with additives such as SiC to promote oxidation resistance. In particular, ZrB₂-SiC and HfB₂-SiC with volume ratios of 80:20 have shown improved oxidation resistance via formation of a passive amorphous borosilicate surface layer.^{4,5} Tantalum additions in the form of TaB₂ or TaSi₂ have been reported to further enhance oxidation resistance by facilitating a highviscosity phase-separated amorphous surface coating.

Metal diborides can be synthesized by reaction between a metal oxide and boron (borothermal reduction):^{9–14} $MO_2(s)+4B(s) \rightarrow MB_2(s)+2BO(g)$. The reaction temperatures are generally lowered by having carbon present, such that the overall boro/carbothermal reaction is given by:¹⁵ $MO_2(s)+2B(s)+2C(s) \rightarrow MB_2(s)+2CO(g)$. Metal borides can also be synthesized by reaction between a metal oxide and boron oxide via a carbothermal reduction:^{16–17} $MO_2(s)+B_2O_3(l, g)+5C(s) \rightarrow MB_2(s)+5CO(g)$. Excess boria is generally required for the above reaction because of B_2O_3 volatilization at elevated temperatures (boiling point of B_2O_3 , i.e., 1 atm vapor pressure, is $1860^{\circ}C$),¹⁸ as well as to compensate for the formation of gaseous boron oxide (e.g., BO) intermediate products which are removed from the reaction zone by the argon gas stream. Homogeneous products with fine particle size have been reported ^{18–20} using this fabrication route. Metal carbides have been observed as inter-

mediate reaction products during metal diboride synthesis because of preferential carbothermal reduction of the metal oxide by carbon. However, the metal diboride is formed eventually if sufficient boron is available, i.e., $MC(s)+B_2O_3(s)+2C(s) \rightarrow MB_2(s)+3CO(g)$.

Chemical solution processing routes refer to methods in which one or all of the components (i.e., metal-bearing, boronbearing, and carbon-bearing) are solubilized in a liquid processing medium. Soluble sources that are used to provide boron include boric acid and boron alkoxides. Numerous soluble carbon-bearing materials have been used to produce metal carbides, including phenolic resins, furfuryl alcohol, sugar, corn starch, petroleum pitch, polyacrylonitrile polymers, cellulose acetate polymers, and diols. Common soluble metal/metal oxidebearing materials are metal alkoxides, metal diketonates, and metal carboxylates. Metal-organic compounds are usually subjected to hydrolysis and condensation reactions to produce polymeric or colloidal metal-oxide precursors.²¹⁻³⁷ Depending on the reaction conditions, the metal-organic compound may also be a source for some of the carbon for the carbothermal reduction reaction.

The most important advantage of solution-processing methods is that more intimate mixing of components (atomic-scale or at least molecular-scale mixing) can be achieved. However, it should be noted that preparation of solutions with atomic- or molecular-scale mixing does not necessarily ensure that the same scale of mixing will be maintained during subsequent processing steps. It is necessary to remove the liquid medium in a manner that avoids segregation of components. For example, molecularscale mixing in the solutions may be maintained by first gelling the solutions before solvent removal. The hydrolysis time, temperature, and atmosphere can be altered to control the grain size and phase distribution in the resulting product, which in turn will factor into the properties of the resulting materials.³⁸⁻⁴⁰ In this work, solution-based synthesis was used in effort to fabricate submicrometer, highly sinterable powders of ZrB₂, and intimately mixed submicrometer powders of ZrB₂ and TaB₂.

II. Experimental Procedure

A flow chart for the solution-based synthesis of ZrB₂ is shown in Fig. 1. The starting Zr-containing material was a 70 wt% zirconium n-propoxide (Zr(OC₃H₇)₄, Alfa Aesar, Ward Hill, MA) in solution with *n*-propanol. The zirconium *n*-proposide ("Zr(OPr)₄") was mixed with 2,4-pentanedione ("acacH"") using molar ratios of 3 (acacH to Zr(OPr)₄) and 2-propanol was used as a mutual diluent. This solution was refluxed (i.e., solution was heated and the vapor formed was condensed and returned to the solution to be heated again) at 170°-195°C for 2 h for the purpose of reacting zirconium *n*-proposide and 2,4-pentanedione to form zirconium diketonate, as illustrated in Fig. 2. The purpose of this was to facilitate a controlled hydrolysis reaction; zirconium n-propoxide otherwise hydrolyzes very rapidly. Refluxing maintains constant concentrations of constituents as reactions occur among them at temperatures at which their volatilities vary substantially. Following refluxing, much of the solvent (about 2/3) was evaporated using a rotary evaporator (Rotavapor R-114, Buchi, Flawil, Switzerland) at 35°C, and then 2-propanol was added back to the sol; the

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Fig. 1. Flow chart for synthesis of zirconium diboride from solutionbased precursors.

purpose of this was to remove remaining 2,4-pentanedione from the solution. These Zr-containing precursors were then partially hydrolyzed, in which a hydroxyl substituted for the *n*-propoxide and pentanedionate (acac) by interaction with water at 50°C for 2 h under acidic conditions (pH in the range 4–5) using a HNO₃/ Zr molar ratio of 0.27 and an H₂O/Zr molar ratio of 24. Hydrolysis is required to facilitate later condensation reactions. A clear solution was observed before and after hydrolysis.

Separately, a boric acid (H_3BO_3 , Fisher Scientific, Fair Lawn, NJ) in water solution with a concentration of 4 wt% was prepared as the boron source, to make a B/Zr ratio of 3. To dilute the boric acid solution, 2-propanol was then added with a propanol/ H_2O ratio of 3. Twenty weight percent phenol-formaldehyde resin (novolac-type; Georgia Pacific, Atlanta, GA) in a 2-propanol solution was added to the boric acid solution to increase the C/Zr ratio to 4.8–6.0.

The mixture of boric acid and phenol-formaldehyde resin was then added to the hydrolyzed Zr-containing solutions. The solutions were concentrated in a rotary evaporator (preventing the constituents from demixing) in a condensation reaction in

Substitution:

which there was a buildup of species with a three-dimensional structure. As solvent was volatilized, a residual mass formed with a sludge-like consistency. This was then dried to powders under vacuum conditions at $120^{\circ}-140^{\circ}$ C (2 h). These powders were subsequently pyrolyzed at temperatures in the range of $800^{\circ}-1100^{\circ}$ C (2 h) in a flowing argon atmosphere in an alumina tube-furnace to produce intimately mixed not-yet-reacted zirconia/boron oxide/carbon mixtures. This temperature range was found to permit near-complete conversion to the desired oxide or carbon constituents, but was not high enough to initiate carbothermal reduction. Pyrolyzed powders were subsequently heat treated at temperatures in the range of $1200^{\circ}-1400^{\circ}$ C (2 h) in flowing argon in a graphite tube-furnace for carbothermal reduction.

For the ZrB₂-TaB₂ composite, the starting Ta-containing material was a tantalum ethoxide solution (i.e., 99.99 wt% Ta(OC₂H₅)₄ in ethanol, HC Starck, GmbH, Germany). The tantalum ethoxide was mixed with 2,4-pentanedione using molar ratios of 3:1 and 1-propanol was used as a mutual diluent. Zirconium n-propoxide/acacH solution was prepared by the same method. Tantalum ethoxide/acacH solution was added to the zirconium n-propoxide/acacH solution to make a Zr/Ta ratio of 3. The resulting solutions were initially refluxed at $\sim 195^{\circ}$ C for 2 h, and then partially hydrolyzed (at 50°C for 2 h) under acidic conditions with a HNO₃/Zr molar ratio of 0.27 and an H_2O/Zr molar ratio of 24. Boric acid and phenolic resin were added to the above hydrolyzed solution to make the molar ratio of C/ (Zr+Ta) = 4.8 and B/(Zr+Ta) = 3.0. The mixture was then concentrated and dried. The dry powder was first pyrolyzed at 800°C to obtain fine-scale mixtures of ZrO₂/Ta₂O₅/B₂O₃/carbon. These powders were then heat treated at 1300°-1800°C in flowing Ar in a graphite tube-furnace in order to carry out the carbothermal reduction reactions to produce the ZrB2-TaB2 mixture.

X-ray diffraction (XRD, Model PW1800, PANalytical, Almelo, the Netherlands) was used to determine the phases present after various heat treatments. Scanning electron microscopy (SEM, Model 1530, LEO Electron Microscopy Inc., Oberkochen, Germany) was used to evaluate the powders for shape, size, and extent of agglomeration. For SEM evaluation, powders were pressed onto carbon tape adhering to an SEM stub. These were then coated with gold via sputtering. Fourier transform infrared spectroscopy (FTIR, Nexus 870, Nicolet Instrument Corp., Madison, WI) was performed on zirconium *n*-propoxide and zirconium diketonate (Fischer Scientific, Pittsburgh, PA).



Fig. 2. Reactions for precursor synthesis



Fig. 3. Fourier transform infrared spectroscopy spectra of the starting material (Zr *n*-propoxide), the solution after refluxing, and a commercial zirconium diketonate.

III. Results and Discussion

(1) Submicrometer ZrB_2

Triethyl borate was initially used as the boron source for precursor synthesis. Solutions containing triethyl borate were evaluated by adding them before or after refluxing. In the three evaluated solvents, ethanol, 2-propanol, and 1-butanol, the boron in solution became a member of the volatile species; no zirconium diboride was formed through carbothermal reduction. Boric acid in a water and 2-propanol solution did form a nonvolatile boron species in solution.

Figure 3 shows FTIR spectra obtained from the starting compound (zirconium *n*-propoxide), the solution after refluxing, and a commercial zirconium diketonate. The figure confirms that from the refluxing step, zirconium *n*-propoxide reacted with acacH to form zirconium diketonate. In general, zirconium *n*-propoxide undergoes more rapid hydrolysis reactions than the corresponding zirconium pentanedionate, and this has resulted in uncontrolled precipitation of relatively large precursor particles during the hydrolysis step. Therefore, zirconium *n*-propoxide was first refluxed (195°C, 2 h) with 2,4-pentanedione in order to partially or fully convert the zirconium alkoxy groups to a chelated zirconium diketonate structure.

An idealized reaction to produce stoichiometric ZrB_2 by carbothermal reduction is given by

$$\operatorname{ZrO}_2(s) + \operatorname{B}_2\operatorname{O}_3(l,g) + 5\operatorname{C}(s) \rightarrow \operatorname{ZrB}_2(s) + 5\operatorname{CO}(g)$$

However, the necessary ratio of boron to zirconium was found to be $\sim 3:1$ instead of 2:1 as dictated by the reaction stoichiometry. Excess boron oxide was required to form ZrB₂ because of B₂O₃ volatilization at elevated temperatures.

Figure 4 shows XRD patterns for dried precursor powders that were heat treated at various temperatures. The as-dried



Fig. 4. X-ray diffraction (XRD) patterns for ZrB_2 powders (as batched: B/Zr = 3, C/Zr = 5.0). Patterns corresponding to 800° and 1100°C were exposed to a pyrolysis heat treatment of 5°C/min to the indicated temperatures, holding for 2 h in an alumina tube furnace under flowing argon. XRD patterns corresponding to higher indicated temperatures were first exposed to the above pyrolysis step, and then placed in a graphite tube furnace for further heat treatment. This entailed heating at 80°C/min to a temperature 75°C lower than final temperature, 40°C/min to a temperature 35°C lower than final temperature, 20°C/min to a temperature 15°C lower, and 5°C/min to a temperature 5°C lower, and finally 1°C/min to the indicated final soak temperature. Specimens were then soaked for 2 h.





Fig. 5. Plot of weight loss versus temperature for ZrB_2 and ZrB_2 –TaB₂ dried powders. Weight losses indicated for 600°–800°C are from soaks at those temperatures for 2 h. For all higher indicated temperatures, indicated weight losses are from pyrolysis heat treatments at 800°C for 2 h, followed by heat treatments at the indicated temperatures for 2 h. Heating rates for pyrolysis were 5°C/min. Higher temperature heat treatment heating schedules were as indicated in the caption to Fig. 4.

precursor was XRD-amorphous. After heat treatments at 800° and 1100° C, monoclinic zirconia (*m*-ZrO₂) with a trace concentration of tetragonal zirconia (*t*-ZrO₂) were detected. Crystalline B₂O₃ and carbon were not detected, implying that these phases



Fig. 6. Scanning electron microscopy photomicrograph a of ZrB_2 sample heat treated at 1300°C for 2 h in a graphite tube furnace.

were present in amorphous form. Initial formation of ZrB_2 was observed after heat treatment at 1200°C, while the intensity of *t*-ZrO₂ increased compared with m-ZrO₂ in the range 1100°– 1250°C. Zirconia phases reduced to minor levels at 1300°C, and were not observed at 1400°C.

Weight loss measurements (Fig. 5) imply that the carbothermal reduction proceeded extensively above 1100° C, and taperedoff after heat treatments at 1300° C. The calculated weight loss from the above carbothermal reaction (in which no gaseous reactant escapes and only CO(g) is removed) is 55.4%. Figure 6 shows an SEM photomicrograph of a sample (initial composition



Fig. 7. X-ray diffraction (XRD) patterns for heat treated ZrB_2 -TaB₂. XRD patterns corresponding to 600°-1100°C were exposed to a pyrolysis heat treatment of 5°C/min to the indicated temperatures, holding for 2 h in an alumina tube furnace in flowing argon. XRD patterns corresponding to higher indicated temperatures followed heating schedules as enumerated in the caption to Fig. 4.



Fig. 8. Scanning electron microscopy micrograph of ZrB₂-TaB₂ heat treated at 1300°C for 2 h.

was C/Zr = 5.0, B/Zr = 3.0) heat treated at 1300° C showing nearly spherical particles of sizes 200-600 nm, with necking apparent between the particles.

(2) ZrB₂-TaB₂ Submicrometer Powder Mixture

XRD patterns for ZrB₂-TaB₂ heat treated to various temperatures are shown in Fig. 7. Tantalum zirconium oxide (TaZr_{2.75}O₈) was detected after heat treatment at 700°C. This phase was at its highest concentration at 1000°C and was resorbed above 1250°C. TaC was observed after heat treatments at 1100° and 1150°C. TaC was an intermediate product, which reacted with B_2O_3 at ~1150°C to form TaB₂:

$$2\text{TaC}(s) + 4\text{C}(s) + 2\text{B}_2\text{O}_3(l) \rightarrow 2\text{TaB}_2(s) + 6\text{CO}(g)$$

ZrB₂ first appeared at 1150°C. There was a significant increase in peak intensity for this phase over the range 1250°-1400°C. Between 1400° and 1600°C, ZrB₂ and TaB₂ formed a solid solution as evidenced by the merging of their respective XRD peaks after heat treatment at and above 1600°C.

The weight loss during heat treatment of the ZrB2-TaB2 mixture is shown in Fig. 5. Weight loss increased abruptly from 1100° to 1300°C due to carbothermal reduction, as was the case for ZrB₂ alone. This terminated at 1300°C. Figure 8 depicts the microstructure of the ZrB₂-TaB₂ powder heat treated at 1300°C for 2 h. Particle sizes appear in the range of 200-600 nm.

IV. Conclusions

Submicrometer spherical particles of ZrB2 and a ZrB2-TaB2 mixture were synthesized via a solution-based method. Zirconium n-propoxide was refluxed with 2,4-pentanedione to form zirconium diketonate, which facilitated controlled hydrolysis and condensation reactions, in turn forming intimately mixed precursors. Phenol-formaldehyde and boric acid were solution additives providing carbon and B₂O₃. After pyrolysis heat treatments to form oxides and carbon, carbothermal reduction heat treatments yielded the diboride powders.

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