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A Solvothermal Approach for the Preparation of Nanostructured Carbide and Boride Ultra-High-Temperature Ceramics

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The use of a solvothermal process for the synthesis of tantalum carbide (TaC) and lanthanum hexaboride (LaB_6) powders in fused-quartz test tubes is reported in order to demonstrate the synthesis of these powders using thermal and chemical ignition techniques and to prove that the process is of a self-propagating high-temperature synthesis type, obviating the need for an autoclave. X-ray powder diffraction showed phase pure powders with crystallite sizes of 25 and ~80 nm, while dynamic light scattering showed average particle sizes of 97 and ~130 nm, for TaC and LaB_6, respectively. The data demonstrates that the powders have a very low level of agglomeration. Scanning electron microscopy shows that the TaC powders have a spherical morphology, while the LaB_6 powders have a mixture of cubic and spherical morphologies.

I. Introduction

Transition metal carbides, such as tantalum carbide, are some of the most refractory ceramics known (having melting temperatures up to ~4000 K). Besides being refractory, other beneficial properties include thermomechanical stability, thermochemical stability, corrosion and wear resistance, good creep and fatigue resistance, unique optical and electronic properties, high emissivity at elevated temperatures, and catalytic characteristics.[1–8] These materials are of particular interest in the aerospace industry, where reentry conditions and internal rocket conditions result in harsh environments with demanding specifications. In addition to carbides, transition metal borides are also relevant materials for aerospace applications. In the case of zirconium diboride/silicon carbide composites, the oxidation resistance can be significantly enhanced with additions of lanthanum hexaboride to provide outstanding behavior for temperatures up to 2400°C.[9]

Solvothermal synthesis for carbide materials has been independently demonstrated by Hu,[10] Gu,[11] Ma,[6] and their coworkers. The technique is historically defined as synthesis in a nonaqueous solvent by the application of temperature and pressure and is done within the confines of an autoclave. This can result in heavily agglomerated powders due to the long processing times. Typical reactants include chloride compounds and alkali/alkaline earth metals where the metals reduce the chloride reactants and provide nascent seeds to form the desired materials, but other reactants, including elements, have been used to replace chloride compounds in some instances. Due to the use of an autoclave for the process, the reaction is not directly observable. Lack of direct observation has made the fundamental understanding of this technique difficult. For purposes of this study, solvothermal synthesis will be redefined to include the synthesis in a heated solvent, but without pressure. Specifically, the focus of this work is to demonstrate a unique solvothermal synthesis approach where synthesis is performed in transparent fused-quartz test tubes, rather than in an autoclave, and to demonstrate the viability of using the technique to make carbide and boride nanopowders such as tantalum carbide (TaC) and lanthanum hexaboride (LaB_6), while at the same time allowing direct observation of the reactions taking place during the process. This study confirms that the process is similar to a self-propagating high-temperature synthesis (SHS) process, obviating the need for an autoclave and long processing times, and producing fine and unagglomerated powders.

II. Experimental Procedure

Reactant mixing was performed in an argon-filled glove box. Three types of samples were prepared: (1) thermally ignited TaC, (2) thermally ignited LaB_6, and chemically ignited LaB_6. For the case of the thermally ignited TaC synthesis, 5.57 g of tantalum (V) chloride (99.8%, Alfa Aesar, Ward Hill, MA) and 0.56 g of carbon (Lampblack 101, Degussa, Parsippany, NJ) were mixed using a mortar and pestle to achieve homogeneity. The mixture was added to a fused-quartz test tube with 1.62 g of lithium (granular, 99%, Sigma-Aldrich, St. Louis, MO) and sealed with a rubber stopper. A 50-g batch, using 92.8 g of tantalum chloride, 9.3 g of carbon, and 27.0 g of lithium, was also performed in a 600 mL stainless-steel beaker to demonstrate scale-up. The stoichiometric equation for the process is

$$TaCl_5 + C + 5Li \rightarrow TaC + 5LiCl$$

The reactants were mixed to obtain the TaC product, but with additional carbon and lithium in amounts of 3× carbon stoichiometry and 3× lithium stoichiometry to guarantee that the process proceeded to the right.

A similar procedure was used for the synthesis of LaB_6. Lanthanum (III) chloride hydrate (99.9%, Alfa Aesar), boron (Sigma-Aldrich), and lithium granules were used. The amounts of lanthanum (III) chloride hydrate, boron, and lithium for the thermally ignited sample were 3.82, 2.02, and 0.97 g, respectively, which correspond to 2× boron stoichiometry and 3× lithium stoichiometry. For the chemically ignited sample, the reactant amounts were the same except for the amount of boron, which was reduced to 1.01 g, corresponding to 1× boron stoichiometry. The reaction stoichiometries were determined according to the following equation:

$$LaCl_3 + 6B + 3Li \rightarrow LaB_6 + 3LiCl$$

After mixing, the closed sample tubes were removed from the glove box for ignition underneath a chemical fume hood. Before ignition, the test tubes were hand rolled to achieve mixing of the lithium granules with the rest of the reactants. The thermally

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ignited samples were lowered into a tube furnace that was held at a temperature of 548 K, just above the self-ignition temperature of lithium, after loosening the rubber stoppers to allow for outgassing. Once ignition occurred, the sample was immediately removed from the furnace and allowed to air quench. For the chemically ignited sample, the rubber stopper was removed from the test tube. Water was added into the test tube until ignition occurred and the sample was allowed to air quench.

After air quenching, the samples consisted of solid reaction products surrounded by solidified lithium. The products were removed from the test tubes by adding water and forming lithium hydroxide, thus, freeing the reaction products. The products were then poured into a 250 mL beaker. Enough water was added to create a 100 mL suspension, which was magnetically stirred for 15 min, followed by ultrasonication for 15 min, and magnetic stirring for another 15 min. The suspension was centrifuged at 11 000 rpm for 5 min, decanted, and allowed to dry. The dried powders were lightly ground in a mortar and pestle to prepare them for washing procedures.

For washing, the TaC samples were magnetically stirred with 100 mL of concentrated nitric acid (15.8*N*) for 30 min, followed by ultrasonication for 30 min, magnetic stirring for another 15 min, and centrifuging at 11 000 rpm for 5 min. Two water rinses were performed by adding water to the centrifuge tubes and ultrasonicating for 5 min before centrifuging again. A final ethanol rinse was performed in a similar manner. After pouring of the supernatant, the sample was allowed to dry in air for 24 h before mixing with a mortar and pestle and storing for characterization. A modified washing procedure was used for the 50-g batch of TaC. Three water washes, using a procedure similar to the nitric acid wash, were performed before drying. The washing procedure for the LaB_6 samples is described elsewhere.[12]

The samples were characterized by powder X-ray diffraction on a Siemens D5000 instrument (Siemens, New York, NY) by scanning from 15° to 85° 2θ using a step size of 0.04° 2θ and a dwell time of 2 s after dispersing the powders onto a zero-background holder. Jade 8 software was used to estimate the average crystallite sizes using the Williamson–Hall technique. For TaC, the analysis software was also used to perform profile fitting and unit-cell refinement to determine the lattice parameter. The lattice parameter was used to determine the compound stoichiometry according to the equation $C/Ta = 6.398a - 17.516$.[13] Dynamic light scattering (DLS) on a Nanotrac™ ULTRA instrument (Microtrac, Inc., Montgomeryville, PA) was used to determine the particle size distribution of 0.01 g of powder dispersed in 25 mL of deionized water. The DLS samples were allowed to magnetically stir for 24 h and were ultrasonicated for 5 min before the measurements were taken. Each DLS measurement consisted of an average of five 30 s runs as is recommended by the instrument manufacturer and in conjunction with ASTM standard E2490-09. Scanning electron microscopy (SEM) was performed on a FEI™ Quanta 200F instrument (FEI Company, Hillsboro, OR) to observe particle morphology and supplement particle and crystallite size analyses. SEM samples were prepared by dispersing 0.01 g of powder into 25 mL of acetone, magnetically stirring for 1 h, ultrasonicating for 10 min, drop coating onto a silicon wafer, drying, and then carbon coating. Specific surface area (SSA) measurements were performed using a Tristar 3000 BET surface area analyzer (Micromeritics, Norcross, GA) after degassing in argon for 24 h at 423 K. Density measurements were performed by helium pycnometry using an AccuPyc II 1340 (Micromeritics, Norcross, GA) and was used with SSA measurements to calculate an average crystallite size according to $6000/(SSA \times \rho)$, where SSA is in m^2/g and ρ is the density in g/cm^3.

III. Results and Discussion

Direct observation of the solvothermal reaction suggests that it is a fast, self-sustaining reaction, requiring only ignition. Ignition can be achieved either thermally or chemically. To thermally ignite a sample, the self-ignition temperature of the lithium metal must be exceeded by the application of heat. Chemical ignition can be achieved by reacting lithium with water to produce lithium hydroxide and hydrogen. Either process results in a strong exothermic reaction that propagates the combustion wave. Once the system is ignited, molten lithium is formed, which serves as the solvent for the rest of the reaction. The temperatures achieved during ignition are well above the decomposition temperatures of the chlorides (~513 K for $TaCl_5$ and ~1273 K for $LaCl_3$ versus reaction temperatures as high as ~1653 K) and therefore the reaction to form TaC will proceed from the elements. The reactions to form TaC and LaB_6 from their elements are exothermic, having adiabatic flame temperatures of 2700 and 2800 K, respectively.[14] The energy from the reaction has the capability of driving the temperature of the solvent up to, but not exceeding, the vaporization temperature of the lithium until the reactants are depleted.

The higher the exothermicity of the reaction, the more likely this process will work for a given system. Faster heating and cooling rates can be achieved with this approach when compared with synthesis in a thick-walled autoclave vessel. This can inhibit grain growth during the process and prevent secondary reaction/crystallization events from occurring during a dwell or slow cool. Furthermore, the apparatus is simpler, costs much less, and can accommodate larger batch sizes more readily than an autoclave. To demonstrate the ease of scale-up a 50-g batch was prepared in a larger container.

Figure 1 illustrates the X-ray diffraction patterns and crystallite sizes for the three small-scale samples. Results show that single-phase TaC and LaB_6 samples were obtained and the average crystallite sizes were 25, 84, and 81 nm for the TaC, thermally ignited LaB_6, and chemically ignited LaB_6, respectively. Phase purity is obtained even in the case of the chemically ignited LaB_6. This is significant because this sample was exposed to oxygen from dissociation of water molecules as well as from the fact that the sample stopper was removed before the reaction, which means that synthesis is essentially performed in air. A minor amount of lanthanum borate was formed as a consequence of this, but was removed during the washing procedure. The source of ignition did not result in a difference in the average crystallite size of the LaB_6 powders, suggesting that the mechanism for the synthesis is the same regardless of how the reaction is started and further supports the idea that the reaction proceeds by self-propagating synthesis from the elements. The TaC compound stoichiometry, determined by lattice refinement, was 0.94. The 50-g batch was nearly phase-pure,

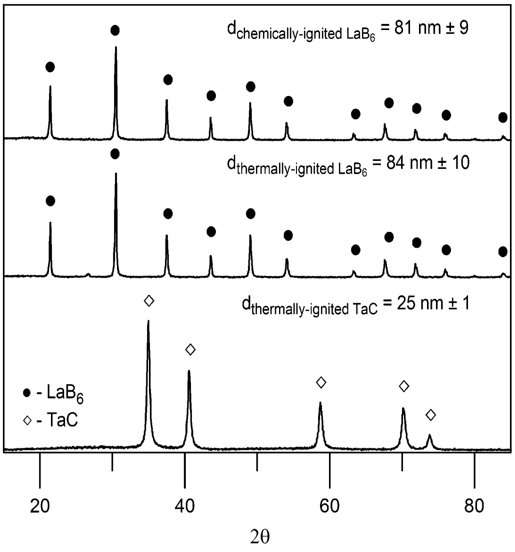

Fig. 1. X-ray diffraction patterns for the TaC and LaB_6 powders (*d* is the crystallite size).

containing a minor amount of tantalum metal. The decrease in phase purity is believed to be a result of mixing, where localized regions were carbon deficient, and indicates that process optimization is required. The crystallite size for the large batch-size was 25 nm and the compound stoichiometry was 0.94 indicating no change from the smaller batch size.

Figure 2 illustrates the DLS results for the three small-scale samples. TaC has an average particle size of 97 nm with an upper-tail distribution that falls off rapidly (the majority of particles are below 200 nm). Similarly, the majority of particles are below 200 nm for the large-scale batch, but the average particle size was 73 nm, indicating a small improvement in the particle size distribution. The average particle sizes of the two LaB_6 samples have a small bimodal peak in the upper-tail distribution. The second mode occurs around 500–600 nm and is more prevalent in the chemically ignited sample. A useful figure of merit to characterize the amount of hard agglomeration is a ratio between the average particle size and the average crystallite size. These figures of merit are 3.9, 1.6, and 2.0, for the TaC, thermally ignited LaB_6, and chemically ignited LaB_6, respectively, which suggests a very low state of agglomeration for the powders. The figure of merit for the 50-g TaC batch is 3.0, indicating that scaling of the process actually assists in achieving a lower level of agglomeration. Ma *et al.*[6] reported a crystallite size of 40 nm for their TaC powders from SEM imaging, noting that the powders are agglomerated due to their fine size (particle necking between particles is clearly evident from the images, indicating significant hard agglomeration. Gu *et al.*[11] report a crystallite size of 15–40 nm and slight agglomeration from TEM analysis. Neither analysis presents the true particle size to obtain a figure of merit. Thus, we propose from the visual data that both sets of powders are heavily agglomerated due to the long processing times and slow cooling from the use of an autoclave.

SEM for the three samples are shown in Fig. 3. TaC has a near-spherical morphology and it is clear from the images that the individual grains are very small, in agreement with the crystallite and particles size results. The LaB_6 samples appear to have a mixture of cubic and near-spherical morphologies. The cubic faces in LaB_6 correspond to the lower energy {100} planes of the cubic crystal structure in this material.[15] The cubic morphology arises during washing, but the presence of near-spherical morphologies indicates the mechanism is not complete under the current washing procedure.[12] Larger grains up to 1 μm are evident for the LaB_6 samples, but the majority of grains appear to be in submicrometers and below 300–400 nm, which agrees well with the upper limit of the left-hand side of the curve in the bimodal distribution of the DLS results. The larger grains are associated with the upper-tail peak of the right-hand side of the curve in the bimodal distribution, which is centered around 500–600 nm with the upper limit approaching 1 μm. Darker patches that blur portions of the LaB_6 images in certain locations are most likely the result of either residual boron or lithium that was not fully removed during the washing procedure and would require further optimization to eliminate. Distinct particle necking is not clearly observed and the images complement the crystallite size and particle size distributions obtained from XRD and DLS.

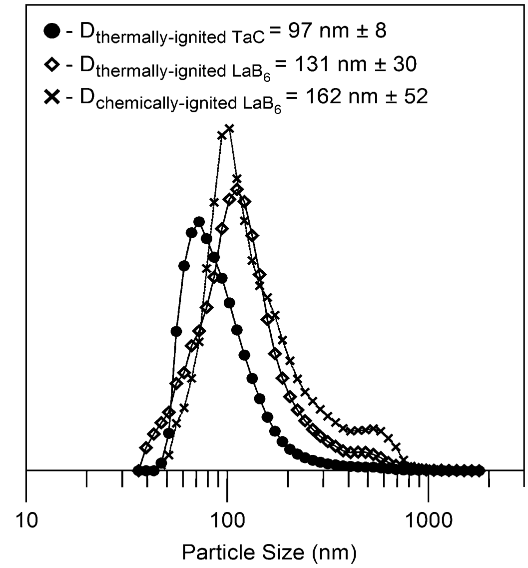

Fig. 2. Particle size distributions for the TaC and LaB_6 powders (D is the number-average particle size).

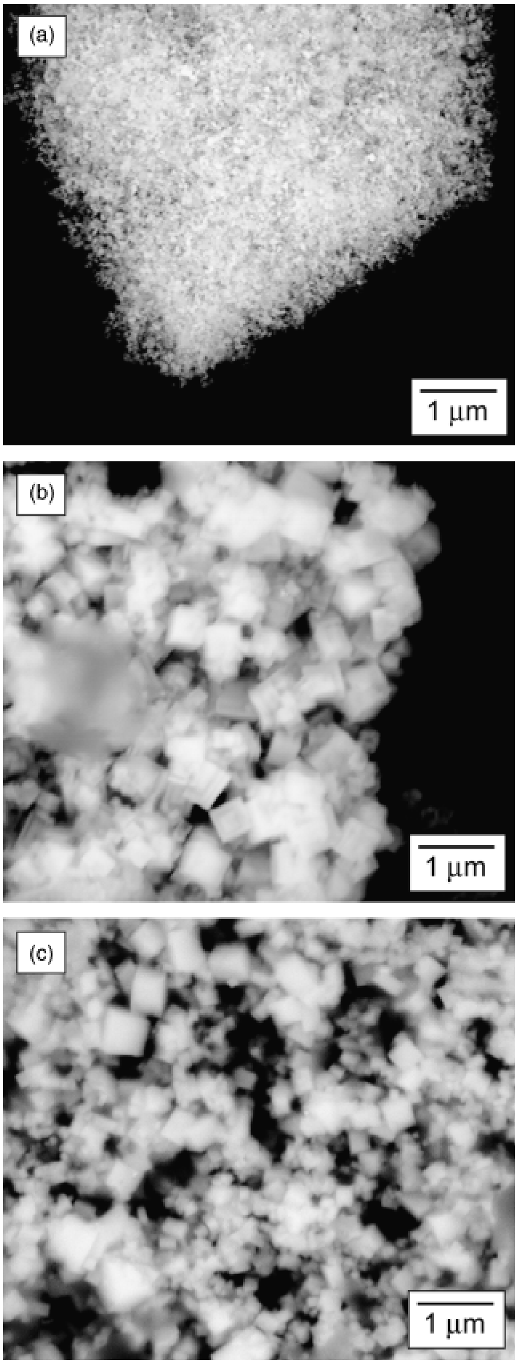

Fig. 3. Backscattered scanning electron micrographs of (a) TaC, (b) thermally ignited LaB_6, and (c) chemically ignited LaB_6.

The SSA for the small-scale and large-scale synthesis of the TaC samples were 39.9 and 19.5 m^2/g, respectively, while the measured densities were 7.6 and 9.7 g/cm^3, respectively, much lower than the theoretical density of 13.9 g/cm^3. The estimated average crystallite sizes using the surface area and density data were 20 and 32 nm, respectively, in good agreement with the value of 24 nm determined by X-ray diffraction. The SSA of the thermally ignited and chemically ignited LaB_6 samples were 6.6 and 7.0 m^2/g, respectively, while the density measurements were 2.9 and 3.0 g/cm^3, and also much lower than the theoretical density of 4.7 g/cm^3. The estimated average crystallite sizes from this data are 313 and 285 nm and are larger than the average crystallite sizes determined by X-ray diffraction (84 and 81 nm, respectively) as well as larger than the average particle sizes determined by DLS (131 and 162 nm, respectively), elucidating the difficulty of extracting particle or crystallite size information from SSA and density measurements. In the case of the LaB_6 density values, the large discrepancy may be a result of the low-density phase that was observed in Fig. 3. The discrepancies in the SSA, density, and average crystallite size data require further evaluation and will be presented in a future communication. Likewise, carbon and oxygen analysis cannot be performed until the state of the surfaces after the washing procedure is better understood.

IV. Conclusions

A new approach to solvothermal synthesis, without pressure and using both thermal and chemical ignition techniques, has been demonstrated. Very little external energy input is needed to carry out this process, suggesting a SHS mechanism. The process has been demonstrated for obtaining two compounds that are very exothermic by reaction from their elements, TaC and LaB_6. The characterization of the TaC and LaB_6 powders demonstrates that this technique is suitable for obtaining nanocrystalline nonoxide materials and is attributed to the fast reaction kinetics. Furthermore, the figures of merit that were obtained relating to particle dispersion indicate that the level of hard agglomeration of the samples is low. This unique approach will aid in the development of nanocrystalline ultra-high-temperature ceramics, and composites of them, and has the potential to satisfy other applications that require nanocrystalline and unagglomerated nonoxide powders. More understanding of the powder surfaces after using this synthesis method and analysis of oxygen and residual carbon are necessary.

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