A Convenient Inorganic Solvent Thermal Route to Nanocrystalline Tantalum Diboride

Jianhua Ma*[1] and Yihong Du[2]
[1]*College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou, Zhejiang 325027, P. R. China*
[2]*City College, Wenzhou University, Wenzhou, Zhejiang 325035, P. R. China*

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Nanocrystalline TaB_2 has been prepared via a simple inorganic solvent thermal route by the reaction of metallic magnesium powders with tantalum pentoxide and boric acid in an autoclave at 650 °C. X-ray powder diffraction patterns indicate that the product was hexagonal tantalum diboride. Scanning electron microscopy images show that it consisted of particles with an average size of about 40 nm. The product was also studied by BET and TGA.

Tantalum diboride (TaB_2), like borides of Ti, Zr, Cr, and other transition metals, is well known for its high melting point, outstanding hardness, high thermal conductivity, good chemical stability, extreme refractoriness, and good wear resistance.[1,2] Because of these attractive properties, TaB_2 has extensive applications in many fields, and it is a diboride with the same favorable characteristics as other refractory borides. For example, they have been used as high-temperature materials, surface-protection materials, and wear-resistant materials. Besides these properties, it is meaningful to synthesize nanocrystalline TaB_2 as the nanosized powders have other unique properties, such as the lower sintering temperature for bulk materials.

Traditionally, tantalum diboride has been synthesized by various methods. Crystalline TaB_2 can be deposited using chemical vapor deposition of $TaCl_5$ and B_2H_6 in the temperature range 773–1200 K.[3] The deposits obtained with B_2H_6 have an extremely small crystal size and contain amorphous boron when the deposition temperature is below approximately 873 K but are substoichiometric in boron above this temperature. TaB_2 single crystals can be grown by floating zone and the Al solution methods.[4] Crystals grown from Al solution are hexagonal needle-like TaB_2 single crystals 0.3–3 mm in size without a second phase. Tantalum diboride (TaB_2) can be deposited on a quartz substrate from a gas mixture of $TaCl_5$, BCl_3, H_2, and Ar at a temperature between 900 and 1300 °C.[5]

In this paper, nanocrystalline tantalum diboride has been synthesized via a simple inorganic solvent thermal route by the reaction of metallic magnesium powders with tantalum pentoxide and boric acid in an autoclave at 650 °C. In this route, a mixture of sodium chloride and magnesium chloride acts as inorganic solvent in the synthesis of nanocrystalline tantalum diboride. Tantalum pentoxide is the tantalum source and boric acid is the boron source.

In this research, a mixture of the same weight of anhydrous sodium chloride and anhydrous magnesium chloride powder was used as inorganic solvent in the reaction. All of the manipulations were carried out in a dry glove box with flowing nitrogen gas. In a typical experiment, 0.004 mol (about 1.768 g) of analytical grade tantalum pentoxide, 0.016 mol (about 0.989 g) of analytical grade boric acid and 0.070 mol (about 1.701 g) of metallic magnesium powders were put into a mortar, mixing with the above inorganic solvent (about 15 g). Then, the mixture was put into a stainless steel autoclave. After sealing under argon atmosphere, the autoclave was heated at 650 °C for 10 h, followed by cooling to room temperature in the furnace. The product obtained from the autoclave was washed several times with absolute ethanol, dilute aqueous HCl solution, and distilled water to remove impurities. Finally, the product was washed three times with absolute ethanol to remove water. The final product was vacuum-dried at 60 °C for 12 h. Black powders were obtained.

The obtained sample was analyzed by powder X-ray diffraction (XRD) on a Rigaku Dmax-γA X-ray diffractometer using Cu Kα radiation (wavelength $\lambda = 1.54178$ Å). The morphology of the sample was examined on a Hitachi 800 transmission electron microscope. The specific surface area of the sample was measured by the Brunauer–Emmett–Teller (BET) method (Model ASAP 2000, Micromeritics, Norcross, GA). The average diameter of the powders (specific surface diameter) was estimated using the specific surface area. Thermogravimetric analysis was performed on a thermal analyzer (Model: TA-50) below 1200 °C in air at a rate of 10 °C·min^{-1} to study its thermal stability and oxidation behavior.

Figure 1 shows the XRD pattern of the prepared sample. There are eight obvious diffraction peaks in this pattern. And all these diffraction peaks ((001), (100), (101), (002), (110), (111/102), (200), and (201)) at different d space can be indexed as hexagonal tantalum diboride. Refinement gives the cell constants, $a = 3.090$ Å and $c = 3.266$ Å, which are consistent with values reported in the literature ($a = 3.080$ Å, $c = 3.270$ Å) (JCPDS card no. 75-1047). No evidence of impurities such as metallic tantalum, tantalum oxides, or other tantalum borides, can be found in this XRD pattern.

The morphology of the TaB_2 sample was investigated by transmission electron microscopy. The TEM image of the TaB_2 is shown in Figure 2. In Figure 2a, the sample shows that it consists of particles with an average diameter of 40 nm. These particles exhibit slightly agglomerated particle morphology due to the ultrafine size of the sample. Figure 2b shows a selected area electron diffraction (ED) pattern of crystalline TaB_2. The ED pattern also confirms the crystallinity of TaB_2, in which

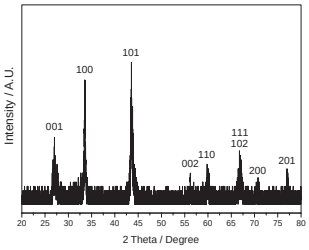

Figure 1. XRD pattern of the as-prepared sample.

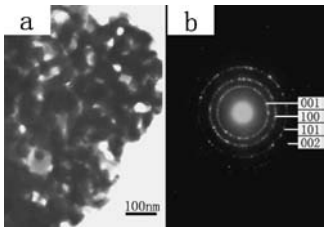

Figure 2. TEM and ED images of the as-prepared TaB_2.

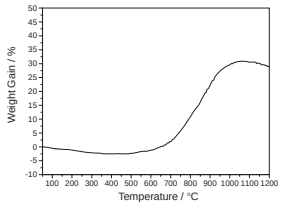

Figure 3. TGA curve heated under flowing air for the TaB_2 sample.

the diffraction ring diameters and intensities again correspond well to the hexagonal TaB_2. These rings can be indexed as (001), (100), (101), and (002).

We also studied the particle size of the sample by measuring the specific surface area of the powders with the Brunauer–Emmett–Teller (BET) method. In our result, the sample has a value of $10.4\,m^2/g$. So the average diameter of the powders (specific surface diameter) is estimated according to the equation ($d = 6/\rho S$, where $d =$ the estimated average diameter of the powders, $\rho =$ the density of the sample, $S =$ specific surface area of the powders) using the specific surface area on the assumption that the powder shape is spherical and that the density of the powder is $11.15\,g{\cdot}cm^{-3}$. The estimated average diameter of the powders is about 52 nm which is a little larger than the value observed from the TEM image, suggesting the agglomeration of primary particles.

The thermal stability of these nanosized TaB_2 powders was investigated in air under different temperatures. A typical TGA profile studied at temperatures below 1200 °C in flowing air is shown in Figure 3. From the TGA curve, we find that the weight gain of the sample has not changed significantly below 600 °C. A slight weight loss indicates that this possibly arises from evaporation of absorbed water on the surface of the sample. But the quantity of the adsorbed water is very small. The onset of the oxidation of the TaB_2 sample is found to begin at about 600 °C, which indicates that the sample is oxidized by oxygen to form tantalum oxide and boron oxide. As the temperature rises, the amount of the formed tantalum oxide and boron oxide becomes bigger, suggesting that the oxidation rate of the sample becomes faster. Finally, the sample can be oxidized thoroughly at 1050 °C. When the temperature exceeds 1050 °C, the weight gain becomes smaller and smaller. This is because B_2O_3 can be evaporated at this high temperature (about 1000 °C).[6] Thus, the evaporation of B_2O_3 results in the final weight gain being less than the theoretical one (43.44%). We know that TaB_2 is recognized as the potential candidate for high-temperature structural applications. But in this paper, the size of the prepared TaB_2 is very small. The surface energy of TaB_2 particle becomes higher in contrast with the bulk one. It can be oxidized by oxygen at relatively lower temperature. But it has good thermal stability below 600 °C. When 0.5 g of TaB_2 was added to the $1.0\,mol{\cdot}L^{-1}$ HCl or NaOH solution, its quality did not change even after 48 h, and the XRD pattern was as before. Therefore, the sample is stable either in acid medium or in alkali one.

In our experiments, as the temperature rose, the boric acid decomposed generating boron trioxide and water vapor. The water vapor reacts with metallic magnesium powders, forming H_2 gas and magnesium hydroxide which subsequently decomposes into magnesium oxide and water vapor. So the pressure in the autoclave may be very high owing to the formed H_2 gas. At the reaction temperature, tantalum pentoxide and boron trioxide can be reduced by metallic magnesium powders to produce nascent tantalum and nascent boron. Because of the higher activity of nascent tantalum (Ta*) and boron (B*), they can react with each other forming TaB_2. The high pressure in the autoclave would be helpful for reducing the reaction temperature and enhancing the reaction speed. Therefore, the possible total reaction process can be represented as the following,

$$Ta_2O_5 + 4H_3BO_3 + 17Mg = 2TaB_2 + 17MgO + 6H_2 \quad (1)$$

In our present inorganic solvent thermal route, the mixture of sodium chloride and magnesium chloride acts as a molten salt. As the temperature rises, this mixture becomes liquid (melting point: 425 °C). So it can serve as an inorganic solvent to control the reaction speed and the particle size. Since the diffusion coefficients in the liquid state are higher than those in the solid state, the molten salt can accelerate the kinetics by enhancing diffusion. Besides, since the formed H_2 gas may be very high in the autoclave at the reaction temperature, it is helpful to carry out this reaction in an autoclave. And the high pressure in the autoclave may help to reduce the reaction temperature. The molten salt can absorb the reaction enthalpy released from this process and maintain a relative low reaction temperature. And the product prepared in our route tended to be nanosized.

In summary, nanocrystalline TaB_2 has been prepared via a simple inorganic solvent thermal route in an autoclave at 650 °C. It consists of particles with an average size of 40 nm. The molten salt, the mixture of sodium chloride and magnesium chloride, acting as inorganic solvent during the reaction, may be important in the formation of nanocrystalline TaB_2 with a narrow particle size distribution. The product has good thermal stability and oxidation resistance below 600 °C.

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