Mechanochemical synthesis and characterization of TiB₂ and VB₂ nanopowders

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Abstract

A novel method for the synthesis of transition-metal boride nanopowder has been developed using a mechanochemical reaction between LiBH₄, LiH and transition-metal chloride (TiCl₃ and VCl₃) by high energy ball milling. This method successfully produces TiB₂ and VB₂ particles dispersed within a soluble LiCl matrix. Subsequent washing with distilled water, ethanol and acetone to remove the LiCl matrix phase yields TiB₂ and VB₂ nanopowders of 15–60 nm particle size. From the X-ray diffraction patterns and high resolution transmission electron microscopy image, it is found that each particle is polycrystalline consisting of 3–5 nm crystallites. Neither particle nor crystallite size are increased significantly after heating at 680 °C.

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1. Introduction

Transition-metal borides such as TiB₂, ZrB₂, CrB₂ and VB₂ are promising high-temperature materials due to their unique properties such as high melting point, high hardness, excellent wear resistance, high electrical conductivity, exceptional resistance to acids and molten metals [1–9]. Traditionally, these transition-metal borides were prepared by high-temperature methods [7,10] such as direct reactions between transition metals or transition-metal oxides with elemental boron above 1000 °C. Recently, several groups have synthesized TiB₂ nanopowders [11–14]. Bates et al. [11] employed a chemical reaction between NaBH₄ and TiCl₄ in a solvent to produce amorphous precursor powder which was subsequently heat treated between 900 and 1100 °C to obtain nanocrystalline TiB₂. Axelbaum et al. [12,13] synthesized nanometer-sized TiB₂ particles by a gas phase combustion reaction between sodium, TiCl₄ and BCl₃. Gu et al. [14] have also synthesized TiB₂ nanopowders via a solvothermal reaction between sodium, boron and TiCl₄ at 400 °C.

Among various synthetic routes to prepare nanostructured materials, mechanochemical synthesis by high energy ball milling has been recognized as an effective and simple way of producing nanocrystalline, amorphous and other non-equilibrium nanostructured powders, mainly through a solid-state reaction [15]. Chloride mediated mechanochemical reactions in particular have been very effective in producing metallic and inorganic nanoparticle [16]. In this process, displacement reactions during ball milling produce composite structures of nanoparticles embedded in chloride matrices. The nanoparticles are subsequently recovered by removing the chlorides through simple washing.

The purpose of this study is to develop a novel method for synthesizing transition-metal boride nanopowders at room
temperature. For this purpose, the following mechanochemical reactions have been studied to synthesize TiB2 and VB2 nanopowders.

$$\text{TiCl}_3 + 2\text{LiBH}_4 + \text{LiH} \rightarrow \text{TiB}_2 + 3\text{LiCl} + 4.5\text{H}_2 \uparrow \quad (1)$$

$$\text{VCl}_3 + 2\text{LiBH}_4 + \text{LiH} \rightarrow \text{VB}_2 + 3\text{LiCl} + 4.5\text{H}_2 \uparrow \quad (2)$$

The microstructural features of the synthesized powders have been characterized. The phase compositions as well as the nanostructures of the synthesized powders have also been characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM) with electron energy loss spectroscopy (EELS).

2. Experimental procedure

The raw materials used in this study were TiCl3 (99%), AlCl3 (99.9%), LiBH4 (95%) and LiH (95%), all from Sigma-Aldrich. Mixtures of the raw materials with molar ratios corresponding to reactions (1) and (2) were prepared. As a process control agent, excess LiCl (Fluka, 99%) was added to each mixture in order to prevent an increase in temperature during milling. 3 g of each mixture was charged into a tool steel bowl of 150 ml internal volume with an O-ring seal under an Ar atmosphere in a glove box. The milling media were WC−Co balls, 9 mm in diameter, and the ball-to-powder weight ratio (BPR) was approximately 30:1. High energy ball milling was carried out for up to 4 h continuously using a planetary ball mill (Retsch PM 200) with a rotation speed of 500 rpm.

To remove the LiCl produced as a by-product according to reactions (1) and (2), the as-milled powders were rinsed several times in distilled water, ethanol and acetone. Following rinsing, the powders were recovered from slurries by means of filtration with cellulose acetate membrane filters (average pore size of 0.1 μm). The recovered powders were dried for 1 day in air at ambient temperature.

The phase compositions of the synthesized powders were analyzed by XRD using Cu Kα radiation (Bruker D8 Advance). Their average crystallite size was estimated using the Scherrer formula [17]. The particle morphology and size distribution were analyzed by a TEM (FEI TECNAI G2 F20) operating at 200 kV with an in-situ heating holder (Gatan 628.Ta) at elevated temperature as well as at room temperature.

The microstructural features of the synthesized powders were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM) with electron energy loss spectroscopy (EELS).

3. Results and Discussion

Table 1 summarizes thermodynamic functions concerning reactions (1) and (2) calculated by Thermo-Calc [18]. Because the Gibbs energy change of these reactions, $\Delta G$, is negative at ambient temperature, these displacement reactions should be thermodynamically possible.

The large negative enthalpy change of these reactions implies that quite a large amount of heat would be released during milling and thus the vial temperature would increase significantly. Because a significant increase in temperature might induce the particle growth of the reaction products, it is important to keep temperature as low as possible during the mechanochemical process in order to obtain nanoparticles. The addition of a diluent phase that does not participate in the reaction such as NaCl has been regarded as an effective way for preventing a significant increase in temperature [19,20]. For this purpose, LiCl was added to the raw materials so that the volume fraction of LiCl in the reaction products would be about 90%.

The XRD patterns of as-milled powders after milling for 4 h indicate that LiCl is present as a major phase, as shown in Fig. 1(a) and (b). Borides can also be identified, although their peak intensities are relatively weak due to the large volume fraction of LiCl. It is not easy to judge if reactions (1) and (2) are complete after milling from these results alone. Fig. 1(c) and (d) shows XRD patterns of the rinsed powders without LiCl. The broad peaks of TiB2 ($a=3.038$ Å, $c=3.2392$ Å, ICSD # 55001) and VB2 ($a=2.99761$ Å, $c=3.0562$ Å, ICSD # 14414) are clearly observed. Since other phases are not seen except the boride phases, it seems that reactions (1) and (2) are almost complete. Actually, there were very weak peaks of LiOH·H2O in XRD patterns following rinsing in distilled water (not included here). The presence of LiOH·H2O found in the water-rinsed product is due to the presence of ~6 vol.% LiOH in the as-purchased LiH [21]. However, they disappear after rinsing in ethanol and acetone. Both the crystallite sizes of TiB2 and VB2 estimated by the Scherrer formula taking into account the instrumental broadening are similar (about 4 nm).

![Fig. 1. XRD patterns of as-milled by mechanochemical processing; (a) reaction (1), (b) reaction (2) and rinsed powders; (c) TiB2 (d) VB2.](image-url)
impingement of boride particles effectively during milling as hard agglomerates are rarely observed. TEM analyses of individual particles reveal that their primary particle size varies in the range between 15 and 60 nm. A significant difference in the primary particle size and the shape between TiB$_2$ and VB$_2$ was not observed. The primary particles seem to be polycrystalline since the crystallite sizes from XRD are much smaller than the primary particle sizes from TEM analysis.

High resolution TEM images of TiB$_2$ at room temperature and in-situ heated at 680 °C for an hour are presented in Fig. 3(a) and (b), respectively. As-synthesized TiB$_2$ particles consist of 3–5 nm nanocrystallites (Fig. 3(a)), which is in good agreement with the size from XRD. The crystallite size distribution is quite narrow, although it is generally known that the control of the size distribution is rather difficult using mechanochemical reactions. Fig. 3(b) shows that the crystallite size increases up to 5–10 nm after heating at 680 °C. However, the growth is not significant even at elevated temperatures compared to other nanocrystalline metals [22]. The strong covalent character of the bonding of TiB$_2$ might have retarded the lattice diffusion in TiB$_2$ and accordingly suppressed the grain growth effectively. A significant increase in particle size was not observed after heating.

Since transition-metal borides are usually produced by high-temperature reactions between transition metal and boron above 1000 °C [7,10], it is very difficult to obtain nanosized powders. Some transition-metal chloride mediated chemical reactions between 400 and 1000 °C have recently been attempted to prepare TiB$_2$ nanopowders [11–14]. However, these reactions usually include toxic solvent or need high-temperature reactors. The mechanochemical reactions at room temperature employed in this study provide a simple cost-effective way for producing TiB$_2$ and VB$_2$ nanopowders. Besides TiB$_2$ and VB$_2$, this mechanochemical method can be applicable to the preparation of other transition-metal boride nanopowders.

4. Conclusions

A mechanochemical reaction between LiBH$_4$, LiH and transition-metal chloride has been exploited to synthesize transition-metal boride nanopowder. LiCl that does not take part in the reactions have also been introduced to prevent impingement of product particles during milling and a large increase in temperature due to exothermal reactions. TiB$_2$ and VB$_2$ nanopowders have been successfully prepared by this method. TEM analysis reveals that the individual particle size of the synthesized powders lies between 15 and 60 nm. High resolution TEM images show that each particle consists of 3–5 nm nanocrystallites, which is consistent with XRD analysis. After TEM in-situ heating at 680 °C, a slight increase to 5–10 nm in
crystallite size is observed without a significant change in the particle size.

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References