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Properties of titanium and zirconium diborides obtained by self-propagated high-temperature synthesis

D.D. Radev, M. Marinov

Institute of General and Inorganic Chemistry, Sofia 1113, Bulgaria

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Abstract

Self-propagated high-temperature synthesis (SHS) of TiB_2 and ZrB_2 is carried out in a steel reactor under Ar. The SHS is initiated by a current pulse of 60 A and 40 V. It is shown that the interparticle contacts play a significant role in the successful proceeding of the synthesis reactions. The products obtained have similar morphology. X-ray data show the presence of well-crystallized phases of TiB_2 and ZrB_2. Chemical analyses indicate a high boron content in the products. The properties of TiB_2 powders synthesized from the same initial titanium and boron reagents by both SHS and mechanochemical synthesis are compared.

Keywords: Self-propagated high-temperature synthesis; Titanium diboride; Zirconium diboride

1. Introduction

The diborides of titanium and zirconium possess properties which put them among the leading materials suitable for high performance application [1–3]. The peculiarities of the synthesis methods used determine a number of physical, chemical and technological properties of the materials obtained. Recently developed non-conventional synthesis methods of refractory and superhard compounds provide some valuable properties of the resulting products. Among these methods, self-propagated high-temperature synthesis (SHS) and mechanochemical synthesis have shown considerable technological and economic advantages [4–6]. The properties of titanium and zirconium compounds obtained by SHS are described in Refs. [7–9]. In a previous article [10], the properties of mechanochemically synthesized TiB_2 by explosion kinetics has been studied. It is of interest as an experimental proof if, after initiation, the reactions of explosive mechanochemical syntheses proceed by an SHS mechanism. The properties of TiB_2 powders synthesized from the same initial titanium and boron reagents by both SHS and mechanochemical methods are compared in the present work. The conditions of SHS of TiB_2 and ZrB_2 as well as some physical and chemical properties of the products obtained are also described.

2. Experimental details

Powdery amorphous boron (mean particle size below 10 μm, purity 98%) (Merck), titanium (purity 99%) and zirconium (purity 97%) (Fluka) were used as reagents for SHS of TiB_2 and ZrB_2. Stoichiometric amounts of metal and boron powders were utilized to obtain TiB_2 and ZrB_2. The powdery mixtures were homogenized in a planetary mill. To prevent contamination from materials of milling accessories, polyamide bowls and steel balls covered with Teflon were used. Cylindrical pellets measuring 25×11(diam.) mm^2, which contained the reagents, were produced by pressing in a steel die. Pressures were varied from 100 to 900 MPa. SHS of TiB_2 and ZrB_2 was carried out in a stainless steel reactor under a protective atmosphere of Ar. The pellets were placed between two graphite electrodes in the reactor (Fig. 1). The synthesis reactions were initiated by a current pulse of 60 A and 40 V. XRD patterns were taken under Cu Kα radiation using a Philips counter diffractometer. Powdery TiB_2 and ZrB_2 were utilized as standards (Johnson Matthey, Alfa Products). They contained 68.8 wt.% Ti and 31.1 wt.% total B as well as 80.7 wt.% Zr and 19.1 wt.% total B respectively. No traces of free B were discovered. The morphology and sizes of the initial metal particles and of the products were studied by SEM. Chemical analysis methods

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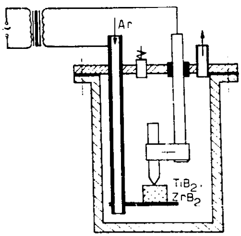

Fig. 1. Reactor for SHS.

were used to establish the amounts of total boron and the presence of free metals (Ti, Zr) in the products. The total boron content was determined by converting the boron into orthoboric acid (H_3BO_3), complexing by mannitol ($HOCH_2(CHOH)_4CH_2OH$) and titration by sodium hydroxide (NaOH). The contents of free Ti and Zr were determined as TiO_2 and ZrO_2 after dissolving TiB_2 and ZrB_2 in mixtures of H_2SO_4 and HNO_3.

3. Results and discussion

An electron micrograph of the initial Zr powder is shown in Fig. 2. The particles have an isometric shape and fine sizes, the average particle size being 1–5 μm. The initial Ti particles are studied by SEM [10]. They are characterized by a clearly expressed lengthened shape and a rough dispersivity. The lengths of some particles often exceed 100 μm.

The SHS reactions have been started by a single current pulse. After turning off the current source the synthesis reaction flows with a peculiar hissing sound. The adiabatic temperatures during SHS of TiB_2 and ZrB_2 and the melting points of the products are almost the same [11]. For systems like these, syntheses under conventional combustion conditions are possible.

The X-ray diffraction profiles of the products and the metal borides used as standards are shown in Fig. 3 and Fig. 4. The X-ray spectra of the products (Fig. 3(a), Fig. 4(a)) reveal the presence of well-crystallized phases of TiB_2 and ZrB_2. The relatively lower intensity of the peaks of TiB_2 (Fig. 3(a)) is an indirect proof for the smaller sizes of primary particles of the products obtained by SHS. Phase analyses have shown traces of Ti and ZrO_2 in the products.

SEM of TiB_2 obtained by SHS is shown in Fig. 5. The particles are characterized by a comparatively narrow size distribution. Owing to the high temperature of SHS, most of them form aggregates. Their mean particle size is 40–60 μm. The same morphology is inherent in the SHS ZrB_2 particles. Their mean size is smaller (5–15 μm) and they show the same tendency to form aggregates (Fig. 6). The presence of many edges with small curvature radii is a premise for the

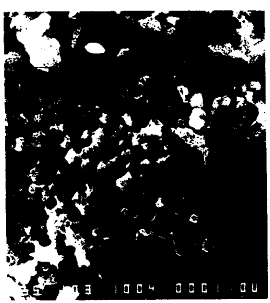

Fig. 2. Scanning electron micrograph of initial Zr particles, ×10 000.

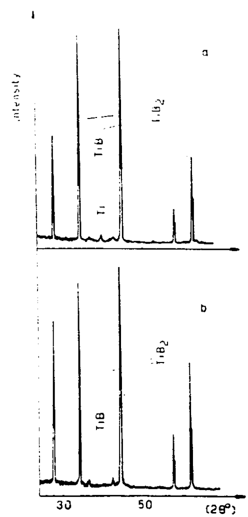

Fig. 3. XRD patterns of TiB_2: (a) product, (b) standard.

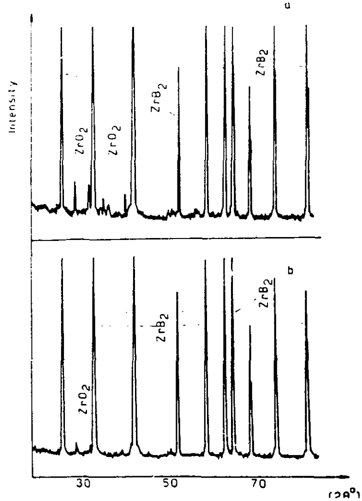

Fig. 4. XRD patterns of ZrB_2: (a) product, (b) standard.

high abrasive ability of hard material particles obtained by SHS.

Chemical analysis has shown the presence of 2.12 wt.% free Ti in TiB_2. The amount of total boron is 29.83 wt.%. The content of total boron in ZrB_2 is 18.94 wt.%. Free Zr is not observed. It is found that

Fig. 5. Scanning electron micrograph of TiB_2 particles obtained by SHS, ×780.

Fig. 6. Scanning electron micrograph of ZrB_2 particles obtained by SHS, ×3200.

the content of ZrO_2 in the reagent and in the product is the same. The presence of ZrO_2 traces registered by XRD is due to the high chemical activity of fine initial Zr particles and their partial oxidation before the synthesis reaction. Because of the high adiabatic temperatures during SHS, part of the boron evaporates. The content of combined boron may be enhanced by adding a 1–2 wt.% boron excess to the reaction mixture.

The coarse dispersivity of the initial Ti powder reduces the contact area among metal and boron particles in the pellets before the synthesis. SHS of TiB_2 is carried out successfully after densification of the reagents with pressure exceeding 700 MPa. Even then some amount of unreacted Ti is observed in the product. The high dispersivity of the initial Zr powder facilitates SHS of ZrB_2. The synthesis reaction proceeds successfully after pressing the pellets containing reagents at 200 MPa. It is evident that the properties of the reagents are of great significance for SHS and determine, to a large extent, the physical, chemical and technological characteristics of the compounds synthesized. The high values of the adiabatic temperatures during combustion is another factor determining the properties of TiB_2 and ZrB_2 obtained by SHS.

The use of powdery metal reagents (Ti and Zr) quite different in size and morphology allows elucidation of the influence of their physical properties on the characteristics of the products obtained. In contrast, thermodynamic data on the Ti–2B and Zr–2B interactions and peculiarities of the synthesis process determine some general properties typical of the SHS. Formation of aggregates and their 'moon' surface are the reasons for the high grinding ability of the products. A similar morphology is peculiar to other refractory compounds obtained by SHS. It is established that the SHS method ensures better abrasive properties of the superhard compounds than do other synthesis methods [12]. A high chemical purity of products is another advantage of the SHS. The only source of impurities in the products may be the reagents used. The production of cheap pure boron or the use of boron-containing reagents are preconditions for industrial applications of the SHS.

Comparison of properties of titanium diboride obtained by SHS and those produced mechanochemically from the same reagents (Ti+2B) reveals significant differences. Some physical and chemical properties of mechanochemically synthesized TiB_2 are described in Ref. [10]. One can suggest that after initiation the explosive mechanochemical synthesis flows by an SHS mechanism. It is hard to believe that one synthesis mechanism has led to such different products. The mechanochemical synthesis takes place under the effect of a series of factors: local high temperatures and pressures, formation of active surface and accelerated diffusion processes due to the presence of structural defects. The properties of TiB_2 particles obtained mechanochemically by explosion kinetics are similar to those of TiB_2 synthesized by alloying after 80 h mechanical treatment under an inert Ar atmosphere [13].

Simultaneously with new methods, traditional synthesis methods are also being developed to obtain TiB_2 with a fine particle size and a high sinterability [14].

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