

COMPARATIVE STUDIES ON THE HIGH-TEMPERATURE
AND MECHANOCHEMICAL SYNTHESIS OF TITANIUM
DIBORIDE

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Abstract

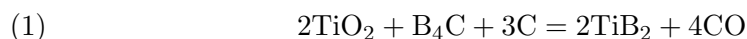
The present work shows two approaches to obtain titanium diboride (TiB_2). The traditional high-temperature carbothermal reduction synthesis is performed using boron carbide (B_4C) as boron source. The direct mechanochemical synthesis is accomplished in a planetary mill using boron and titanium powders as reagents. The synthesis reaction proceeds by explosive mechanism after 90 min of intense mechanical treatment. Here using SEM, XRD and analytical chemical methods, we examine the morphological properties of the products obtained by both synthesis methods. These properties are responsible for the sinterability of the product and determine the possibility to produce dense bodies by the methods of the powder metallurgy.

Key words: titanium diboride, mechanochemistry, high-temperature synthesis

Introduction. The TiB_2 is a typical representative of the transition metal-like refractory borides from IV–VI group. It possesses high melting point of 3200°C , high hardness values of 30.0 GPa, an excellent resistance to oxidation at elevated temperatures and pronounced stability in contact with metal melts and slags of Al, Cu, Mg, Zn, Cd, Fe, Pb [1–3]. Evaporators, crucibles, nozzles, cutting tools and wear resistant coatings are among the articles manufactured from titanium diboride using the specific methods of the powder metallurgy [4, 5]. An important application is the use of TiB_2 cathodes in the electrochemical reduction of alumina to aluminum metal [6]. The TiB_2 is one of the promising armour application ceramics for both personnel and vehicle protection offering most of the

required properties as high hardness, compressive strength, elastic modulus and ballistic efficiency [7]. Recently, TiB₂ particles have been used as a Pt support material in proton-exchange membrane (PEM) fuel cells [8]. The synthesis methods are decisive for the set of chemical, morphological and technological properties of titanium diboride powders. The traditional high-temperature synthesis methods have some disadvantages leading to inconstancy of the product composition due to the boron evaporation in the course of the high-temperature treatment, degradation of the furnace constructive materials and contamination of the product, high energy losses, etc. Here, using SEM, TEM, XRD and methods of analytical chemistry, we show the differences in morphology of TiB₂ powders obtained by the traditional high-temperature, so-called “boron carbide” synthesis and by direct mechanochemical synthesis.

Experimental. The classical synthesis of TiB₂ was carried out in a high-temperature furnace *Degussa* subjected with a graphite resistive heater at 1800 °C under protective Ar atmosphere according to reaction (1):



A stoichiometric amount of the reagents was blended in a polyethylene container using planetary mill *Fritsch*. The over stoichiometric amount of B in the form of 5 wt.% B₂O₃ has been added to the reagents to compensate for the boron losses as a result of evaporation during the high-temperature synthesis. The temperature change was registered by an optical pyrometer and the rate of its rising was 10°·min⁻¹. A stoichiometric amount of amorphous boron (produced by *Aldrich*, 97.0% purity) and titanium powder (produced by *Fluka*, 99.0% purity) were used as reagents in mechanochemical synthesis of TiB₂. The SEM images of Ti and B powders are shown in Figs 1, 2. Boron particles have mean size of 1–5 μm. The SEM pictures of titanium reveal aggregated interconnected particles with smooth surfaces and mean size of 30–50 μm. The mechanical treatment of reagents was carried out in a planetary mill using stainless steel reactors and milling balls with diameter of 10 mm. This type of high-energetic milling apparatuses is very often used in mechanochemistry. Its high effectiveness is based on the specific construction providing antiparallel movement vectors of supporting disk and milling containers, a complicated trajectory of milling bodies and the high values of accelerations achieved in the course of the mechanical treatment of the reagents.

Wet chemical analytical methods were used to determine the boron content in the products. Boron has been determined by complexing with mannitol C₆H₈(OH)₆ and titration with sodium hydroxide (NaOH) in the presence of indicators: 0.2% solution of methyl red (CH₃)₂NC₆H₄N=NC₆H₄(COOH) and 1% solution of phenolphthalein (C₂₀H₁₄O₄) till obtaining “onion-yellow” colour.

Results and discussion. Figure 3 reveals SEM image of TiB₂ particles obtained by the boron-carbide synthesis according to Rect. 1. The picture shows

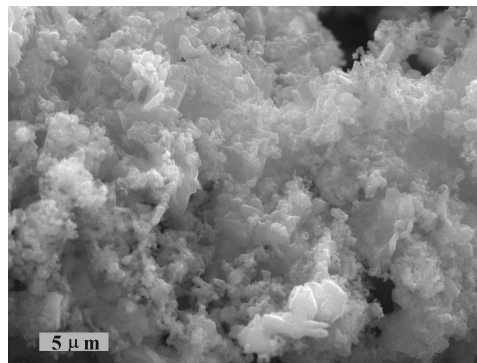
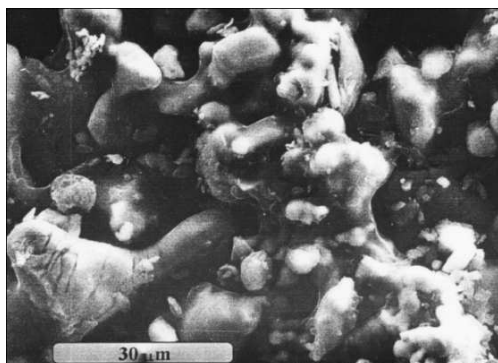


Fig. 1. SEM of the initial Ti particles, $\times 1200$

Fig. 2. SEM of the initial B particles, $\times 4000$

particles with smooth surfaces and means size of 5–10 mkm. The size distribution of TiB_2 powder is uneven and a fraction of particles with sizes of about 1 mkm is also present. Formation of aggregates bigger than 20 mkm, resulting from the high synthesis temperature, is also registered. Similar powders of TiB_2 need additional process of milling to obtain product with smaller particle size and hence higher sinterability, suitable to produce articles by the methods of powder metallurgy. The milling process would introduce some contaminants from the milling accessories due to the high hardness and abrasion ability of TiB_2 particles. Additional tedious process of acid cleaning is necessary to remove these contaminations. The presence of strong covalent bonds in the structure of TiB_2 determines its excellent mechanical properties and high chemical stability. At the same time, these bonds impede the mass transfer during densification of TiB_2 by the specific techniques like pressureless and activated sintering, hot pressing, hot isostatic pressing, etc. The methods of powder metallurgy are the only way to obtain dense bodies from titanium diboride powders and hereby to utilize in practice the properties of that valuable material. The results of XRD analysis shows that the product consists only of TiB_2 phase. The analytical chemical methods reveal the presence of 29.9 wt.% combined boron in the product. This amount corresponds to the composition $\text{Ti}_{1.04}\text{B}_{1.96}$, which is the lowest limit of the homogeneity area of B in the TiB_2 [9]. Being a compound with a large area of homogeneity, it is always a problem to obtain TiB_2 with a stoichiometric amount combined B (31.1 wt.%), using high-temperature synthesis methods due to the boron evaporation. Therefore, it is necessary to introduce some amount of B_2O_3 over the stoichiometry into the reagents. Granulation of the reagents is another technological trick leading to better contact between particles of the reagents and to improved gas penetrability during the synthesis, thus providing conditions for obtaining a high quality product with a random distribution of the boron content.

The mechanochemical synthesis of TiB_2 proceeds in a planetary ball mill by an explosive mechanism after 90 min of intense mechanical treatment. Due to the

high enthalpy of the TiB_2 formation, after the period of mechanical activation, the process of self-propagating combustion synthesis takes place. Milling-induced combustion was first observed and described by TSCHAKAROV et al. [10] during the mechanochemical synthesis of metal chalcogenides from a mixture of elemental powders. Subsequently, a number of similar reactions were reported to occur during chemical reduction of oxides with reactive metals under the influence of intense mechanical treatment. The appearance of new active surfaces, increased contact between particles of reagents, presence of points of local heats and areas of increased pressure are among the reasons for initiation of the combustion synthesis. The morphological change of Ti particles in the process of the mechanochemical synthesis of TiB_2 is studied in [11], where before the reaction of combustion, formation of globular aggregates containing reagents has been registered. Similar behaviour of reagents during their mechanical treatment has also been observed during mechanical synthesis of Ni-Cr and Ti-Ni alloys [12, 13].

Figure 4 shows SEM image of randomly distributed in size TiB_2 particles obtained by the explosive mechanochemical synthesis. The product has mean particle size of 1–5 mkm, which is a precondition for high contact area between particles and their higher sinterability in the process of high temperature densification. The chemical analysis shows the presence of 29.2 wt.% combined boron in the composition of the TiB_2 . This amount corresponds to the compound with a stoichiometry $\text{Ti}_{1.06}\text{B}_{1.94}$. Probably the product also contains, except the main phase of TiB_2 , traces of TiB , which has not been detected by the XRD analysis. The direct mechanochemical syntheses of products similar to these of titanium and zirconium borides with high values of enthalpy of formation ($-323 \text{ kJ}\cdot\text{mol}^{-1}$) are very dangerous, and special safety measures should be undertaken during experimental process. Opening the reactors prior to the synthesis is extremely dangerous as the penetration of fresh air could cause strong explosion

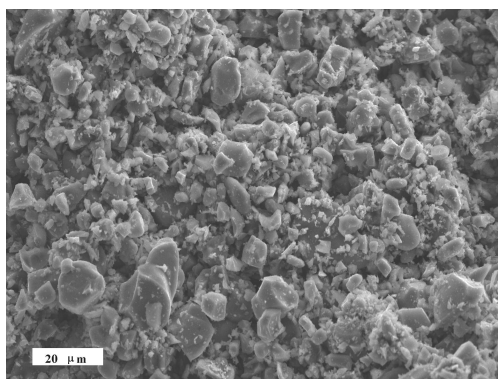


Fig. 3. SEM of TiB_2 obtained by high-temperature synthesis, $\times 1000$

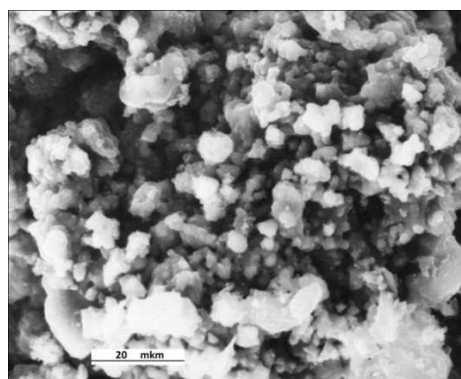


Fig. 4. SEM of TiB_2 obtained by mechanochemical synthesis, $\times 2000$

with participation of the milling bodies. Manipulation, exploration and storage of mechanically activated metal powders are also very dangerous due to the pyrophoric properties of similar metal powders and the high burning temperatures of the latter. Luckily, the methods of mechanochemistry offer synthesis ways more appropriate of practical viewpoint. The method of mechanically activated thermal synthesis allows synthesis at significantly lower temperatures, which is a precondition for obtaining products with fine grain sizes. The potential of mechanically activated processes for materials synthesis was first demonstrated by BENJAMIN [14] who devised “mechanically alloying” for oxide-dispersed nickel- and iron-based super alloys. This marked a new era of successfully employing mechanically activated process in material synthesis, and it was followed by the extension and application of this novel technique to a wide range of structural and functional materials, including intermetallics and metal matrix composites, magnetic materials, semiconductors, and more recently nanocrystalline ceramic materials. There exists a variety of techniques based on the intense milling of reagents in high-energy apparatuses like planetary type mills and attritors, for example mechanical alloying, mechanical milling, mechanical disordering, mechanically assisted thermal or self-propagating synthesis, etc. A detailed study on the mechanism of mechanical alloying of nanocrystalline TiB_2 powders has been done and step by step formation of the end product has been shown [15]. Pure TiB_2 has been obtained by the method of mechanical alloying after 280 h of mechanical treatment of Ti and B mixture in an Ar protective atmosphere [16]. Due to the high energy losses and low productivity similar results contain only theoretical meaning.

Conclusion. Here we demonstrated the peculiarities of two synthesis methods and the properties of TiB_2 obtained by the classical carbothermal and direct mechanical synthesis. Every method determines a set of specific morphological properties of the powdery products which are decisive for their technological characteristics, e.g. fluidity, pres- and sinterability, etc. and which are responsible for the behaviour of powders during production of the end bodies by the technology of the powder metallurgy. The technological advantages of the mechanochemical synthesis are obvious when compared with the traditional synthesis methods. High-temperature processes and the corresponding equipments, processes of homogenization and grinding of powders typical of the classical high-temperature syntheses are avoided. The product obtained is finely dispersed, which is a precondition for high sinterability of TiB_2 powder. At the same time, except the above-mentioned disadvantages of the direct synthesis by explosive mechanism, the pure elements used as reagents are more expensive compared with the starting materials used in the classical high-temperature synthesis methods. Investigations in the field of the mechanically-assisted thermal synthesis are probably the successful way for arrangement of a technology combining the advantages of the synthesis methods described here.

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