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Properties of TiB_2 powders obtained in a mechanochemical way

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Abstract

Mechanochemical synthesis of TiB_2 powders was achieved in a planetary mill. The product obtained, whose physical and chemical properties were investigated, was a single-phase powder, possessing submicronic particle size. Microstrain of the lattice was registered by X-ray studies. The amount of combined boron was comparatively high. These properties were preconditioned for high activity of the substances obtained, especially during sintering. A mechanism for the synthesis is proposed.

1. Introduction

Titanium diboride, which belongs to the refractory transition metal borides, has high hardness (34.8 GPa), good toughness, a high melting point (2900 °C) and a good corrosion resistance. It has stable thermal shock behaviour, conducts heat well and is resistant to oxidation [1–4]. On this basis, titanium diboride and the materials obtained from it was appropriate for high performance application. The modern industrial methods of TiB_2 powder synthesis and the product properties are described in ref. 3. In the past, non-conventional methods of preparing superhard refractory materials have been developed including self-propagating high-temperature synthesis, plasmochemical synthesis and mechanochemical synthesis [5–8]. Each of these methods ensures a specific combination of technological advantages and unique properties of the products.

The present paper describes the conditions of mechanochemical synthesis of TiB_2 powders and reports the results obtained on the physical and chemical properties of the product.

2. Experimental details

Titanium powder (99%) and amorphous boron (98%) from Merck were used for the synthesis. Titanium had a mean particle size of 40–63 μm, while the particle size of boron was below 10 μm. The reaction was carried out in a Pulverisette-5 centrifugal planetary mill, developed by Professor Rumpf. The power of the apparatus was 0.55 kW. A stainless steel bowl and milling balls were used. The reactor volume was 80 ml. The milling bodies, spherical in shape, had diameter of 10 mm, weight 3.5 g each, and total volume 50 ml. The rotation rate was 270 rev min^{-1}. The functioning of the apparatus is demonstrated by the vectors of forces affecting the milling bodies (Fig. 1)*. The high acceleration values (12 g) achieved in this kind of apparatus and the complicated paths of the milling bodies determine the efficiency during mechanochemical synthesis.

The synthesis proceeded under air. The shape and size of the particles of the initial Ti powder and the product were established by electron microscope analysis [9]. The specific surface area of the synthesized powder was determined by the Brunauer–Emmett–Teller method (N_2 at −196 °C). The phases presented in the product were determined by X-ray analysis under CoKα radiation. Powdery TiB_2 (Ti–68.8 wt.%, combined with B–31.0 wt.%) was utilized as a standard**. The spectra

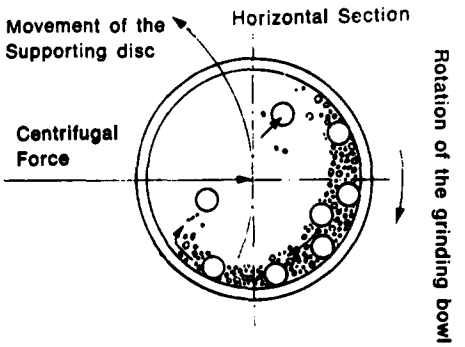

Fig. 1. Scheme of vectors of forces during milling.

*According to the range of application (Fritsch GMBH).
**Production of the Johnson Matthey Alfa Products.

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of the standard and mechanochemically synthesized product were compared.

3. Results and discussion

The mechanochemical interaction proceeded according to the reaction:

$$2B + Ti = TiB_2 \quad (1)$$

between reagents taken in a stoichiometric ratio.

Figure 2 presents the electron micrograph of initial Ti particles. They have a lengthened shape characteristic and metal powders prepared by centrifugal pulverization. The synthesis occurred by explosion kinetics after 80 min treatment of the powder mixture in a planetary mill.

Figures 3(a) and 3(c) show X-ray patterns of the reagents after 60 min treatment as well as the product obtained. No phase changes of the reagent composition have been observed before interaction. The titanium powder acquires pyrophoric properties and its inflammation may occur several days after mechanical treatment has stopped. It is dangerous to open the reactor before interaction because fresh air penetrating the reactor may cause an explosion. A comparison of the X-ray patterns of standard powder (Fig. 3(b)) and mechanically synthesized TiB_2 shows the product obtained to be single phase. X-ray diffraction profile analysis shows microstrain in crystallites of the product.

The electron micrograph of mechanochemically synthesized TiB_2 in Fig. 4 shows particles close to submicronic sizes with uniform size distribution. The shapes

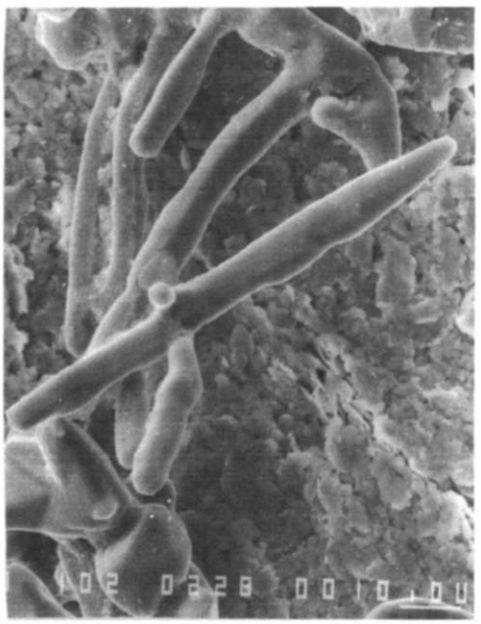

Fig. 2. Ti particles before interaction (×1000).

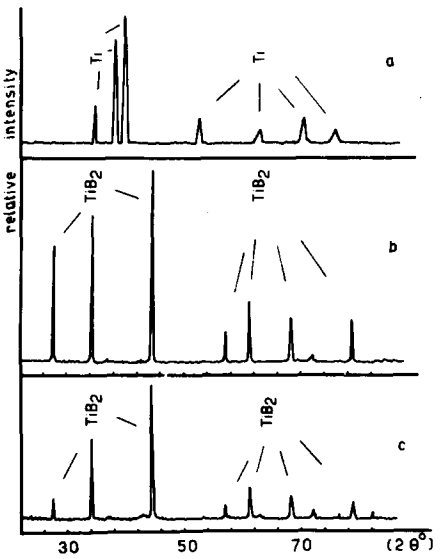

Fig. 3. X-ray diffraction patterns for powders: (a) before and (c) after interaction.

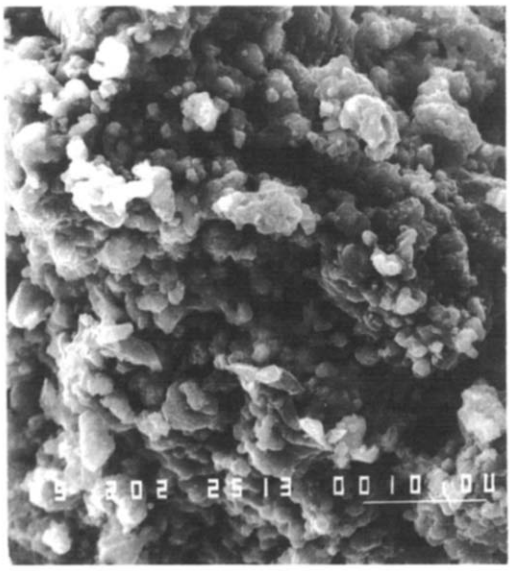

Fig. 4. Mechanochemically synthesized TiB_2 particles (×2000).

are similar to those of iron particles obtained by pulverization by air (RZ method). In addition, the particles of mechanochemically synthesized product are about 10 times smaller.

The specific surface area of the powders obtained was 1.54 $m^2 g^{-1}$, and the mean particle size calculated for an idealized shape was 0.86 μm.

The amount of combined boron was determined by alkalimetric titration of mannitol–boric acid with an NaOH solution. The boron content in TiB_2 was 28.84 wt.%. The amount of combined boron may perhaps be enhanced by attaining a 3–5 wt.% boron excess into the reagents. This method is used in industrial TiB_2 synthesis when 5 wt.% B_2O_3 are introduced into the

reaction mixture of TiO_2, B_4C and C, and in self-propagating high-temperature synthesis when boron is taken in amounts exceeding stoichiometry by 2–3 wt.%. No free Ti and B are found.

Because of the high value of the enthalpy of formation of TiB_2 probably after the initiation, self-propagating high-temperature synthesis takes place. This assumption needs experimental confirmation, *e.g.* by comparison of the properties of TiB_2 particles synthesized by both methods.

The technological advantages of the mechanochemical synthesis are obvious. High-temperature processes and furnaces, homogenizing and grinding of the powders are avoided. The product obtained is finely dispersed and has a defect structure which increases the sinterability of TiB_2 powder. The ability of the sintered materials to inherit the properties of the initial powders necessitates studying of the correlation between the synthesis method and the product properties.

References

1 G. Samsonov, T. Serebryakova and V. Neronov, *Boridy,* Moskwa, Atomizdat, 1975.

2 L. Sigl and K. Schwetz, in D. Emin (ed.), *American Institute of Physics, Conf. Proc. 231, 1990, Boron-Rich Solids,* New York, 1990, p. 468.

3 G. Schwier, in Shigeyki Somiya (ed.), *Ceramic Science and Technology at the Present and in the Future,* Uchida Kokakuho, Tokyo, 1981, p. 35.

4 T. Watanabe and S. Kouno, *Am. Ceram. Soc. Bull., 61* (9) (1981) 970.

5 A. Merjanov and U. Borovinskaya, *Dokl. AN SSSR, 204* (2) (1972) 336.

6 E. Knyshev, *J. Less-Common Met., 47* (1976) 273.

7 R. Hancock, British Patent No. 1 309 660, 1973.

8 J.J. Lin and S. Nadiv, *Mater. Sci. Engi., 39* (2) (1979) 193.

9 H.-C. Chao, in H.H. Hausner (ed.), *Modern Developments in Powder Metallurgy, 5, Materials and Properties,* Plenum Press, New York, 1971, p. 369.