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Preparation of TiB_2 sintered compacts by hot pressing

HIDEAKI ITOH, SHIGEHARU NAKA
Synthetic Crystal Research Laboratory, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464, Japan

TSUNEAKI MATSUDAIRA, HIROSHI HAMAMOTO
Toyota Central Research and Development Laboratories Inc., Nagakute-cho, Aichi Pref. 480-11, Japan

A sintered compact of titanium diboride (TiB_2) was prepared by hot pressing of the synthesized TiB_2 powder, which was obtained by a solid-state reaction between TiN and amorphous boron. Densification of the sintered compact occurred at 20 MPa and 1800° C for 5 to 60 min with the aid of a reaction sintering, including the TiB_2 formation reaction between excess 20 at% amorphous boron in the as-synthesized powder (TiB_2 + 0.2B) and intentionally added 10 at% titanium metal. A homogeneous sintered compact of a single phase of TiB_2, which was prepared by hot pressing for 30 min from the starting powder composition [(TiB_2 + 0.2B) + 0.1Ti], had a fine-grained microstructure composed of TiB_2 grains with diameters of 2 to 3 μm. The bulk density was 4.47 g cm^{-3}, i.e. 98% of the theoretical density. The microhardness, transverse rupture strength and fracture toughness of the TiB_2 sintered compact were 2850 kg mm^{-2}, 48 kg mm^{-2} and 2.4 MN m$^{-3/2}$, respectively. The thermal expansion coefficient increased with increasing temperature up to 400° C and had a constant value of 8.8×10^{-6} deg^{-1} above 500° C.

1. Introduction

A sintered compact of titanium diboride (TiB_2) is expected to be applied to an abrasive, corrosion-resistant or electrode material, since TiB_2 has a unique combination of properties: high melting point (2790° C), low density (4.53 g cm^{-3}), high microhardness (3400 kg mm^{-2}) and good electrical or thermal conductivity [1]. Since TiB_2 is one of the covalently bonded ceramic materials with less sinterability, it is important for the industrial application of TiB_2 compacts to establish an appropriate sintering procedure of TiB_2 using a fine-grained starting powder with favourable activity [2]. Several papers [3–5] have been published on the sintering of TiB_2 by hot pressing in the presence of sintering aids or binders, without which TiB_2 sintered compact is difficult to prepare.

In previous papers [6, 7], we have developed a new synthetic procedure of titanium diboride powder by a solid-state reaction between titanium nitride and amorphous boron powders. Crystalline TiB_2 powder, having an average grain size of about 1 μm, was prepared through a mild and controlled formation reaction of TiB_2. The object of the present paper is to investigate the contraction behaviour during hot pressing of TiB_2 using the starting TiB_2 powder which was synthesized by the above procedure. The microstructure of the sintered compacts and mechanical or thermal properties are also described.

2. Experimental procedure

2.1. Starting powder for hot pressing

TiB_2 powder was synthesized by a solid-state reaction between titanium nitride powder (Japan New Metals Co.; average grain size 0.8 μm) and amorphous boron powder (Rare Metallic Co.; average grain size 0.9 μm) [7]. Each powder was pretreated at 600° C for 60 min in vacuum (5×10^{-5} torr) so as to eliminate the adsorbed gaseous species. They were subsequently mixed at the molar ratio B/TiN = 2.2 and were heat-treated at 1400° C for 360 min. The synthesized TiB_2 powder containing 20 at% amorphous boron, which will be referred to as (TiB_2 + 0.2B), was well dispersed and had a particle size of 0.5 to 2 μm. Thus in-laboratory synthesized powder was added by 10 at% of a commercial titanium powder (Osaka Titanium Co.; average grain size 8 μm) to keep the stoichiometry of B/Ti = 2.0 in the powder. This assorted powder [(TiB_2 + 0.2B) + 0.1Ti] was supplied for a starting powder of hot pressing as well as as-synthesized powder.

2.2. Sintering procedure and evaluation of the sintered compacts

The starting powder was formed into a disk of 40 mm in diameter under 20 MPa, and was degassed in a vacuum (5×10^{-3} torr) at 600° C for 60 min, after which the specimen was hot pressed at 1800° C for 5 to 60 min in an argon atmosphere under 20 MPa pressure. As-prepared sintered compact (diameter 40 mm; thickness 5 mm) was identified by X-ray diffraction and the fractured surface was observed by scanning electron microscope (SEM). The bulk density of the sintered compact was measured by Archimedes' method. Vickers microhardness was measured under 200 g

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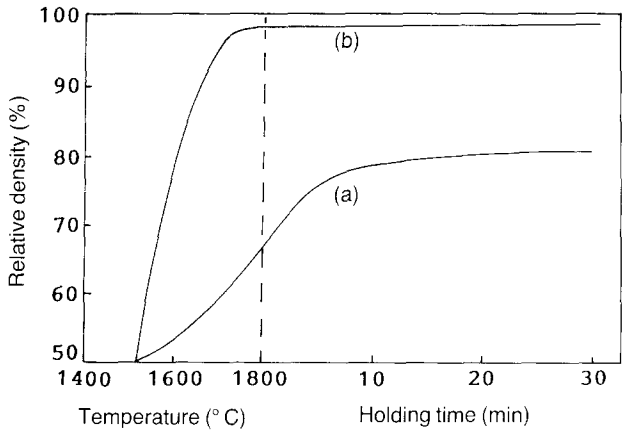

Figure 1 Variation of the relative density of specimens with heating temperature and holding time during hot pressing. Starting powder composition: (a) TiB_2 + 0.2B, (b) (TiB_2 + 0.2B) + 0.1Ti.

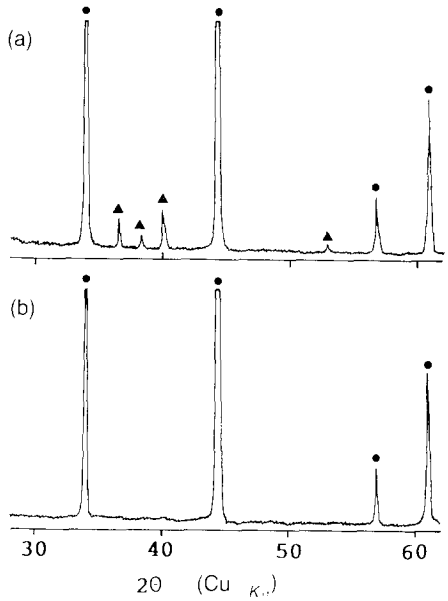

Figure 2 X-ray diffraction patterns of the specimen (a) before and (b) after hot pressing for 30 min. Starting powder composition: (TiB_2 + 0.2B) + 0.1Ti; ● TiB_2, ▲ Ti.

load and fractured toughness (K_{Ic}) was measured by the indentation method. Transverse rupture strength (σ_{3b}; three point bending test) and the linear thermal expansion coefficient (TEC) of the electric spark machined specimen with the dimensions 3 × 4 × 40 mm were also measured.

3. Results and discussion

3.1. Hot pressing behaviour of TiB_2

Figure 1 shows a contraction behaviour of TiB_2 compact during hot pressing, where the relative density of the compact is represented as a function of heating temperature up to 1800° C (heating rate 25° C min^{-1}) and holding time at the soaking temperature of 1800° C. The relative density on the vertical axis was determined from the relative volume change of the compact, which was calculated by the stroke of the piston against the initial density of the compact. A contraction of the specimen is initiated at about 1500° C. In the case of the specimen having the starting powder composition of the synthesized powder (Fig. 1a) (TiB_2 + 0.2B), a gradual increase in relative density is observed up to 1800° C. The contraction continued in the initial 10 min of treatment at 1800° C, and a poor densification (about 75% of relative density) was observed even in the holding time over 10 min. When using the titanium added powder (Fig. 1b) (TiB_2 + 0.2B) + 0.1Ti, however, a rapid and marked contraction of the specimen occurs in the heating process, attaining the relative density of about 98% at 1750° C. A constant relative density of 98.2% is maintained at the soaking temperature of 1800° C.

Figure 2 shows the X-ray diffraction patterns of the specimen (a) before and (b) after hot pressing, in which the starting powder composition is (TiB_2 + 0.2B) + 0.1Ti. Strong diffraction peaks corresponding to the synthesized TiB_2 and weak diffraction peaks corresponding to the added titanium metal can be identified in specimen (a). After the hot pressing, only the diffraction peaks of TiB_2 are observed in Fig. 2b, which verifies that all the added titanium metal reacted with amorphous boron in the synthesized powder, with the result of formation of a single phase of TiB_2 compact.

Figure 3 shows micrographs of the fractured surface of the sintered compacts of the starting powder compositions (a) TiB_2 + 0.2B, and (b) (TiB_2 + 0.2B) + 0.1Ti for the hot pressing time of 30 min. Many pores are seen in specimen (a), having less sinterability and

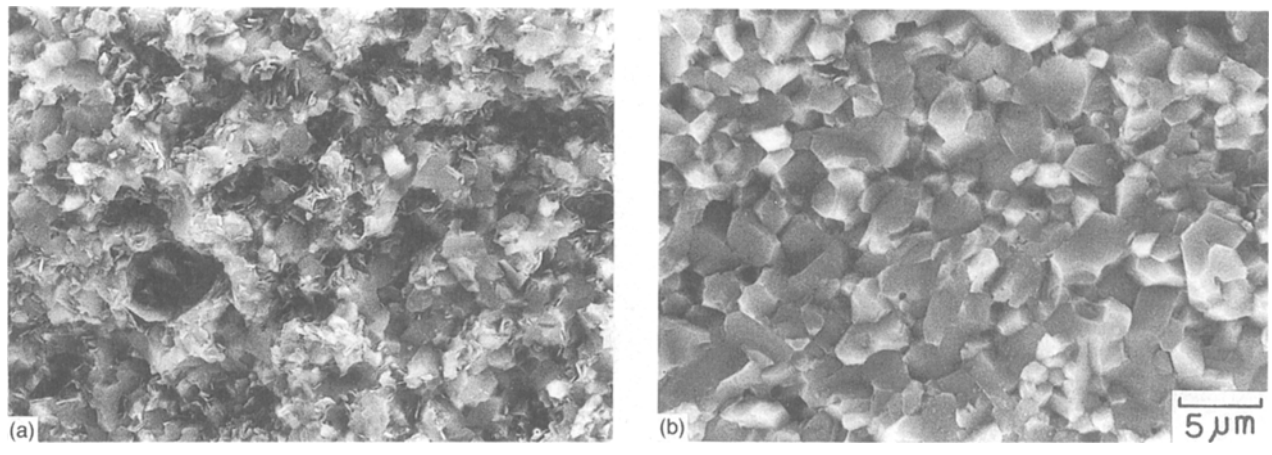

Figure 3 Micrographs of fractured surface of the sintered compacts. Starting powder composition; (a) TiB_2 + 0.2B, (b) (TiB_2 + 0.2B) + 0.1Ti; treatment time 30 min.

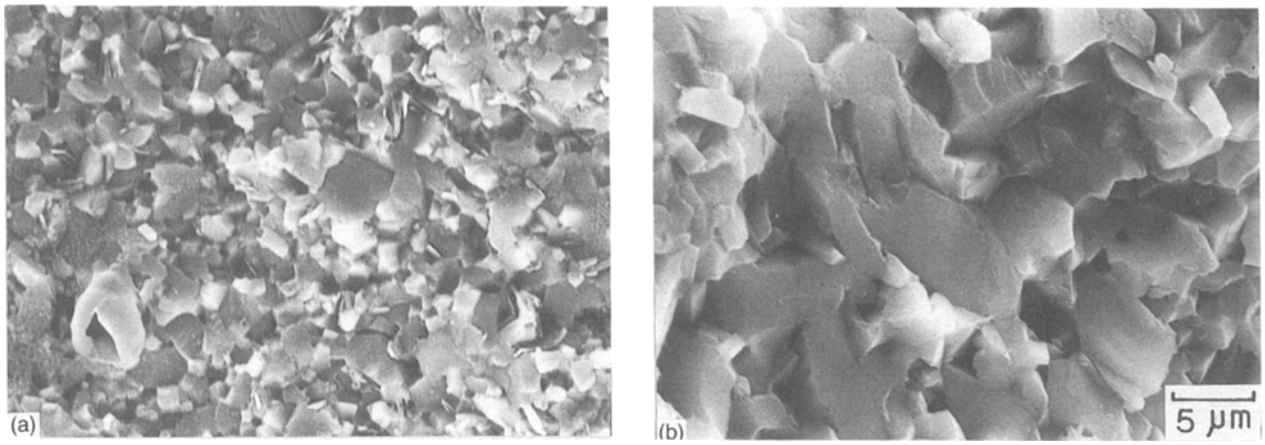

Figure 4 Micrographs of the fractured surface of the TiB_2 sintered compacts. Starting powder composition: (TiB_2 + 0.2B) + 0.1Ti; hot pressing time (a) 5 min, (b) 60 min.

a low density of 3.75 g cm^{-3} (83% of the theoretical density), while a fully sintered microstructure can be observed in specimen (b), the density of which is 4.47 g cm^{-3} (98% of theoretical). It is confirmed from Figs 1–3 that the densification of the sintered compact is promoted by the reaction sintering, which includes the exothermic formation reaction of TiB_2 between added titanium and amorphous boron [7, 9].

3.2. Microstructure and properties of TiB_2 sintered compact

Figure 4 shows micrographs of the fractured surface of the TiB_2 sintered compact with varying hot pressing times (5 and 60 min), where the starting powder composition is (TiB_2 + 0.2B) + 0.1Ti and the hot pressing temperature was kept constant at 1800° C. At an early stage of sintering (see Fig. 4a), the grain size in the sintered compact is as large as the starting powder and the relative density is 97.5% (see Fig. 5). Densification proceeds at the treatment time of 30 min (see Fig. 3b) and the sintered TiB_2 grains with diameters of 2 to 3 μm are seen to develop a homogeneous microstructure, having appropriate particle joining and neck growth. Grain growth is further promoted at treatment time as long as 60 min (see Fig. 4b), in which coarse grains having diameters of about 10 μm are found. The active and fine-grained TiB_2 powder synthesized in our laboratory would contribute to such neck and grain growth, which is not observed in using a commercial TiB_2 powder (grain size 5 to 10 μm) as a starting powder.

Figure 5 shows a dependence of hot pressing time at 1800° C on the relative density and microhardness of the sintered compact. The relative density increases slightly as the hot pressing time increases and attains 98% of theoretical at 30 to 60 min. The microhardness is considerably low (Hv ~ 2700 kg mm^{-2}) at the hot-pressing time of 5 min, probably due to less interparticle bonding between TiB_2 grains as shown in Fig. 4a. At treatment times of over 30 min, the microhardness is mostly constant as high as 2850 kg mm^{-2}.

The influence of hot pressing time at 1800° C on the transverse rupture strength and the fracture toughness of the TiB_2 sintered compact is shown in Fig. 6. The transverse rupture strength has a maximum value of 48 kg mm^{-2} at the hot pressing time of 30 min, which suggests that the strength of the sintered compact is highly sensitive to the microstructure. In contrast, the fracture toughness increases slightly from 5 to 30 min and has a constant value of 2.4 MN m$^{-3/2}$ over 30 min. From Figs 4–6, the best sinterability which gives high hardness, transverse strength and fractured toughness is obtained at the hot pressing time of 30 min at the sintering temperature of 1800° C.

Figure 7 shows the temperature dependence of the linear thermal expansion coefficient (TEC) of the TiB_2 sintered compact, which was obtained by hot pressing of the specimen (TiB_2 + 0.2B) + 0.1Ti at 1800° C for

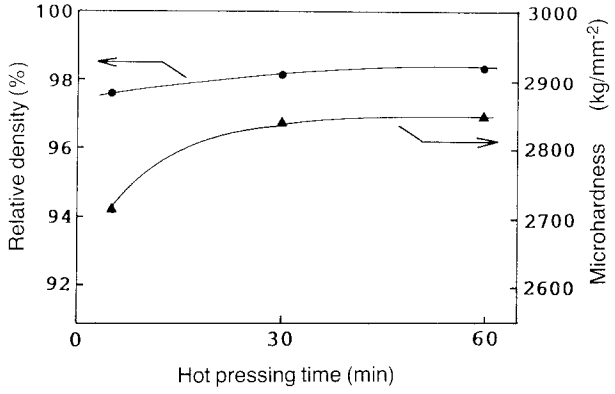

Figure 5 Relative density and microhardness of the TiB_2 sintered compact against hot pressing time.

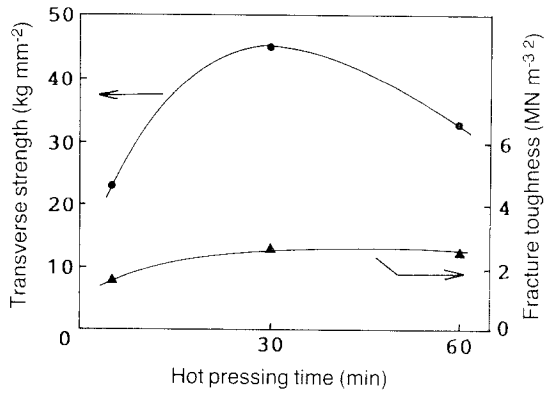

Figure 6 Transverse strength and fracture toughness of the TiB_2 sintered compact against hot pressing time.

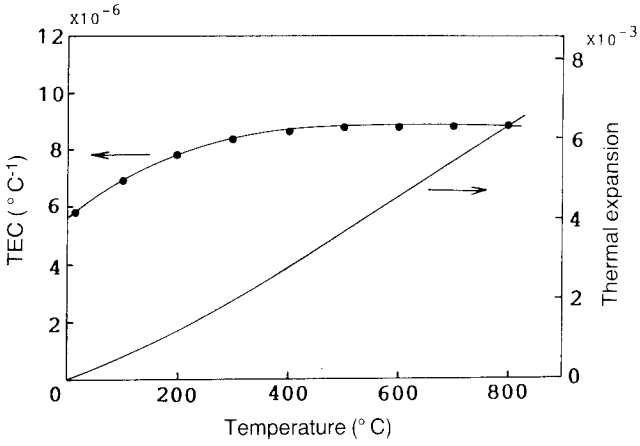

Figure 7 Temperature dependence of thermal expansion coefficient (TEC) of the TiB_2 sintered compact.

30 min. The TEC increases with increasing temperature up to 400° C and had a constant value of $8.8 \times 10^{-6} deg^{-1}$ above 500° C.

4. Conclusions

TiB_2 powder, which was synthesized by a solid-state reaction between TiN and amorphous boron, was hot pressed at 1800° C for 5 to 60 min under 20 MPa in an argon atmosphere. The following results were obtained in relation to the hot pressing behaviour, microstructure and properties of the sintered compact.

1. A homogeneous single-phase sintered compact of TiB_2 was prepared by a reaction sintering at 1800° C for 30 min, which accompanies the TiB_2 formation reaction between excess amorphous boron in the synthesized powder and intentionally added titanium metal.

2. The fine-grained microstructure of the sintered compact, having direct interparticle bonding between TiB_2 grains of about 2 to 3 μm in diameter, was obtained as a result of densification by reaction sintering. The bulk density was $4.47 g cm^{-3}$, that is, 98% of the theoretical density. The microhardness, transverse strength and fracture toughness of a single phase of TiB_2 sintered compact were $2850 kg mm^{-2}$, $48 kg mm^{-2}$ and $2.4 MN m^{-3/2}$, respectively. The thermal expansion coefficient increased with temperature up to 400° C and had a constant value of $8.8 \times 10^{-6} deg^{-1}$ above 500° C.

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