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Synthesis of TiB_2 powder from a mixture of TiN and amorphous boron

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TiB_2 powder was synthesized by solid state reaction using amorphous boron and TiN as a source of titanium. The TiB_2 formation did not occur at all in a nitrogen atmosphere even at 1400° C. TiB_2 formed above 1100° C in argon and hydrogen atmospheres. The only crystalline phase of TiB_2 powder was favourably synthesized at 1400° C for 360 min in an argon atmosphere from a starting powder with a composition containing excess boron (B/Ti = 2.2). The synthesized powder was well dispersed and had a particle size of 0.5 to 2 μm. The powder activity was evaluated by sintering at 4 GPa and 1300 to 1600° C for 15 min.

1. Introduction

Titanium diboride (TiB_2) has a high melting point (2790° C) and microhardness ($H_v = 3370\,\text{kg}\,\text{mm}^{-2}$) as well as good electrical and thermal conductivities [1]. The combination of these properties, in addition to the chemical stability in reducing atmospheres and in molten metals or salts, is expected to render it attractive for unique applications in metal evaporation boats, electrodes, wear resistant tools, etc. [2]. In order to prepare a TiB_2 sintered compact which fulfils these industrial applications, it is necessary to synthesize TiB_2 with a favourable powder activity [3–5].

Among the several methods for synthesis of TiB_2 powder [4–10], the solid state reaction between titanium and boron is one of the most convenient processes for mass-production of TiB_2. However, the heat of formation of TiB_2 ($280\,\text{kJ}\,\text{mol}^{-1}$) is so high [11] that a rapid formation of TiB_2 occurs accompanied by a melt formation. This process is not appropriate for the synthesis of TiB_2 powder, because it is difficult to control the reaction [7, 12].

Fig. 1 shows the free energy changes (ΔG) for various titanium boride formation reactions as a function of temperature. The free energy changes in the $Ti + B = TiB$ and $Ti + 2B = TiB_2$ systems have extremely negative values, almost independent of temperature, which suggests the difficulty of controlling the formation reaction between titanium and boron. On the other hand, the free energy change for the formation reaction

$$TiN(s) + 2B(s) = TiB_2(s) + 1/2N_2(g)$$

alters to negative above 500° C with a gradual decrease in ΔG in a higher temperature range. While the ΔG for the system

$$TiN(s) + B(s) = TiB(s) + 1/2N_2(g)$$

is positive up to about 1900° C. The formation reaction of TiB_2 would be controlled without a burst reaction by using TiN as a titanium source.

In the present paper, a new synthesis process for obtaining TiB_2 powder is presented which uses the solid state reaction from a mixture of TiN and amorphous boron. The synthetic conditions of TiB_2 powder with a grain size of 0.5 to 2 μm was investigated in the temperature range 1000 to 1500° C. Properties of the synthesized TiB_2 powder are described, including the sintering results of the TiB_2 powder under high pressure and temperature conditions.

2. Experimental procedure

2.1. Synthesis of TiB_2 powder

The starting powders for the preparation of TiB_2 were TiN powder (Nihon Sin-Kinzoku Co., average particle size 0.8 μm, purity > 99 wt %) and amorphous boron powder (Rare Metallic Co., average particle size 0.9 μm, purity 96.6 wt %). Amorphous boron powder, as-received, contains volatile impurities (H_2O, oxygen, etc, 2.4 wt %) and metal impurities (magnesium, aluminium, iron, silicon, etc, 1.0 wt %). As-received TiN and amorphous boron powders were separately pretreated in alumina boats at 600° C for 60 min in vacuum (5×10^{-5} torr) in order to eliminate the adsorbed gaseous species. The powder which was mixed in agate mortar at the mole ratios of B/TiN = 2.0 and 2.2, was treated at 1000 to 1500° C for 0 to 360 min in a stream of argon, hydrogen or nitrogen (flow rate $50\,\text{ml}\,\text{min}^{-1}$). Net boron content (96.6 wt %) in amorphous boron powder as-received, was used for the calculation of the atomic ratio.

2.2. Analysis of the treated powder

The treated specimen was identified by X-ray diffraction. The relative amount and crystallinity of crystalline

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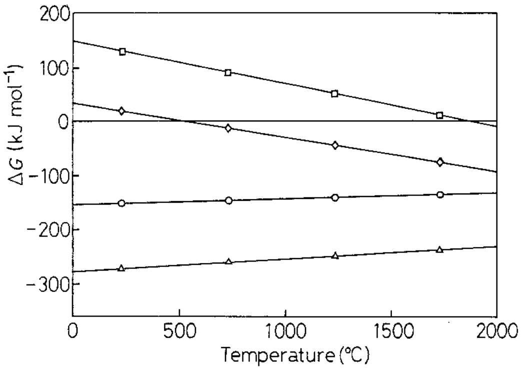

Figure 1 Plot of ΔG against temperature for various titanium boride forming reactions: (○) Ti + B = TiB, (△) Ti + 2B = TiB_2, (□) TiN + B = TiB + $1/2N_2$, (◇) TiN + 2B = TiB_2 + $1/2N_2$.

phase in the specimen were evaluated by the normalized intensities of selected diffraction lines. The lines for evaluation were 2 0 0 of TiN and 1 0 1 of TiB_2, respectively. Normalized relative intensities were determined by the peak height ratio (I/I_{Si}), where I_{Si} shows the intensity of the 2 0 0 line of silicon (purity 99.99 wt %).

The grain shape and grain size of the treated powder were examined by scanning electron microscopy (SEM). The atomic ratio of B/Ti in the specimen was measured by inductively coupled plasma (ICP) emission analysis.

2.3. Sintering of the synthesized powder

As-synthesized powder, which contains 20 at. % amorphous boron in excess of the stoichiometric composition of TiB_2, was mixed with 0 to 10 at. % titanium powder (Nihon Sin-Kinzoku Co., average particle size 15 μm, purity 99%) and then pressed at 20 MPa at room temperature. The green compact was sintered at 4 GPa and 1300 to 1600° C for 15 min using the girdle-type high pressure apparatus.

The sintered density was measured by Archimedes' method and the Vickers microhardness was measured under 200 g load. The fractured surface of the specimen was observed by SEM.

3. Results and discussion

3.1. Synthesis conditions for TiB_2 powder

3.1.1. Effect of treatment atmosphere

The effect of treatment atmosphere on TiB_2 formation was examined using three different atmospheres: argon, hydrogen and nitrogen. Fig. 2 shows the X-ray diffraction patterns of the powders which were treated at 1100° C for 60 min in streams of (a) argon and (b) nitrogen. After treatment in an argon atmosphere, relatively broad peaks of the formed TiB_2 could be observed together with sharp peaks of the unreacted TiN, which correspond to the plots at the initial formation temperature of 1100° C (see Section 3.1.3).

A similar pattern was also obtained in the case of treatment in a hydrogen atmosphere, with no effect of hydrogen on the boride formation being seen. In a nitrogen atmosphere, however, only diffraction lines of TiN could be seen with no detection of TiB_2.

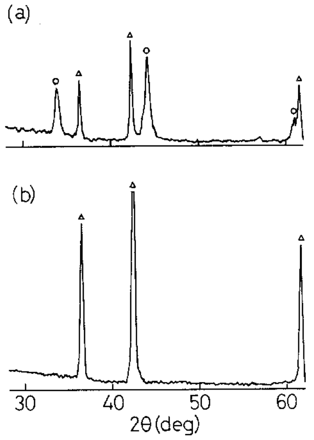

Figure 2 X-ray diffraction patterns of the specimens treated at 1100° C for 60 min and B/TiN = 2.2; (○) TiB_2, (△) TiN. (a) Treated in argon, (b) treated in nitrogen.

At a treatment temperature of 1400° C, the diffraction intensities of TiB_2 increased in both argon and hydrogen atmospheres. However, TiB_2 was not formed at all even at 1400° C in the case of treatment in a nitrogen atmosphere, as shown at 1100° C in Fig. 2b. This result indicates that the reaction is suppressed in the presence of nitrogen in the treatment atmosphere. Boride formation would proceed in atmospheres excluding nitrogen. In the present paper, TiB_2 was prepared in an argon atmosphere.

3.1.2. Effect of composition of the mixed starting powder

Fig. 3 shows the X-ray diffraction patterns of as-synthesized powders, where the mixed starting powders having the mole ratio of B/TiN: (a) 2.0 and (b) 2.2, were treated at 1400° C for 360 min in an argon atmosphere. At the mole ratio of B/TiN = 2.0, which corresponds to the stoichiometric composition of TiB_2 (Fig. 3a), weak peaks of unreacted TiN could be observed in addition to the strong TiB_2 peaks. At this stoichiometric mole ratio (B/TiN = 2.0), a small amount of TiN remains unreacted at the treatment temperature of 1400° C and a treatment time of 360 min. On the other hand, only strong TiB_2 peaks were confirmed in the case of B/TiN = 2.2 (Fig. 3b), which contains 20 at. % boron in excess of the stoichiometric

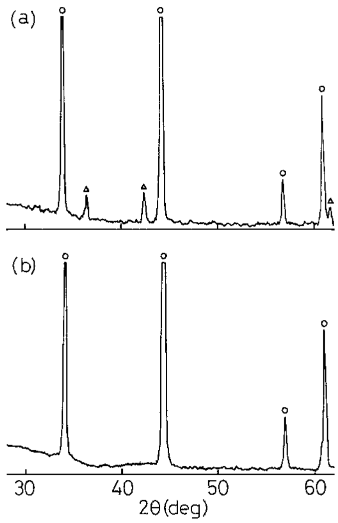

Figure 3 X-ray diffraction patterns of the specimens treated at 1400° C for 360 min in an argon atmosphere: (○) TiB_2, (△) TiN. (a) B/TiN = 2.0, (b) B/TiN = 2.2.

composition of TiB_2. Apparently TiB_2 was obtained as the only crystalline phase, when completion of boride formation was attained using a starting powder with a composition containing excess boron. No detectable difference in the B/Ti ratio in the specimen could be measured by ICP emission analysis before and after heat treatment. As-synthesized powder, therefore, would contain 20 at. % free amorphous boron. This synthesized powder will be written as (TiB_2 + 0.2 B) in this paper.

3.1.3. Effects of treatment temperature and time

Fig. 4 shows the treatment temperature dependence of the relative intensity of TiN and TiB_2 and the weight loss of the treated specimen, where the mixed powder with the mole ratio of B/TiN = 2.2, was heated in the temperature range 1000 to 1500° C for 60 min in an argon atmosphere. At 1000° C, TiN was identified as the only crystalline phase and hence remained unreacted below 1000° C. Amorphous boron could not be detected by X-ray diffraction. The formation of TiB_2 was observed above 1100° C and the amount of TiB_2 formed increased gradually up to 1300° C, as indicated by the weight loss curve. In contrast, the relative intensity of TiN decreased, which suggests that the relative amount and crystallinity of TiN would be decreased due to the boride formation from TiN and amorphous boron. Although a remarkable increase in the relative intensity of TiB_2 was seen above 1300° C, the completion of the reaction was attained even at 1500° C, as shown by the presence of a small amount of residual TiN.

Fig. 5 shows the relative intensities of TiN and TiB_2, and the weight loss of the treated specimen as a function of holding time at 1400° C and B/TiN = 2.2 in an argon stream. The intensity of TiB_2 increases greatly up to 120 min and becomes saturated at 360 min, while that of TiN decreases asymtotically to $I/I_{Si} = 0$ and disappears at 360 min. The weight loss, by a net evolution of nitrogen gas from the specimen, increases gradually and the theoretical value of 18% at the end point of the reaction is also attained after 360 min. It is concluded from the above results that the only crystalline phase of TiB_2 powder can be synthesized by means of a mild formation reaction at a holding time of 360 min.

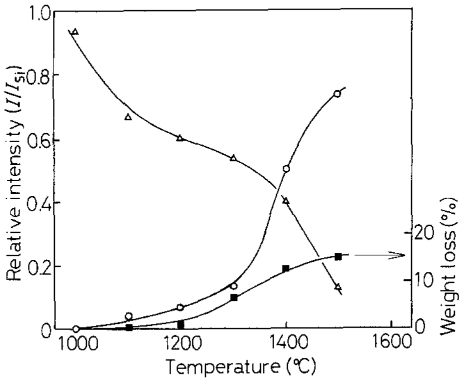

Figure 4 Relative intensity of TiB_2 and TiN, and weight loss of the specimen as a function of treatment temperature at a holding time of 60 min in an argon atmosphere and B/TiN = 2.2: (○) TiB_2, (△) TiN, (■) weight loss.

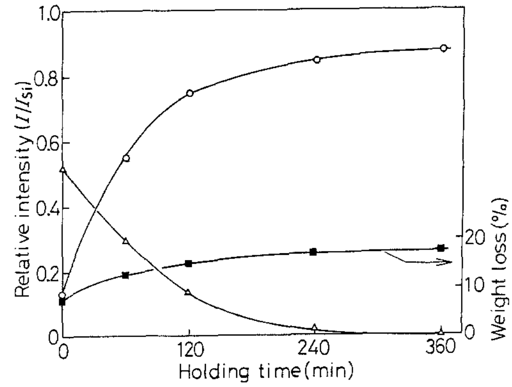

Figure 5 Variation of relative intensity of TiB_2 and TiN, and weight loss of specimen as a function of holding time at 1400° C in an argon atmosphere and B/TiN = 2.2: (○) TiB_2, (△) TiN, (■) weight loss.

3.1.4. Morphology of the synthesized powder

Fig. 6 shows an SEM photograph of synthesized TiB_2 powder obtained at 1400° C for 360 min in an argon atmosphere using the starting powder of B/TiN = 2.2. The particle size is 0.5 to 2 μm, which is similar to that of the starting TiN powder. TiB_2 powder cannot be distinguished from 20 at. % amorphous boron. The powder is considered to be well dispersed, as agglomeration and grain growth of the TiB_2 particle formed are rarely observed.

3.2. Sinterability of the synthesized powder

Fig. 7 shows the variations of Vickers microhardness and density of the sintered compacts with sintering temperature (1300 to 1600° C) under a high pressure of 4 GPa for 15 min. Two kinds of powder were

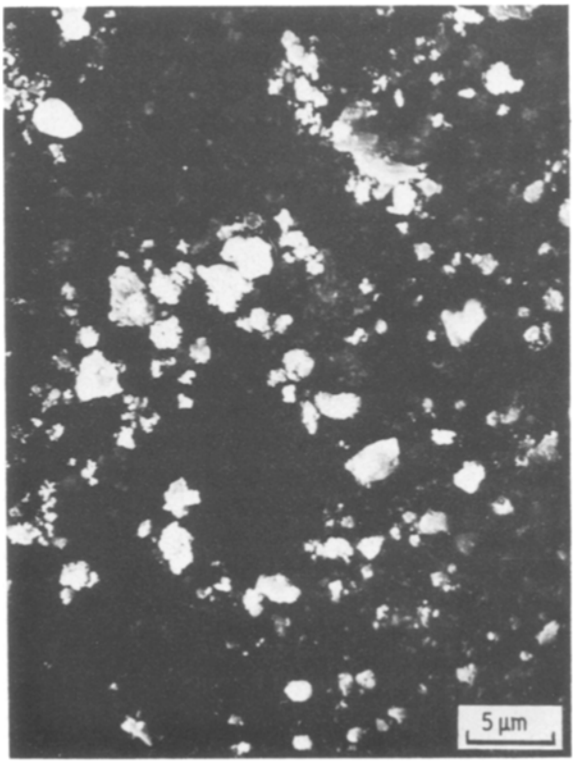

Figure 6 Scanning electron photomicrograph of TiB_2 powder synthesized at 1400° C for 360 min in an argon atmosphere and B/TiN = 2.2.

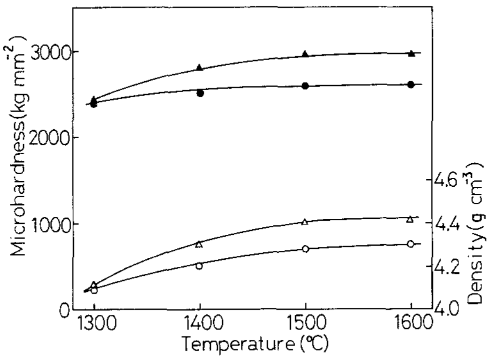

Figure 7 The density (○, △) and microhardness (●, ▲) of the sintered compacts as a function of temperature at 4 GPa for 15 min. (○, ●) $TiB_2 + 0.2B$, (△, ▲) $(TiB_2 + 0.2B) + 0.1Ti$.

sintered: one is as-synthesized powder which contains 20 at. % amorphous boron ($TiB_2 + 0.2B$), and the other is the powder in which 10 at. % titanium was added to the as-synthesized powder represented by $(TiB_2 + 0.2B) + 0.1Ti$. This powder has a composition corresponding to stoichiometric TiB_2. The microhardness and density of the compacts obtained from both powders increase progressively with sintering temperature and are saturated at 1500 to 1600° C. The compact sintered from as-synthesized powder ($TiB_2 + 0.2B$) has a microhardness of 2600 kg mm^{-2} and a density of 4.30 g cm^{-3} at a sintering temperature of 1600° C, while sintered compact from the powder with added titanium ($(TiB_2 + 0.2B) + 0.1Ti$) has higher values of microhardness (2950 kg mm^{-2}) and density (4.44 g cm^{-3}). It is confirmed that the sinterability of the as-synthesized powder is increased by addition of 10 at. % titanium powder. No titanium metal phase was identified by X-ray diffraction even in the specimen with added titanium. The densification of the compact is considered to be promoted by reaction sintering, which is accompanied to be promoted by reaction sintering, which is accompanied by the formation of TiB_2 from amorphous boron and added titanium. This TiB_2 sintered compact has the stoichiometric composition of TiB_2.

Fig. 8 shows the SEM photographs of fractured surfaces of the compacts sintered under high pressure and temperature of 4 GPa and 1600° C for 15 min. The sintered compact with no added titanium (Fig. 8a) contains many micropores and the relative density was 95% theoretical. The effect of titanium addition is found in the microstructure of the sintered compact in Fig. 8b, where the number of micropores decreased and the relative density increased up to 98%.

The synthesized TiB_2 powder was sintered by hot-pressing at 20 MPa and 1800° C for 60 min. TiB_2 sintered compact prepared from the mixed powder ($(TiB_2 + 0.2B) + 0.1Ti$) had a high density (4.45 g cm^{-3}) and a high microhardness (2850 kg mm^{-2}) [13]. The TiB_2 powder prepared in the present work shows a favourable powder activity for sintering.

4. Conclusions

TiB_2 powder was synthesized by the solid state reaction from a mixture of TiN and amorphous boron. The rapid formation reaction of TiB_2 was controlled by using TiN compound instead of titanium metal. The following results were obtained in relation to the effects of atmosphere (argon, hydrogen or nitrogen), treatment temperature (1000 to 1500° C) and time (0 to 360 min) on the formation reaction of TiB_2, as well as evaluation of grain size and powder activity.

1. TiB_2 formation did not occur in a nitrogen atmosphere even at 1400° C, but TiB_2 was formed above 1100° C in argon and hydrogen atmospheres. The only crystalline phase of TiB_2 powder was favourably synthesized at 1400° C for 360 min in an argon

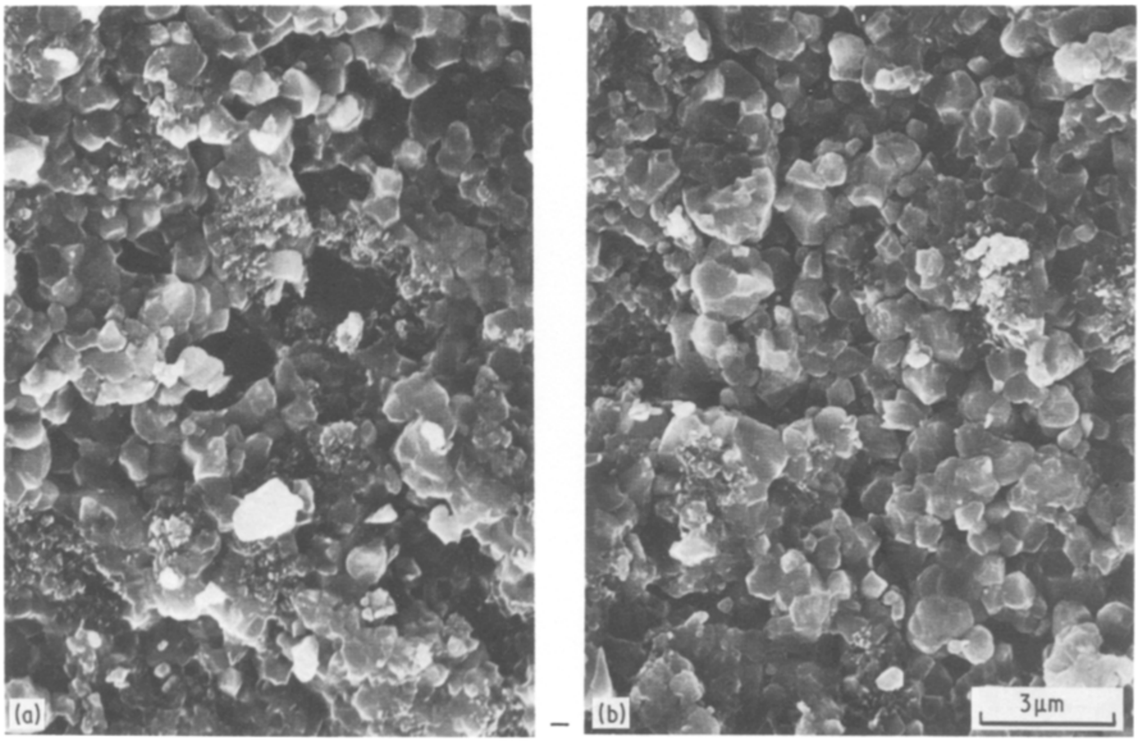

Figure 8 SEM photographs of the fractured surfaces of the compacts sintered at 4 GPa, 1600° C and 15 min. (a) $TiB_2 + 0.2B$, (b) $(TiB_2 + 0.2B) + 0.1Ti$.

atmosphere using a starting powder of a composition containing excess boron (B/TiN $= 2.2$).

2. The synthesized powder ($TiB_2 + 0.2B$) was well dispersed and had a particle size of 0.5 to 2 μm, which is similar to that of starting TiN powder.

3. The synthesized powder was sintered under high pressure and temperature conditions. TiB_2 sintered compact, having the stoichiometric composition of B/Ti $= 2.0$, was obtained by addition of 10 at. % titanium powder to the synthesized powder. The densification of the compact could be promoted by reaction sintering, which is accompanied by the formation of TiB_2 from excess amorphous boron and added titanium.

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