Preparation of titanium diboride TiB$_2$ by spark plasma sintering at slow heating rate

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Abstract

A systematic study of the spark plasma sintering of TiB$_2$ starting from mixture of elemental powders was performed to investigate the temperature distribution between pressing tool and sinter body. The reaction mechanism and time-dependant evolution of the sintering behavior are established. The simultaneous application of pulsed high dc current and load leads to a microstructure with needle-shaped grains. Electron backscattering diffraction analyses show the preferred orientation of small crystallites parallel to the pressing direction.

Keywords: Spark plasma sintering; Titanium diboride; Microstructure

1. Introduction

Titanium diboride (TiB$_2$) is a refractory intermetallic compound with excellent hardness, corrosion resistance and electrical conductivity. It is difficult to sinter TiB$_2$ by common methods because of its low self-diffusion rate. Therefore, we investigated the spark plasma sintering (SPS) route for obtaining TiB$_2$.

The SPS system is a combination of a hot press and a pulse current generator [1]. The technique has been developed for compaction of various metals, ceramics and composites. In the SPS process, dc current pulses with several hundred or thousand amperes and a duration of about 3 ms passed through the green good, while mechanical pressure is applied. SPS is postulated to generate sparks between powder particles due to the pulsed current. The effects caused by the SPS are not yet understood clearly. However, our experimental results show the activating effect of the pulsed current [2]. The temperature measurement in the SPS system employed is typically performed in two regions: a low-temperature region between room temperature and 1200 °C, in which the measurement is done by thermocouple inside the die wall. In the high-temperature region (600–2000 °C), the measurement of the surface temperature of the die wall is done by a pyrometer.

It is known that the temperature inside the sample is mostly different from the temperature that is used to control the process (temperature of the die or the die wall surface, respectively). The difference depends on the heating rate, the electrical conductivity of tools and sample, the thermal insulation and other parameters. Many works have been done to simulate the temperature distribution with FEM methods [3,4] or to measure the sample temperature by thermocouples [2,5–7]. Most of these investigations show the temperature distribution while sintering at temperatures lower than 1000 °C [6].

In this study, the analysis of the temperature distribution between sample and die was done during the SPS synthesis of TiB$_2$. The reaction between titanium and boron is exothermic for the binary phases—titanium monoboride...
(TiB) and TiB$_2$. Because of this, the reactions can be easily observed by temperature changes inside a sample.

2. Experimental

Commercial Ti powders (Chempur GmbH, 99.5%, -200 mesh) and amorphous B (Alfa Aesar, 99.99%, 325 mesh) were used as starting materials. The powders were mixed in a molar ratio of Ti:B = 1:2 and then treated in a swing mill (ZrO$_2$ milling set, 25 Hz, 30 min).

The synthesis was carried out by using a SPS 515-S system (Sumitomo Coal Mining Co., Ltd., Japan). To analyze the known occurrence of differences between the temperatures measured on the surface of the graphite die and the temperatures inside the die [8], a measurement of the sample temperature with a second thermocouple placed inside the die was performed. This thermocouple was plunged through the upper punch and fixed with zirkonia-based cement with the measurement tip 4 mm deep inside the sample. For the analysis of sample temperatures lower than 1200 K, K-type thermocouples were used. For higher temperatures, W-5% Re/W-26% Re-thermocouples with a flexible $\varnothing = 0.7$ mm Ta-mantle (THERMOCOAX GmbH, Germany) were used. These thermocouples can be used up to temperatures of about 1850 °C.

The SPS preparation was carried out in dynamic vacuum. An uniaxial pressure of about 40 MPa in the die was applied during the entire process.

After the reaction, the bulk samples were ground and polished to remove the thin surface layer. The samples were then treated in a swing mill (ZrO$_2$ milling set, 25 Hz, 30 min).

The orientation of single grains in the microstructure was carried out by means of the electron backscattering diffraction (EBSD). These investigations were made with the system INCA Crystal 300 (Oxford instruments), which is mounted to a SEM FEI XL 30 (formerly PHILIPS). EBSD mapping was made at magnification 500. The step width of the measuring points was 1 μm. The measured maps were evaluated with regard to the grain size, grain shape and crystallographic orientation.

3. Results and discussion

3.1. Temperature behavior and chemical reactions

In the Ti–B binary system, following reactions may take place during heating of the mixture of the elemental powders:

$$\text{Ti} + \text{B} \rightarrow \text{TiB} \quad \Delta G(R, 1000 \text{ K}) = -157 \text{kJ/mol}, \quad (1)$$

$$\text{Ti} + \text{TiB}_2 \rightarrow 2\text{TiB} \quad \Delta G(R, 1000 \text{ K}) = -6.3 \text{kJ/mol}, \quad (2)$$

$$\text{Ti} + 2\text{B} \rightarrow \text{TiB}_2 \quad \Delta G(R, 1000 \text{ K}) = -308 \text{kJ/mol}. \quad (3)$$

The Gibbs free energy $\Delta G$ of formation reactions (1)–(3) have been calculated using the thermodynamic data [9]. $\Delta G$ values of all the three reactions are negative, which indicates that all the reactions can take place. Although $\Delta G$ of reaction (3) is the most negative, Ti and TiB$_2$ can further react to form TiB due to the small negative value of the free energy of reaction (2). For this reason, TiB$_2$ will be converted to TiB as long as the average B concentration in the reaction zone is less than 18 mass% [10].

After milling, XRD powder patterns do not show reaction between the powders. Subsequently, the pre-milled powder mixture is SPS treated stepwise from room temperature to 900 °C with a heating rate of 20 °C/min (Fig. 1). The first strong compaction of the powder mixture below 200 °C is a result of the particle movement and deformation due to applied pressure. Chemical reactions cannot be observed. Below 700 °C, powder XRD showed the reflections of $\alpha$-Ti and a strong amorphous background. The sample temperature is slightly lower than the temperature measured in the die. The origin of this behavior is the lower electrical conductivity of the powder mixture compared with the graphite material of the die.

In the temperature region above 450 °C (measured in the die), the densification rate increases again. While this occurs, the sample temperature becomes higher in comparison with the die wall temperature (Fig. 1). The reason for

![Fig. 1. Die and sample temperature and the punch displacement for SPS treatment of the powder mixture Ti + 2B$_{amorphous}$ below 900 °C. Temperature measurement was done with thermocouples (cf. text).](image)
this is the additional heat of the exothermic reactions. Because of this, the second step of densification represents the solid-state reactions between amorphous B and Ti to TiB₂ (reaction (3)) and—in a second step, by excess of Ti—to TiB (reaction (2)). Above 700 °C reflections of TiB and TiB₂ are visible in the powder XRD patterns (Fig. 2).

Independent of the high negative Gibbs free energy for reaction (3), there is no indication for a self-sustaining process under the SPS conditions applied. The displacement/temperature vs. time diagrams indicate a diffusion-controlled solid-state reaction, which can be deduced from comparison with the SPS processing of the elemental powder mixture of nickel with aluminium (Fig. 3). In this case, the mixed powders react spontaneously within seconds. The temperature in the sample increases rapidly in comparison with the temperature in the die. An important criterion for the classification of a reaction is the value of the heating rate. Lower heating rates increase the conversion rate by solid-state reactions and inhibit solid–liquid processes that are necessary for self-sustaining interaction [11,12]. A self-sustaining reaction between Ti and amorphous...
B within the SPS setup is possible at heating rates higher than 100 °C/min. Under that conditions, reaction leads frequently to the destruction of the pressing tool. Because of this, the heating rate for further experiments in the high-temperature region was chosen to be always lower than 25 °C/min.

In the further experiments between 600 and 1900 °C, the temperature measurements were done by a pyrometer on the surface of the die. To minimize the thermal radiation, the die was covered with graphite fleece. The measuring spot of the pyrometer was focused on the hole, which is normally used for the thermocouple. The temperature increases while sintering with about 300 °C/min from room temperature to the minimum temperature for the pyrometer (570 °C). This step needs about 120 s. Higher temperatures were tuned with the chosen heating rate. The temperatures given below (if not mentioned explicitly) are temperatures of the die.

At about 930 °C, the displacement of the punches increases strongly (Fig. 4). This compaction step extends over 400 °C. The temperature in the sample is close to the α/β-transition temperature of Ti (882 °C [13]). The allotropic phase transition leads to the formation of Ti-metal surfaces without oxide layers and, therefore, with a high reactivity. α-Ti is measurable in the powder XRD up to 900 °C (Fig. 2). This supports the chemical reactions (1)–(3) within the green hood. At temperatures higher than 1300 °C, TiB cannot be detected by XRD, the powder diffraction pattern showed only TiB2 (Fig. 5).

During this step of reaction, the electrical behavior of the powder mixture changes from insulating to electrical

![Fig. 7. Microstructure of Ti+2B powder mixtures SPS treated for 30 min at 900 °C (a, b), 1100 °C (c, d), 1500 °C (e, f), 1600 °C (g) and 1800 °C (h). Optical micrographs (a, c, d, g, h) and SEM images (BSE contrast: b; d; SE contrast e) are shown.](image_url)
conductivity. At temperatures below the onset of the reaction, the die temperature is higher than the temperature in the sample. During the reaction, the sample temperature increases faster than the die temperature, which is typical for materials with an electrical conductivity better than graphite. At about 1400 °C sample temperature, the displacement of the punches come close to zero.

At 1680 °C, the displacement increases again rapidly (Fig. 4). The sample temperature decreases temporarily at the onset of the displacement step. This can be explained by the formation of a liquid phase with a composition close to the Ti-rich eutectic composition. The liquid phase reacts with the remaining amorphous B and TiB, forming the final product TiB₂.

In contrast to some information in the literature [14], a homogeneity range for TiB₂ could not be detected by measuring the unit-cell parameters on SPS-treated samples with the starting atomic composition TiₓB₁₀₀₋ₓ/C₀ₓ (27 < x < 45) at 1500 °C.

By the use of die temperatures higher than 1700 and 1800 °C, the displacement of the punches can be understood by the thermal expansion of the pressing tool and the sample (Fig. 6). At higher temperatures an additional compaction of the sample is measurable. This shrinkage is originated in the re-crystallization and re-sintering of TiB₂, which should start above 1900 °C [15].

3.2. Microstructure

Up to 900 °C, the microstructure consists of irregularly shaped, often elongated particles that were loosely packed. The size of the single particle corresponds to the particle size of the used powders (Figs. 7a,b). The bright field images show two phases inside the metallic particles, with one of them having the needle-like morphology (Figs. 7c,d). Electron probe micro-analysis showed that these grains consist of TiB, embedded in a matrix of Ti. At 1000 °C, the porosity of the sintered body is decreased and a TiB₂ diffusion layer around the former Ti grains is visible. Up to 1200 °C, the microstructure evolution is not completed.

Fracture surfaces showed fractured particles with outer layer formed by TiB₂ and needle-shaped TiB grains inside the particles (Fig. 8a). Higher sintering temperatures between 1200 and 1300 °C lead to porous samples that were build from TiB₂ scurf with loose inter-particle contact (Figs. 8b,c). Single disc-like particles were up to 200 μm in length and show a thickness of about 10–20 μm. A part of the scurf is spliced perpendicular to the short axis. SEM investigations lead to the conclusion that between the upper and lower part of the scurf TiB is still present. This is in good agreement with the XRPD data and explains the worse mechanical properties of the samples.

In the range between 1450 and 1500 °C the microstructure changes drastically (Figs. 7e, f). The formation of the liquid phase results in a microstructure with small irregular-shaped grains. The porosity is small (less than 5%) and inhomogeneously distributed. There are a large number of mostly oval-
shaped regions with a size up to 50 μm in length and 20 μm broad, which have a significant lower density than other parts of the microstructure. These regions have a preferred orientation perpendicular to the pressing force and consist of small rod-shaped idiomorphic TiB₂ crystals (Fig. 8d).

Higher sintering temperatures lead to grain growth and a more homogeneous microstructure. Some rod-like grains showed anisotropic growth, which results in grains lengths up to 100 μm (Figs. 7(g, h)).

3.3. EBSD analysis

The orientation of single grains in the microstructure was carried out by means of the EBSD technique on three sections of the sample with the nominal composition TiB₂ after SPS treatment at 1600 °C for 30 min. All sections were perpendicular to each other; their orientation with respect to the applied pressure direction is shown in Fig. 9. Regarding the form of the crystallites, all three maps show a similar picture (Fig. 10). The microstructure consists predominantly of needle-shaped TiB₂ crystallites. The pattern quality images also show this clearly. The crystallite shape was evaluated by the aspect ratio. Crystallites most frequently appear with an aspect ratio between 1.3 and 4.0. Crystals with a high aspect ratio are rather rare.

The distribution of grain size reveals small crystals having the highest frequency. Their areas are between 30 and 150 μm². Large crystallites (500–1500 μm²) appear rarely in all three sections. A correlation between grain size and grain shape was observed: the small crystallites have a small aspect ratio, whereas the large crystallites normally have a big aspect ratio.

Fig. 10. Crystal orientation maps (left) and pattern quality images (right) of sections 1 (a, b), 2 (c, d) and 3 (e, f) together with the color key (g).
The grain orientation in the three sections investigated is visualized with the crystal orientation maps (COM, Fig. 10). From the quality patterns a partial fiber-like texture may be imagined in all three sections. According to the COMs, the fiber axes are nearly parallel to the crystallographic [0 0 0 1] direction. A significant alignment of the [0 0 0 1] axes of the fiber-like crystallites along the pressure direction can be recognized from the COM of Section 3. The forced orientation of the crystallites is probably caused by the interaction of the magnetic field of the dc current during the SPS treatment with the crystal lattice of the TiB₂ [16,17].

4. Conclusions

Starting from the powder mixture of elemental Ti and amorphous B, TiB₂ was synthesized by spark plasma sintering by monitoring the temperature distribution between die and sample. The proposed temperature measurement setup enables the analysis of the chemical reactions during SPS treatment. The slow diffusion-controlled formation of TiB₂ under low heating rate (20 °C/min) can be monitored by the change in the electrical conductivity of the sample. The fast solid–liquid reaction completed the formation of TiB₂. The microstructure of the sintered samples above 1600 °C is dominated by needle-shaped crystallites with main axis parallel to the crystallographic [0 0 0 1] direction in the crystal structure of TiB₂. The crystallites are preferably oriented to the direction of the pressure and DC current.

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