Sinterability of TiB_2 Ceramics Containing Cr and C as the Sintering Aids

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Cr と C を焼結助剤として添加した TiB_2 セラミックスの焼結性

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The effect of Cr and C addition on the sintering process of TiB_2 ceramics was investigated and discussed from microstructural and compositional viewpoints. Simultaneous addition of 6.2 wt% Cr and 1.3 wt% C resulted in high density, high bending strength and high hardness. Results of X-ray diffraction of the TiB_2 composite fired at 900°–1900°C showed that Cr and C reacted with TiB_2 to form CrB and TiC during the sintering process.

Key-words : TiB_2 , Pressureless sintering, Sinterability, Densification, Solid solution, Microstructure

1. Introduction

Titanium boride (TiB_2) has various desirable properties, such as high melting point (2980°C), high hardness (32 GPa), and moderate electrical conductivity ($10^{-5} \Omega \cdot \text{cm}$). TiB_2 has potential uses for wear resistant materials, electrodes for aluminum electrolysis, cathode of CO_2 reduction and parts for vapor deposition.

One of its major disadvantages, however, is poor sinterability, and many attempts are being made to overcome the disadvantage, including hot pressing with sintering aids,^{1,2)} sintering of ultrafine TiB_2 powder synthesized by the arc plasma process without a sintering aid,^{3,4)} and combination with Al_2O_3 , ZrO_2 , SiC or Ti(C, N) to form TiB_2 composite materials.^{5)–9)}

The authors attempted to produce a highly density TiB_2 sintered body by pressureless sintering, and found that TiB_2 could be high densified in the presence of both Cr and C.^{10,11)} However, the function of Cr and C in the densification process of the TiB_2 composite containing Cr and C had not been clarified. In this study, the effect of Cr and C on the sinterability of TiB_2 was investigated.

2. Experimental procedure

Properties of TiB_2 (Cerac Co.), Cr (Soegawa Rikagaku Co.) and C (Mitsubishi Kasei Co.) powders are shown in Table 1. Their average particle sizes and purities are catalogue values, whereas the impurity contents were determined by inductively-coupled plasma emission spectroscopy. The oxygen and carbon contents in the TiB_2 powder was measured using an oxygen and carbon analyzer(Leco

Co.) and the result is given in Table 2.

The powders were blended in the specified ratio and mixed in ethyl alcohol for 24 h using a plastic on-tainer and nylon balls. After drying, the mixture was die-pressed with a pressure of 30 MPa, and subsequently formed into a bar shape (about 10 mm $\times$ 10 mm $\times$ 50 mm in size) by CIP at 300 MPa. The green bodies were packed in a carbon container, and sintered in an electric furnace with carbon heater at 1900°C for 1 h under an argon atmosphere. The heating rate was 15°C/min. After sintering, the sintered bodies were furnace-cooled under argon.

The density of the sintered body was measured by the Archimedeian method.

The sintered body was cut into 4 mm $\times$ 3 mm $\times$ 40 mm bars and polished with a diamond disc to prepare the samples for the 4-point bending test. The measurement was repeated 5 times for each data point, under the conditions of upper span: 10 mm, lower span: 30 mm and crosshead speed: 0.5 mm/min.

The Vickers hardness was measured under the conditions of load: 98N and time: 20 s.

The crystalline phases in the specimens fired at 900°C to 1900°C $\times$ 1 min were identified by powder X-ray diffraction analysis.

Table 1. Average particle size and chemical composition of raw materials.

Material	Average particle size (μm)	Purity(%)	Impurity(%)
TiB_2	2.65	99	Si:0.3, Mg:0.3, Fe:0.2 Al:0.1, Ca:0.01, Cr:0.001
Cr	3.0	99	Fe:0.3, S:0.03, C:0.02 Al:0.01, Si:0.01
C	0.03	99.9	Na:0.01, Ca:0.01, Fe:0.003 Al:0.001, Mg:0.001, Si:0.001

Table 2. Total oxygen and carbon contents of raw materials.

Material	Total oxygen(wt%)	Total carbon(wt%)
TiB_2	0.9	0.6
Cr	0.6	0.0
C	0.2	—

3. Results and discussion

The combinations of Cr and C increased sintered density significantly over that of the sintered bodies containing Cr alone, indicating that the sintering of TiB₂ was greatly accelerated in the presence of both Cr and C. A total aid quantity of 7.5 wt% (Cr/C ratio: 7/1.5, weight: 6.2 wt%Cr–1.3 wt%C) gave a relative density as high as 98%.^{(10),(11)}

Table 3 shows the mechanical properties of TiB₂, TiB₂ containing 7.5 wt%Cr and TiB₂ composite containing 7.5 wt% of Cr and C (Cr/C : 7/1.5), respectively, sintered at 1900°C for 1 h.

The improved mechanical properties resulted conceivably from the increased density.

The TiB₂ compacts containing 6.2 wt%Cr and 1.3 wt%C were fired at 900°C to 1900°C for 1 min. The crystalline phases of TiB₂ composites were determined by powder X-ray diffraction, as given in Table 4. In the sample fired at 1100°C, the diffraction peaks for TiB₂ and Cr₃C₂ were detected. In the sample fired at 1300°C, the diffraction peaks for Cr₃C₂ disappeared, and those for CrB and TiC, although broad, appeared, in addition to those for TiB₂. In the sample fired at 1700°C or higher, sharp diffraction peaks for CrB and TiC were found, in addition to those for TiB₂.

Figure 1 shows the shrinkage curve of the sample containing Cr and C, in which the sintering-induced

shrinkage started between 1100° and 1300°C. No Cr₃C₂ peak was detected, but the peaks of TiB₂, CrB and TiC were detected by X-ray diffraction in the specimens sintered at 1300°C or higher.

The above results suggest that the following reactions took place during the sintering process:

Figure 2 shows X-ray diffraction peaks for TiB₂ (201) plane. It is seen that the diffraction peaks in the sintered body of TiB₂ added with Cr and C shifted towards higher angles from the positions for the

Fig. 1. Linear shrinkage curve of TiB₂-6.2 wt%Cr-1.3 wt%C specimen.

Table 3. Mechanical properties of the TiB₂ composites.

Specimens were fabricated by pressureless sintering at 1900°C for 1 h in argon gas.

Composition (wt%)	TiB ₂ 100%	TiB ₂ -7.5%Cr	TiB ₂ -6.2%Cr-1.3%C
Relative density (%)	78	91	99
Bending strength (MPa)	160	308	405
Vickers hardness (GPa)	3	15	23

Table 4. Crystalline phases of TiB₂-6.2 wt%Cr-1.3 wt%C raw material and the composite fired at 900°C to 1900°C.

Temperature (°C)	Crystalline phases
Raw materials	TiB ₂ , Cr, C
900	TiB ₂ , Cr, C
1100	TiB ₂ , Cr ₃ C ₂
1300	TiB ₂ , CrB, TiC
1500	TiB ₂ , CrB, TiC
1700	TiB ₂ , CrB, TiC
1900	TiB ₂ , CrB, TiC

Fig. 2. X-ray diffraction patterns of TiB₂(201).

(a) TiB₂-6.2 wt%Cr-1.3 wt%C raw material.

(b) TiB₂-6.2 wt%Cr-1.3 wt%C composite sintered at 1900°C for 1 h.

TiB₂ starting powder. We assume that the unit lattice of the TiB₂ crystal in the specimen contracted due to the solid solution, so that the diffraction peaks for TiB₂ shifted towards higher angles.

It is also considered that oxygen (0.9 wt%) and carbon (0.6 wt%) present in the starting powder as impurities (Table 2) affected the sinterability of TiB₂. In particular, the amount of oxygen considered to be present on the starting particle surfaces was decreased by reaction with the carbon present as the impurity and the newly added aid to form CO gas.¹²⁾

It is considered, based on these results, that Cr and C added to TiB₂ reacted to form phases of CrB and TiC during the sintering process, which promoted the bonding between TiB₂ grains, removed pores and contributed greatly to densification of the sintered bodies.

Therefore, a sintered body of TiB₂ having increased density, high strength and high hardness can be obtained by the addition of Cr and C to TiB₂.

4. Conclusions

TiB₂ ceramics was sintered pressurelessly in the simultaneous presence of Cr and C, in order to investigate the effects of these sintering aids on the sinterability of the TiB₂ composites.

Simultaneous addition of Cr and C as the sintering aids accelerated the densification of TiB₂ significantly.

It is considered that the addition of both Cr and C was effective in promoting the bonding between grains and removing pores to achieve high density.

Thus, a sintered body of TiB₂ having increased density, high strength and high hardness can be obtained by the addition of Cr and C to TiB₂.

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