Effect of addition of Cr on the sintering of TiB_2 ceramics

YOUNG S. KANG, SHIN H. KANG, DEUG J. KIM*
Department of Materials Engineering, Sungkyunkwan University, 300 Chunchun-dong, Jangan-gu, Suwon 440-746, Korea
E-mail: kimdj@skku.ac.kr

Titanium diboride has high hardness, wear resistance and high melting point, so it is widely applied as cutting tools, armor materials and metal melting crucibles [1, 2]. However, it is difficult to obtain fully dense bodies due to its strongly covalent nature.

Several investigations have shown that transition metal additives such as Ni and Fe promote the densification of TiB_2. It is considered that the formation of a liquid phase from the additives during sintering led to improvement [3–5]. In our previous work [6], it was found that the simultaneous addition of Cr and Fe improved the density of TiB_2 more effectively than that Fe addition did. However, the reason of the significant density improvement by the simultaneous addition of Cr and Fe to TiB_2 has not been clearly understood.

Since the powder used in the previous work contained 0.25 wt% of Fe as impurity, it was difficult to interpret the effect of the single addition of Cr. The purpose of the present study was to determine the role of Cr during the sintering of TiB_2 by using new grade of TiB_2 powder without Fe impurity.

New F grade of TiB_2 powder (H. C. Starck GmbH, Goslar, Germany) was used as a starting material. The powder did not contain Fe impurity and major impurity was oxygen (1.7 wt%). The average particle size was 2.3 μm which is larger than that of one (0.9 μm) used in the previous study [6]. Chromium (>325 mesh, >99.5% pure) and iron (4–5 μm, >99.5% pure) were added as sintering aids. The total amount of additives was fixed at 1 wt%. The powders were mixed by spex-milling for 30 min in a plastic jar using Si_3N_4 balls and methyl alcohol as media. After milling, the slurry was dried in a rotary evaporator at 70 °C and granulated using a 100-mesh sieve. The granulated powders were die-pressed at 150 MPa to form 15 mm diameter pellets. The specimens were sintered in a graphite crucible using a graphite resistance furnace in a flowing argon atmosphere. The sintering temperature was in the range of 1700–2000 °C for 2 hr and heating rate was 10 °C/min. The temperature was measured by a two-color infrared pyrometer.

The sintered density of the specimen was determined by the Archimedes method. Relative density was calculated using the theoretical densities of the substances added, assuming that only TiB_2, Cr and Fe were present in the sintered body. The sintered materials were sectioned and polished with diamond pastes down to 1 μm. The specimens were etched by electrolytic etching in a KOH solution. The microstructure of the resulting sections then investigated using scanning electron microscopy (S-2150, Hitach, Japan). Average grain sizes of the specimens were determined from these micrographs, using image analyzer (Image Pro-Plus, Media Cybernetics, MD, USA). More than 1000 grains for each specimen were observed to determine the grain size distribution.

Fig. 1 shows the sintered densities as a function of sintering temperature. The maximum sintered density of TiB_2 containing 1 wt% Cr was 77.5%. A great difference of sintered densities of TiB_2 containing 1 wt% Cr was noted between this and previous work [6]; the sintered density of TiB_2 containing 1 wt% Cr in previous work was 92.6%. Although the difference of the size of the two TiB_2 powders was considered, the density of TiB_2 containing 1 wt% Cr in this work was much lower than that in the previous work.

It is well-known that the addition of Fe, even at low content, can enhance the densification of TiB_2. From previous studies [3–5], it was observed that the liquid phase was formed from metallic additives, which played a major role in promoting densification of TiB_2. The melting point of Cr is much higher than that of Fe and decreases rapidly with increasing the Fe content in Cr–Fe solution [7]. Therefore, it is believed that the densities obtained in previous work could be strongly influenced by the Fe impurity. The density of TiB_2 containing 1 wt% Fe reached maximum value of 95.8% at 1900 °C. However, the density decreased with further increase in sintering temperature. When the specimen containing 0.5 wt% Cr and 0.5 wt% Fe was sintered at 1900 °C, the relative density reached to 97.0%, which is higher than that of TiB_2 containing 1 wt% Fe. The decreased density of TiB_2 containing 0.5 wt% Cr and 0.5 wt% Fe with increasing sintering temperature was smaller than that of TiB_2 containing 1 wt% Fe.

Microstructures of the specimens sintered at 1900 °C for 2 hr are shown in Fig. 2. It can be observed that the addition of 1 wt% Fe to TiB_2 enhanced both grain growth and densification of TiB_2. Some grains were observed to be grown exaggeratedly. However, the microstructure of TiB_2 containing 0.5 wt% Cr and 0.5 wt% Fe exhibited a relatively uniform and fine microstructure.

Fig. 3a shows the grain size distributions of TiB_2 containing 1 wt% Fe sintered at 1800, 1900 and 2000 °C. A

*Author to whom all correspondence should be addressed.

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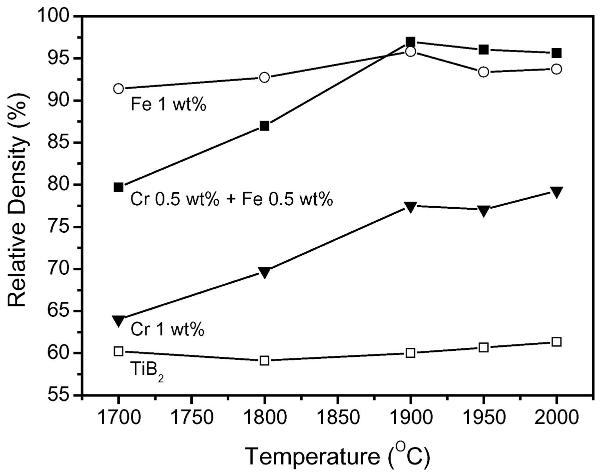

Figure 1 Relative densities of the specimens as a function of sintering temperature.

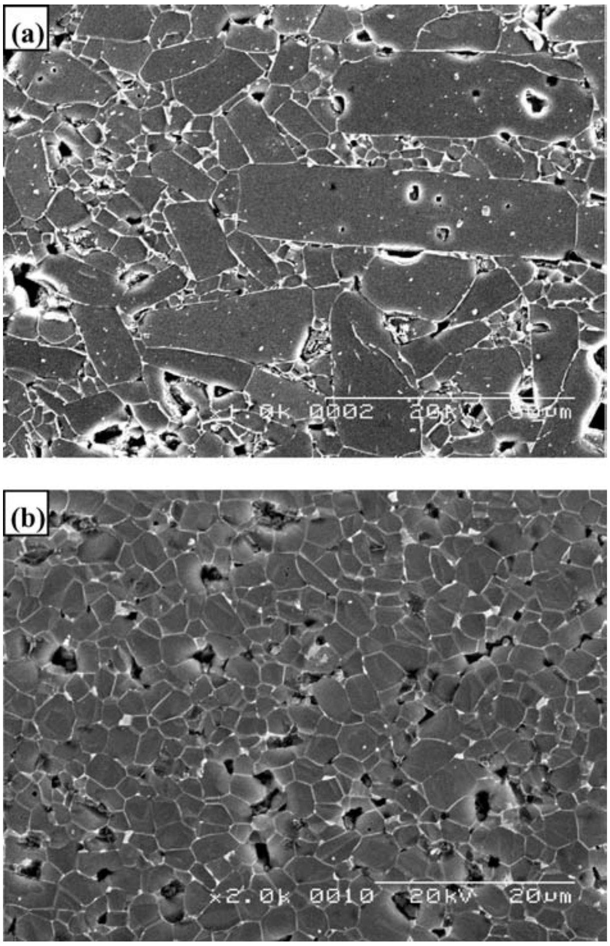

Figure 2 SEM micrographs of TiB_2 containing 1 wt% Fe(a) and containing 0.5 wt% Cr and 0.5 wt% Fe(b) sintered at 1900 °C for 2 hr.

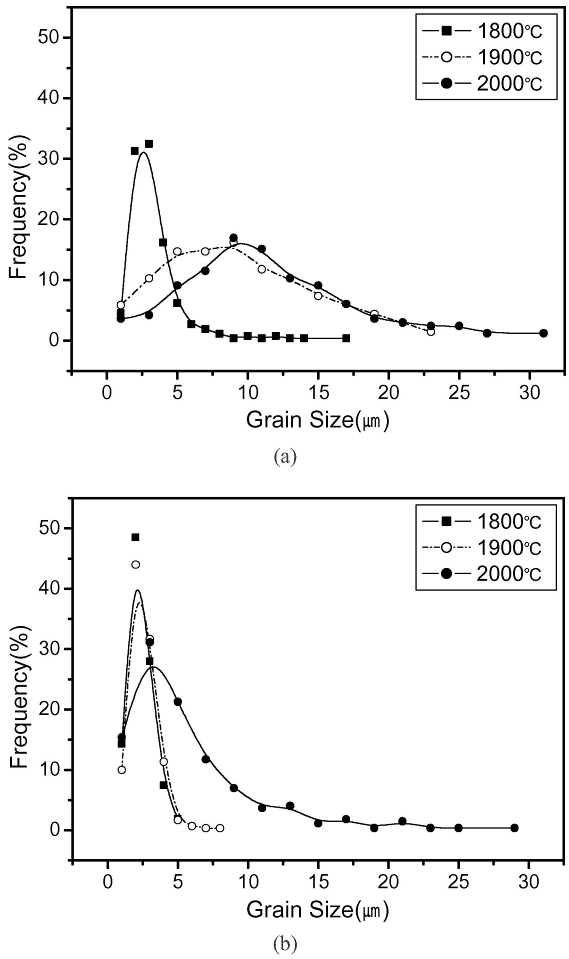

Figure 3 The grain size distributions of TiB_2 containing 1 wt% Fe(a) and containing 0.5 wt% Cr and 0.5 wt% Fe(b) sintered at 1800, 1900 and 2000 °C for 2 hr.

rather narrow distribution in grain size with a few large grains was observed when the specimen was sintered at 1800 °C. With the increase of temperature, a vigorous grain coarsening was observed to occure and then the grain size distribution became broader. It was expected that large grains have grown exclusively at the expense of fine matrix grains.

In contrast, as shown in Fig. 3b, the grain size distributions of TiB_2 containing 0.5 wt% Cr and 0.5 wt% Fe exhibited a narrow distribution with uniform and fine grain size even up to 1900 °C. The microstructure was composed of only fine grains and no abnormally grown large grains were observed, as shown in Fig. 2b. These results suggest that the presence of Cr addition remarkably suppressed the grain growth of TiB_2 containing Fe during sintering at high temperatures. Upon further increase of temperature, however, a few grains started to grow abnormally. Therefore, the grain size distribution was observed to change as like broad grain size distribution of TiB_2 containing 1 wt% Fe, when the specimen was sintered at 2000 °C.

In summary, the simultaneous addition of Cr and Fe was found to enhance more effectively the densification of TiB_2 as compared to that of TiB_2 added with Fe alone. The fine and more narrow grain size distribution of TiB_2 containing 0.5 wt% Cr and 0.5 wt% Fe was observed compared to that of TiB_2 containing 1 wt% Fe. It is suggested that the coarsening of TiB_2 grains could be effectively suppressed by the addition of Cr to TiB_2 containing Fe.

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