Influence of processing condition of Ti, Al, and B₂O₃ mixed powders on the preparation of Al₂O₃–40.5 mass % TiB₂ sintered compact by HIP

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The Al₂O₃–TiB₂ sintered compact was synthesized by a reaction, Ti + 2Al + B₂O₃ = Al₂O₃ + TiB₂, during hot isostatic press (HIP) with mixed powders of Ti, Al and B₂O₃ as starting materials. It was found that pre-cooling at −5°C and milling at 0°C suppress the reaction to proceeding mechanochemically, and extend the time for mixing. Scraping off clung powders inside of container during the milling made powders fine and uniform. The longer milling time and uniformity of the powders achieved by the above treatments made it possible to obtain Al₂O₃–40.5 mass % TiB₂ with 99.5% relative density and Hv = 2800.

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1. Introduction

Although sintered Al₂O₃ is widely used in industries because of its chemical stability, abrasion resistance and high strength, improvement of thermal shock resistance and high-temperature hardness are required. Hybridization of Al₂O₃ with other materials seemed to be an effective way of the improvement, and synthesis of Al₂O₃–TiC and Al₂O₃–TiB₂ composites has reported.1) Dense Al₂O₃–TiB₂ composite containing TiB₂ more than 25 mass % is not available under normal pressure because low sintering ability of TiB₂. Therefore, sintering under high pressure is required. and reactive hot isotropic press (HIP) sintering is considered to be useful to obtain Al₂O₃–TiB₂ composite with higher TiB₂ content.

The authors examined synthesis of Al₂O₃–40.5 mass % TiB₂ compact from reagent grade Ti, Al and B₂O₃ by the reaction (1) with a HIP.

\[ \text{Ti} + 2\text{Al} + \text{B}_2\text{O}_3 = \text{Al}_2\text{O}_3 + \text{TiB}_2 \] (1)

Relative density and micro-hardness of the obtained compact are higher than that of sintered materials synthesized by conventional methods. Texture of obtained compact is, however, not quite uniform that mixing and grinding process of reactants is considered to study in detail.

Equilibrium constants of the reaction (1) are calculated to \( K_{500} = 1.3 \times 10^{124} \) and \( K_{1500} = 5.8 \times 10^{15} \) with thermodynamic data by Barin et al. at 27°C (300 K) and 1527°C (1800 K), respectively.4) 5) These higher values indicate that the reaction (1) can take place not only at HIP temperature of 1500°C but also at low temperatures (0–30°C) during ball-milling of reactant powders mechanochemically. This indicates importance of detailed study on the low temperature process for improvement of the properties of the compact. In this study, the effect of the properties of the mixed powder that consists of Ti, Al, and B₂O₃ used for HIP process was examined.

2. Experimental

2.1 Mixing and grinding of powders

Raw materials used in this study were Ti powder (Kishida Chemicals, spongy 8–16 mesh and 99.5%), Al powder (Mitsuwa Chemicals, 150 mesh and 99.9%), and the B₂O₃ powder (Kishida Chemicals, 99.9%). Figure 1 shows SEM images of the powders. The powders of Ti:Al:B₂O₃ = 1:2:1 in a molar ratio were weighed the amount of 20.0 g and filled in two container made of the tungsten carbide, 64 mm in the inside diameter and capacity 70 cm³ in a glove box replaced by Ar gas. A FRITSCH P-5 planet type ball mill was used for mixing and grinding of powders. Five balls made of the tungsten carbide, 20mm in diameter, and 61 g each, were loaded in containers. The two containers were set in the mill and milling carried out at rotation speeds of 202 and 436 rpm for containers and the container loaded disks respectively. The milling terminated when the reaction (1) occurred and the color of the Thermo-Label, the color of which changes between 40–150°C, changed in one of the two containers. Only the mixed powder in the container which did not show any temperature rise was used for the following processes, because the powders reacted mechanochemically could not sinter densely, even if HIP was used.

The milling was carried out one or two steps. In two-step milling, inside of the container was cleaned between the steps. Details would be found in Section 3.1.

Crystal structure and appearance of the powders were examined by X-ray diffraction (XRD) and the scanning electron microscopy (SEM).

2.2 HIP procedure

The mixed and ground powder was filled in a Pyrex glass tube in the glove box as shown in Fig. 2. After putting a ceramic wool over the powder and inside of the tube was evacuated down to \( 10^{-3} \) Pa by a rotary pump, then the tube was heated at 500°C for 2 h to avoid breakage of the tube in HIP process. After cooling

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the tube down to 200°C in the furnace, throttle part of the tube was melted and sealed in vacuo. The tube was put in a graphite crucible and set in a pressure vessel of HIP equipment (Kobe Steel, O₂-Dr. HIP). Figure 3 shows the temperature and the pressure patterns in the HIP processing. The tube was heated with a molybdenum heater to 700°C, which is above the softening temperature of the Pyrex glass, and Ar gas was introduced to the vessel. Then the tube was heated up to 1500°C at 100 MPa, and it was kept for 1 h.

2.3 Characterization of sintered compact
Density of the sintered compact was measured by hydrostatic underwater weighing method. Ideal density of the Al₂O₃–B₂O₃ composite compact was estimated at 4.19 g cm⁻³ with the densities of TiB₂ and Al₂O₃ as 4.52₁,₆,₉ and 3.99 g cm⁻³. Vickers micro-hardness was measured under the load of 9.8 N and loading time of 20 s. Ideal hardness of the compact was estimated at Hv = 2780 with the micro-hardness of Al₂O₃ and TiB₂ of 2400¹ and 3400² by assuming the low of mixture for hardness.

3. Result and consideration
3.1 Milling of powders for HIP procedure
As described in 2.1, the milling terminated when the temperature of one containers rose, and the period to the termination was defined as “milling limit time”. Figure 4 shows relationship between the temperature of the milling container and milling limit time for the container with or without pre-cooling before milling. For pre-cooled container, the milling limit times were longer than those of the container without pre-cooling. Figure 5 shows XRD patterns of powders in containers with and without temperature rise. It is shown that only Al and Ti were detected for the powder without the temperature rise, whereas peaks of Al₂O₃ and TiB₂ were detected for the powder with the temperature rise, indicating that a mechanochemical reaction (1) occurred for the latter case. Diffraction peak of B₂O₃ was not observed for both specimens. According to the above results, the milling was decided to carry out at 0°C after pre-cooling for 20 min at −5°C.
During the milling, clinging of the powder was observed. **Figure 6** shows XRD patterns of the powder clung onto the ball or wall on the container, as well as not-clung powder (mixed powder). Only Al and Ti were detected from mixed powder, whereas peak of B₂O₃ also appeared from clung powder. Intensity ratio of Al to Ti peaks is larger for clung powder. It is suspected from the result that Al deformed then clung on the ball and surface of the container during milling, and B₂O₃ might adsorb on fresh Al surface. Relatively hard Ti remained in the powder. Once the milled powders have clung to the ball or wall of the mill container during milling, uniform mixing of powders cannot proceed. It is interesting to scrape off clung powders during the milling to examine how the clinging affects properties of sintered compacts.

According to the results above, two types of milling were carried out. Milling-Type 1 was a continuous milling to milling limit time, whereas Milling-Type 2 proceeded in two steps. In Milling-Type 2, continuous milling once stopped at 200 min, and milling started again to the milling limit time after remixing of the mixed powder and scraped off clung one.

**3.2 Features of mixed powder to before HIP procedure**

**Figure 7** shows the X-ray diffraction patterns of powders prepared by Milling-Type 1. Intensity of Al peaks decreases and width of the peaks increases. The tendency of the change in the intensity and the width are similar for Milling-Type 2 (not shown). Diffraction peaks of Ti are the same independent of the time and the milling type. **Figure 8** shows SEM images of powders after milling. It is found that the primary particles agglomerated to make the secondary particles. The secondary particle was composed of pyramidal particles which apex pointed to the center of the secondary particle when the milling time is short (A). With long time milling, corners of the primary particles became rounded and their size became small as shown in (B) and (C).
3.3 Composition, structure, and texture of the compact

Figure 9 shows the X-ray diffraction patterns of the sintered compacts from mixed powders of Milling-Type 1. The peaks of $\text{Al}_2\text{O}_3$ and $\text{TiB}_2$ are found in all specimen indicating that the formation of $\text{Al}_2\text{O}_3$–$40.5$ mass% $\text{TiB}_2$ ($\text{Al}_2\text{O}_3$–$50$ mol% $\text{TiB}_2$) sintered compact. Weak peaks of TiAl$_3$ and/or Ti$_3$Al also appear for the milling limit time of $100$ min. If mixing time of powders was insufficient, distribution of $\text{B}_2\text{O}_3$ could be non-uniform. Reaction of Ti and Al to form the intermetallics could occur where the concentration of $\text{B}_2\text{O}_3$ is low, whereas excess $\text{B}_2\text{O}_3$ could be absorbed by the Pyrex tube. The above hypothesis can explain the formation of the intermetallics between Ti and Al, indicating that milling for longer period is advantageous to achieve uniform sintered compact by HIP.

Figure 10 show the optical micrographs of compacts sintered by HIP. The sintered compact was composed of white $\text{TiB}_2$ and gray $\text{Al}_2\text{O}_3$ phases as shown in (B). The dark color portions seemed to pore, and the number of which is large for short milling limit time (A), and small for the long milling limit time (D). Similar texture and tendency of pore formation was observed in Fig. 11 where the milling of the powder was carried out by Milling Type-2. It should be noted that in Fig. 11(C), milled for the longest time of all, shows the surface without pore. The followings were considered to reason for these textures. The mixed powders including the large grains of about $10\mu$m might not be densely filled to the tubes leaving vacant spaces between them. If $\text{B}_2\text{O}_3$ (mp = $500^\circ$C) and/or Al (mp = $660^\circ$C) has melted to form a liquid phase, the liquid filled the space between solid particles. Figures 10 and 11, however, do not show an evidence of the liquid phase formation and pores. The result indicates that the liquid phase has not formed because of solid-state reaction to taking place between $\text{B}_2\text{O}_3$ and Al or Ti at temperatures lower than $500^\circ$C.

Figure 12 shows the relationship between relative density of the sintered compacts and the milling limit time for the preparation of powder used for HIP. The relative density increases with increasing the milling limit time independent of Milling-Type. The highest value is obtained when the mixed powder was prepared by Milling-Type 2 for (200 + 290) min. Figure 13 shows the relationship between Vickers microhardness and relative density of sintered compacts. The hardness increases almost with increasing relative density and reaches $Hv = 2800$ at $99.5\%$. The value is almost identical to the ideal hardness $Hv = 2780$. Those results indicate that pore density and hardness of sintered compact is closely related to mixing time of powders, and also suggest that Milling-Type 2 is advantageous to obtain the most dense and the hardest $\text{Al}_2\text{O}_3$–$\text{TiB}_2$ compact.
Fig. 11. Optical micrographs of the composite sintered compacts from mixed powders of Milling-Type 2. The powder of the milling limit time of (200 + 100) min was used. (B): (200 + 200) min. (C): (200 + 290) min.

4. Summary and conclusion

Effect of mixing and grinding condition of Ti, Al and B₂O₃ on formation, density, and micro-hardness of Al₂O₃–40.5 mass% TiB₂ sintered compact by HIP was studied, and the following conclusions were obtained.

(1) Milling mixed powders for longer time was extremely important to obtain dense sintered compact by HIP. Longer mixing time without mechanochemical reaction to occur was established by cooling of milling container before and during milling.

(2) Scraping off clung powders inside of container during the milling is advantageous to obtain fine and uniform mixed powders.

(3) The highest values of relative density and hardness of sintered compact obtained in this study were 99.5% and Hv = 2800 respectively.

Fig. 12. Relationship between relative density of the sintered compact and the milling limit time for the preparation of powder supplied to HIP. Milling temperature was 0°C after pre-cooled at −5°C for 20 min. HIP conditions were 1500°C and 100 MPa for 1 h. □: Milling-Type 2 powders were used. ●: Milling-Type 1 powders were used.

Fig. 13. Relationship between the Vickers micro-hardness and the relative density of the sintered compact. □: Milling-Type 2 powders were used. ●: Milling-Type 1 powders were used.

References

6) CRC Materials Science and Engineering Hand Book, Ceramics pp. 50.
8) CRC Materials Science and Engineering Hand Book, Ceramics pp. 50–52.