journal
J. Am. Ceram. Soc., 72 [6] 1047-49 (1989)

Combustion Synthesis of the Titanium-Aluminum-Boron System

Yutaka Taneoka and Osamu Odawara*
Department of Electronic Chemistry, Tokyo Institute of Technology, Nagatsuta,
Midori-ku, Yokohama 227, Japan

Yoshinari Kaieda
National Research Institute for Metals, Nakameguro,
Meguro-ku, Tokyo 153, Japan

TiB_2 and Al base composite powders, which will offer a weight-saving improvement in stiffness, were produced by combustion synthesis of Ti, Al, and B ternary powder mixtures. Finely dispersed TiB_2 was synthesized by reacting a mixture of Ti, Al, and B in the molar ratio of 1:1:4. The grain size of the TiB_2 formed was <0.5 μm, which was much smaller than that obtained from the reaction of a mixture of Ti, Al, and B in the molar ratio 1:1:2. These results are discussed in light of the reaction propagating velocity and heat removal during the combustion synthesis process. [Key words: TiB_2, combustion synthesis, powder, and aluminum.]

TITANIUM DIBORIDE has great potential not only as a refractory material, but also as an electronic material because of its high melting point, hardness, electrical conductivity, and thermal conductivity. For its production, an exothermic and self-propagating solid-state reaction (combustion synthesis) of Ti and B powder compacts has recently received much attention. The characteristics of combustion synthesis of that system have been investigated by several researchers.[1-4] Combustion synthesis has two advantages: (1) heat generated in the exothermic reaction accelerates the process and (2) the resulting TiB_2 is fine grained with a grain size smaller than that of the starting Ti metal. In the combustion synthesis process capable of producing fine-grained materials, the presence of a liquid phase during the process is expected to play an important role. Maksimov *et al.*[3] have investigated the combustion synthesis of the Ti-B-Fe system. By lowering the melting point of the product phase, Maksimov *et al.* obtained finely dispersed TiB_2 (≈ 1 μm) in an Fe matrix.

In the present work, Al is selected because its molten state extends over a large range of temperatures (935 to 2400 K) and it is expected to produce a unique Ti-Al-B composite by combustion synthesis. Using a mixture of Al+2B, it should be possible to synthesize AlB_2. However, the heat of reaction of $Al+2B=AlB_2$ (66.9 kJ) is much smaller than that of $Ti+2B=TiB_2$ (323.8 kJ), and it is expected that the same would be the case regarding their standard free energy of formation. Thus, in the mixture of Ti+Al+2B, it is expected that TiB_2 will form and not AlB_2. However, in using a mixture of Ti+Al+4B, AlB_2 and TiB_2 could be synthesized simultaneously, by using heat evolved from the Ti+2B reaction.

To investigate the effect of Al addition on the reaction of Ti and B mixtures, combustion synthesis has been performed for the Ti+Al+2B and Ti+Al+4B systems as well as for the Ti+2B and Ti+4B powders.

EXPERIMENTAL PROCEDURE

The starting mixtures were Ti (≈ 50 μm), amorphous B (≈ 0.1 μm), and Al (≈ 100 μm) powders. The compositions of the powder mixture investigated in the present work are listed in Table I. The initial powders were mixed in a ball mill for several hours. Each powder mixture was mechanically pressed into a cylindrical sample 25 mm in diameter and 50 mm in height, with a green density of about 50% of theoretical. Then, the test sample was placed in a closed chamber, which was first evacuated and then filled with Ar gas at atmospheric pressure. The test sample was ignited at one end by using an electrically heated W wire (0.5 mm in diameter). The combustion velocity was measured by the conventional method,[5] using two alumel–chromel thermocouples 30 mm apart on the sidewall of sample.

Microstructures of the fractured surface of the end products were observed by scanning electron microscopy (SEM). The phases formed were analyzed by X-ray powder diffraction (XRD).

RESULTS AND DISCUSSION

Figure 1 shows XRD patterns of the end products synthesized from the specific composition mixtures given in Table I. The products synthesized from both Ti+Al+2B and Ti+Al+4B systems were composed of TiB_2 and Al, and those from the Ti+2B and Ti+4B systems were composed of TiB_2. Since the analysis by a wet technique indicated that the element compositions of each product were almost the same as those for the starting powders, it appears that any dispersion or evaporation of starting powders did not occur during the combustion propagation process. Excess B in the Ti+4B and Ti+Al+4B systems could not be identified by the present XRD technique. Zavitsanos and Morris[4] have studied TiB_2 combustion synthesis using a mixture containing Ti+2B with 20 wt% of Al. The added Al was observed to be completely vaporized by the "self-purification" of the combustion synthesis, and the final product was TiB_2 only. However, the present results show that Al also remained in the product, and

Table I. Composition of Starting Powder Mixtures and Experimental Results Obtained in the Present Work

No.	Mole ratio of powder mixture Ti	Al	B	T_{ad} (K)	v_c (mm/s)
1	1	0	2	3203	80–90*
2	1	1	2	2333	51
3	1	0	4	2453	41
4	1	1	4	2139	21

*Extrapolated value from the data obtained by the reactions of Ti+2B powders with adding Al or B from 0.5 to 3 in molar ratios.[6] (The direct data obtained with Ti+2B were distributed from 34 to 149 m/s because of the excessiveness of reaction with amorphous B.)

A. Virkar—contributing editor

Manuscript No. 199044. Received June 27, 1988; approved October 19, 1988.

*Member, American Ceramic Society.

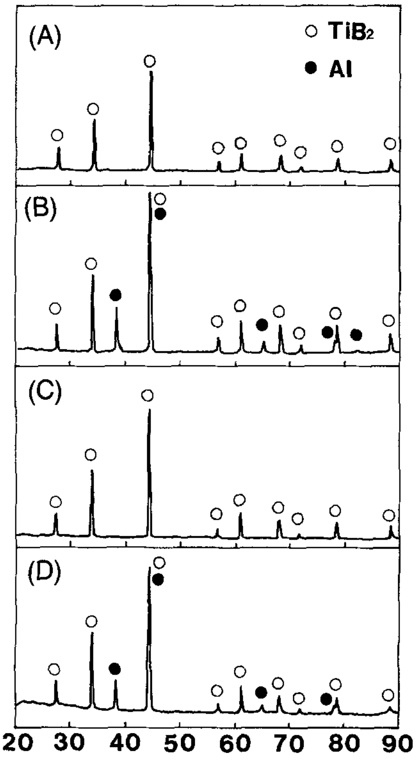

Fig. 1. XRD patterns of products with various compositions of starting powder mixtures: (A) Ti+2B, (B) Ti+Al+2B, (C) Ti+4B, and (D) Ti+Al+4B.

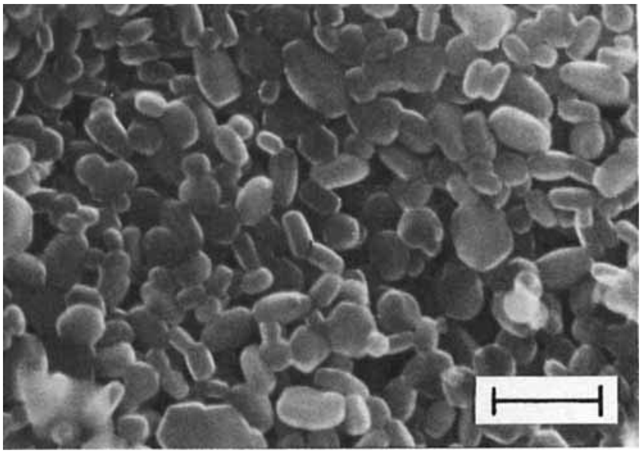

Fig. 2. SEM photograph of the fractured surface of the product obtained from the ternary mixture of Ti+Al+4B (bar=1 μm).

the loss of reactant element was negligibly small, contrary to previous results. Since Zavitsanos and Morris performed the reaction in a vacuum, the vaporized Al dispersed and did not remain in the product.

As shown in Table I, the adiabatic maximum temperature (T_{ad}) calculated from the data of reaction heat was varied by adding Al and/or B, and the combustion velocity (v_c) decreased with increasing amount of Al or B added to the Ti+2B. This means that excess Al or B should hinder the propagation of combustion and should also act as a diluent, which decreases the temperature of the combustion front. The combustion velocity of the sys-

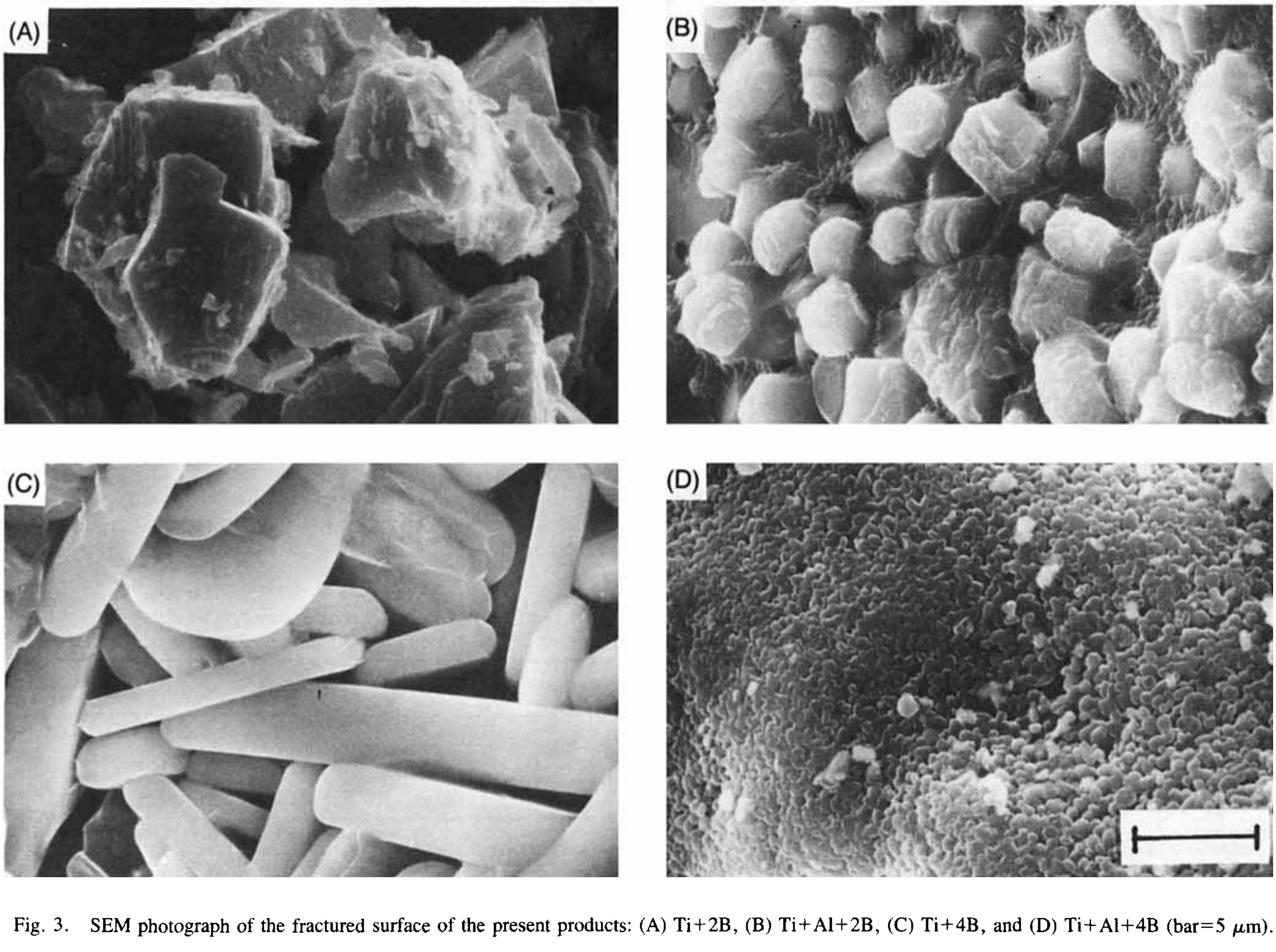

Fig. 3. SEM photograph of the fractured surface of the present products: (A) Ti+2B, (B) Ti+Al+2B, (C) Ti+4B, and (D) Ti+Al+4B (bar=5 μm).

tems tested in the present work considerably increases with the increase of the relative density of the reactant mixture in the region from 40% to 60%.[6] In the case of an aluminothermic reaction, the dispersion of the gaseous phase plays a predominant role in combustion propagation, and, therefore, the combustion velocity decreases with increasing relative density.[7] In view of this difference in the dependence of combustion velocity on the relative density of the sample, the combustion propagation in the present reaction should be affected not by the gaseous phase, but by the amount of heat generated at the combustion front and the preheated zone width in the front.

Figure 2 shows an SEM photograph of a fractured surface of the product synthesized from the reactant composition of the Ti+Al+4B mixture. As can be seen from Fig. 2, the grain size was <0.5 μm, and the particulates were finely dispersed. Similar observation was also made by Brupbacher *et al.*[8] in their experimental work on ceramic–metal composite formation by heating Ti-Al-B powder mixtures in a furnace. However, these authors did not discuss any effect of the composition of Al and B. Addition of Al or B to Ti+2B powders did not significantly change the particle size from that synthesized from Ti+2B, which was about 5 μm, as shown in Fig. 3. Since the starting Ti powder was about 50 μm in size, the size of the TiB_2 produced was about one-tenth of that of the starting Ti.[1] This may be due to the partial melting of Ti behind the combustion front, resulting in the increase of nucleation rate. Addition of Al+2B to Ti+2B did not lead to the formation of AlB_2 in the final product, but a drastic reduction in the particle size of TiB_2 formed was noted. Since such a reduction in particle size was not observed with the addition of Al or B to Ti+2B, the addition of both Al and B must affect the nucleation and growth of produced TiB_2 in the process. As a preliminary result of combustion synthesis in the $Ti+2B+AlB_2$ system, a reduction of particle size similar to that of the Ti+Al+4B system was observed, and the product was also composed of TiB_2 and Al.[6] Considering these results, it is estimated that, in the case of Ti+Al+4B, AlB_2 would be produced during the process of combustion propagation, which would then decompose at high temperature, resulting in lowering the temperature behind the combustion front. The net effect is that TiB_2 particles cannot grow, unlike in other situations studied.

Detailed investigation of the decomposition of AlB_2 showed that AlB_2 decomposed into AlB_{12} and Al at 1200 K, and the AlB_{12} further decomposed into constituent elements at 2300 K.[9] Therefore, considering this decomposition of AlB_2 at high temperatures, it is reasonable to suppose that the final products are TiB_2 and Al even if AlB_2 is produced initially.

CONCLUSION

Finely dispersed TiB_2 and Al composite powders were produced by combustion synthesis of the ternary reactant system of Ti+Al+4B powder mixture. Although the process details are not completely clear at the present time, the formation and decomposition of AlB_2 during the process should play an important role in the fine dispersion of the TiB_2 product.

REFERENCES

[1] J. B. Holt, D. D. Kingman, and G. M. Bianchini, "Kinetics of the Combustion Synthesis of TiB_2," *Mater. Sci. Eng.*, **71**, 321–27 (1985).

[2] Y. Miyamoto, M. Koizumi, and O. Yamada, "High-Pressure Self-Combustion Sintering for Ceramics," *J. Am. Ceram. Soc.*, **67** [11] C-224–C-225 (1984).

[3] Yu. M. Maksimov, A. G. Merzanov, A. T. Pak, L. G. Raskolenko, and B. Sh. Braverman, "High-Temperature Synthesis of the Ti-B-Fe System," *Izv. Akad. Nauk SSSR, Met.*, [2] 219–23 (1985).

[4] P. D. Zavitsanos and J. R. Morris, Jr., "Synthesis of Titanium Diboride by a Self-Propagating Reaction," *Ceram. Eng. Sci. Proc.*, **4** [7–8] 624–33 (1983).

[5] O. Odawara, "Ceramic Lined Pipes Produced by a Centrifugal-Thermit Process," *Trans. Jpn. Inst. Met.*, **26**, 336–44 (1985).

[6] Y. Taneoka, "Effect of Al Addition on Combustion Synthesis of TiB_2"; MS Thesis. Tokyo Institute of Technology, Tokyo, Japan, 1989.

[7] E. I. Maksimov, A. G. Merzanov, and V. M. Shkiro, "Gasless Composition as a Simple Model for the Combustion of Nonvolatile Condensed Systems," *Fiz. Goreniya Vzryva*, **1–4**, 24–30 (1965).

[8] J. M. Brupbacker, L. Christodoulou, and D. C. Nagle, "Process for Forming Metal–Ceramic Composites," U.S. Patent No. 4710348, Dec. 1, 1987.

[9] T. Atoda, I. Higashi, and M. Kobayashi, "Processes of Formation and Decomposition of Aluminum Borides," *Sci. Pap. Inst. Phys. Chem. Res.*, **61**, 92–99 (1967). ☐

---

journal

J. Am. Ceram. Soc., **72** [6] 1049-54 (1989)

Microstructure and Mechanical Properties of Mullite–Silicon Carbide Composites

M. Isabel Osendi,*,* Barry A. Bender,* and David Lewis III*

Naval Research Laboratory, Washington, D.C. 20375–5000

Mullite–SiC-whisker composites were prepared by powder processing using two commercial SiC whiskers. These composites were prepared by sintering rather than hot-pressing. A mullite–SiC-powder composite and a base line mullite material were also prepared for comparison with the two whisker composite materials. Fracture toughness measurements showed significant enhancement in only one of the whisker composite materials. The microstructure of the four materials was examined by scanning electron microscopy and transmission electron microscopy to assist in the explanation of the mechanical behavior of these composites. The examinations suggested that most of the toughening results from second-phase particles, with only limited toughening from effects associated with whiskers per se. In one case, higher toughness was partially associated with the formation of a sialon phase by reaction with the whiskers and the furnace environment. [Key words: mullite, silicon carbide, composites, whiskers, mechanical properties.]

J. J. Petrovic — contributing editor

Manuscript No. 199104. Received May 31, 1988; approved November 11, 1988.

Presented at the 40th Pacific Coast Regional Meeting of the American Ceramic Society, San Diego, CA, November 2, 1987.

*Member, American Ceramic Society.

*Presently at The Instituto de Ceramica y Vidrio, Madrid, Spain.