The Korean Journal of Ceramics, **4** [3] 227 - 230 (1998)

Properties of Hot Pressed Alumina-Titanium Diboride Particulate Composites

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(Received June 12, 1998)

Alumina (Al_2O_3)-Titanium Diborde (TiB_2) particulate composites were fabricated by hot pressing of the powder mixture that was prepared from Self-propagating High Temperature Synthesis (SHS) product and commercial powders. Their properties were examined in order to find feasibility of using SHS for making the high performance ceramic composite. TiB_2 particles obtained by grinding the SHS product were finer than the commercial powders. Hot pressed sample containing the SHS products exhibited higher strength than the one prepared from the commercial powders.

Key words : Alumina, Titanium diboride, Self-propagating high temperature synthesis, Hot pressing

I. Introduction

Alumina based ceramic composites have been studied and developed for structural applications including cutting tools.[1] Titanium carbide particles and silicon carbide whiskers were most widely used for reinforcing the composites. Titanium diboride is known to exhibit as high hardness as and lower electrical resistivity than titanium carbide.[2] While titanium carbide has cubic crystal structure, titanium diboride has hexagonal crystal structure and thermal expansion coefficient along c-axis is significantly larger than that along the other directions.[3] Titanium diboride has been used for toughening the silicon carbide ceramics,[4] zirconia ceramics[5] and alumina ceramics.[2),(6]

SHS was introduced by Merzhanov and Borovinskaya.[7] The process takes advantage of heat generated in order to sustain the exothermic reaction, and it can make any compound as long as the reaction involved produces enough heat. TiB_2 was easily formed by SHS process from titanium and boron because the reaction is highly exothermic.[8] However, price of elemental boron is more expensive than TiB_2, and the process was prohibitive from economic point of view. In this study, boron oxide and titanium oxide instead of B and Ti, respectively were used for making TiB_2 in order to lower cost of fabrication. Aluminum powder was employed for reducing agent of the oxides to make Al_2O_3+TiB_2 composites. Since ratio between Al_2O_3 and TiB_2 of the SHS reaction product was fixed at molar ratio of 5 : 3, which gave 26.5 vol. % of TiB_2 in Al_2O_3 matrix, commercial alumina power was added to the SHS product in order to vary TiB_2 content in the composite.

II. Experimental

TiO_2 powder (GR reagent grade, Shinyo Pure Chemical Co., Osaka, Japan) and B_2O_3 powder (Junsei Chemical Co., Tokyo, Japan) and aluminum powder (-325 mesh, Chang-Sung Corp., Inchon, Korea) were mixed by dry ball milling for 8 hours in polyethylene bottle. Steel balls of 5 mm in diameter were used for mixing. Molar ratio of the three powders was 3 : 3 : 10, which was stoichiometric ratio to make 3 TiB_2 and 5 Al_2O_3. Mixed powder was formed by lever press under 10 MPa into a cylindrical shape of 30 mm in diameter and 20 mm in length. The powder compact was subject to the S.H.S. reaction, which was initiated by tungsten filament in flowing argon atmosphere. The porous reaction product was examined by X-ray diffraction, and was ground by planetary ball milling. Planetary ball milling was carried out for 4 hours by using ethanol, plastic jar and alumina balls of 5 mm in diameter. Ball to powder ratio was 10 to 1. Ground powder was mixed with commercial alumina powder (AKP-30, Sumitomo Chemical Co., Osaka, Japan) by planetary ball milling for 4 hours with ball to powder ratio of 3 to 1. Four kinds of samples were prepared by hot pressing at 1923 K for 0.67 hour under 30 MPa. They were 30 wt% SHS powder +70 wt% alumina powder (TBA30), 60 wt% SHS powder +40 wt% alumina powder (TBA60), and SHS powder only (TBA100). Alumina-17 vol. % TiB_2 composite was also prepared for comparison by using commercial powders; alumina (AKP-30) and TiB_2 (H.C. Starck Co., Berlin, Germany). Hot pressed samples were characterized by the three point flexural strength (3 mm × 4 mm × 20 mm), Microvickers harndess (4.9 N load), and fracture toughness (indentation crack length method

Fig. 1. Pictures of SHS reaction : $3TiO_2+3B_2O_3+10Al=3TiB_2+5Al_2O_3$.

obtained by using 49 N load). Samples were examined by optical microscope and SEM before and after etching in molten KOH salt for 20 seconds, respectively.

III. Results and Discussion

Fig. 1 shows a series of pictures taken during the SHS reaction. It shows that large amount of gas was generated during the reaction, part of which was thought to be moisture absorbed by the powders. B_2O_3 powder was very easy to absorb moisture to make boric acid. Since melting point of B_2O_3 was 723 K,[9] significant amount of it was thought to be lost during the reaction. However, slight increase of B_2O_3 from the stoichiometric ratio in the powder mixture for SHS reaction resulted in alumium borate ($Al_8B_2O_{15}$) while stoichiometric composition produced alumina, titanium diboride and small amount of Al_2TiO_5 as revealed by XRD analysis shown in Fig. 2. Loss of B_2O_3 during SHS reaction left unreacted TiO_2 that reacted with Al_2O_3 to make Al_2TiO_5. Even though reaction temperature was hard to determine due to large amount of the gas generated, color of the flame implied that the temperature was extremely high. Thermodynamic calculation indicated that the reaction temperature was slightly higher than melting point of alumina (2327 K) and much lower than that of titanium diboride (3193 K) if heat dissipated by the gas evolution was ignored. Fig. 3 shows SEM micrograph of the SHS reaction product after grinding. They consisted of very fine particles and coarse particles of a few micrometers in diameter.

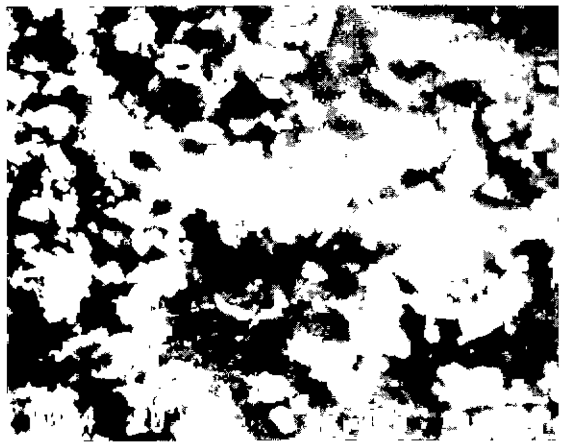

Fig. 3. SEM micrograph of the ground SHS product.

Densities of hot pressed samples prepared by using the SHS reaction product were higher than 99.5% if the reaction product consisted of Al_2O_3 and TiB_2 only. Density of the sample prepared by using the commercial Al_2O_3 and TiB_2 powders was 98.4% theoretical. Fig. 4 shows microvickers hardness values of the samples. Higher hardness of the sample with higher content of TiB_2 was explained by hardness of TiB_2 which was reported to be higher than 30 GPa.[2] Samples TBA30, TBA60 and TBA 100 corresponded to 7 vol%, 14 vol% and 23.7 vol% TiB_2-

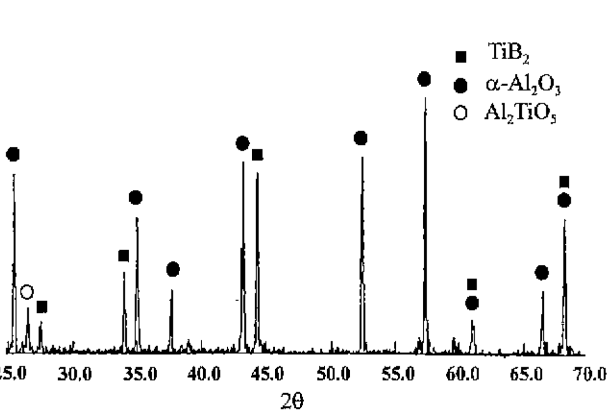

Fig. 2. XRD pattern of the SHS reaction product.

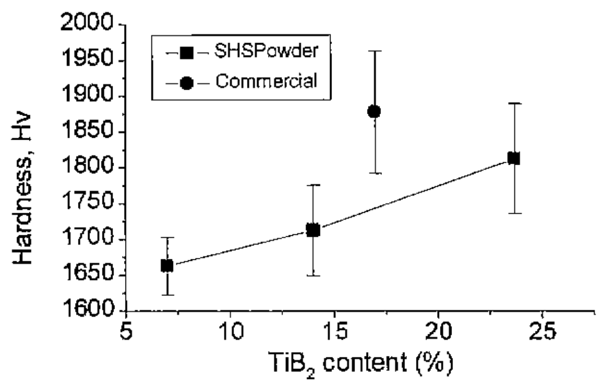

Fig. 4. Microvickers hardness values of the samples: TBA30 : 16.62±0.4 GPa, TBA60 : 17.12±0.63 GPa, TBA100 : 18.12± 0.77 GPa, comparison sample : 18.77±0.86 GPa.

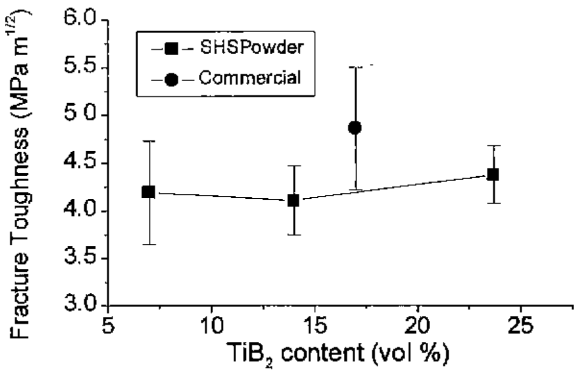

Fig. 5. Fracture toughness values of the samples measured by indentation crack length method : TBA30 : 4.19±0.54 MPa √m, TBA60 : 4.11±0.36 MPa√m, TBA100 : 4.38±0.3 MPa √m, comparison sample : 4.86±0.64 MPa√m.

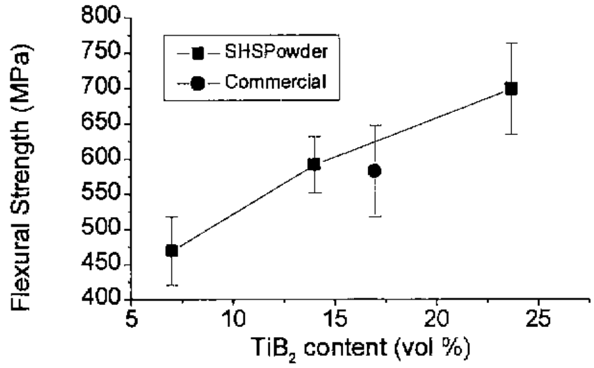

Fig. 7. Three point flexural strength of the samples : TBA30 : 469±49 MPa, TBA60 : 592±40 MPa, TBA100 : 699±64 MPa, and comparison sample : 583±65 MPa.

Al_2O_3 composite, respectively if the SHS product consisted of TiB_2 and Al_2O_3 only. However, the SHS product included not only TiB_2 and Al_2O_3 but also Al_2TiO_5. Reason for lower hardness of sample TBA100 than that of the comparison sample is possibly explained by the presence of Al_2TiO_5 which is thought to have lower hardness than Al_2O_3 or TiB_2(10). Fig. 5 shows the fracture toughness values

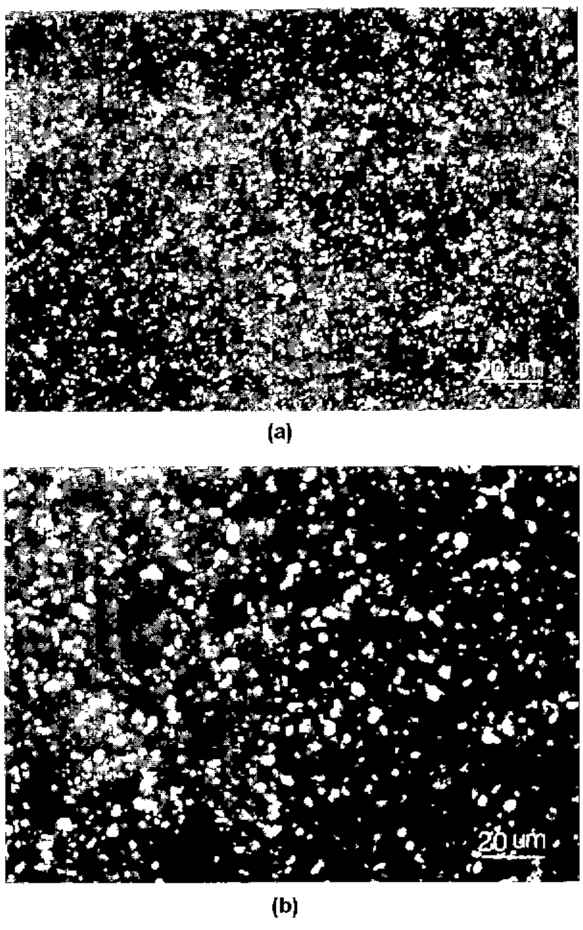

Fig. 6. Optical micrographs of (a) TBA100 and (b) the comparison sample.

according to TiB_2 content. TiB_2 particles were expected to improve the fracture toughness like TiC particles in Al_2O_3-TiC composites.[6] However, the fracture toughness values did not vary much according to TiB_2 content. Principal mechanism for toughening in Al_2O_3-TiB_2 composite was reported as crack deflection around TiB_2 particles.[6] However, thermal expansion difference between TiB_2 and Al_2O_3 was very small and thermal residual stress facilitating crack deflection as in SiC-TiB_2 composite[11] was not expected. Liu and Ownby reported that the fracture toughness of Al_2O_3-TiB_2 composite depended on TiB_2 particle size and showed a maximum when it was 3-6 μm.[12] The reason for lack of dependence of the fracture toughness of the samples on the TiB_2 content was that the TiB_2 particles were too fine. Fig. 6 shows optical micrographs of TBA100 and the comparison sample. Bright spots were the TiB_2 particles, and it is readily recognized that they were much finer in TBA100 than in the comparison sample. Fine particles shown in Fig. 3 should be TiB_2 while larger ones were oxide particles. Fine TiB_2 particles were effective for inhibiting growth of alumina grains. Fig. 7 shows that flexural strength of TBA60 was slightly higher than the comparison sample although the former contained smaller amount of TiB_2 than the latter. Fig. 8 shows the microstructures of the samples after etching. TiB_2 particles were lost during etching and they left pores at the sites. Size of the alumina grains decreased as TiB_2 content increased. Grain size of TBA60 was similar to that of the comparison sample while TBA100 consisted of much finer grains. Fine TiB_2 particles made by SHS reaction inhibited the grain growth and increased flexural strength of the composite.

IV. Conclusions

TiB_2 and Al_2O_3 were formed by SHS reaction of TiO_2, B_2O_3 and Al. Even though small amount of Al_2TiO_5 also formed by the reaction, the mechanical properties of the composite were comparable to those obtained from the sample prepared by using commercial TiB_2 and Al_2O_3

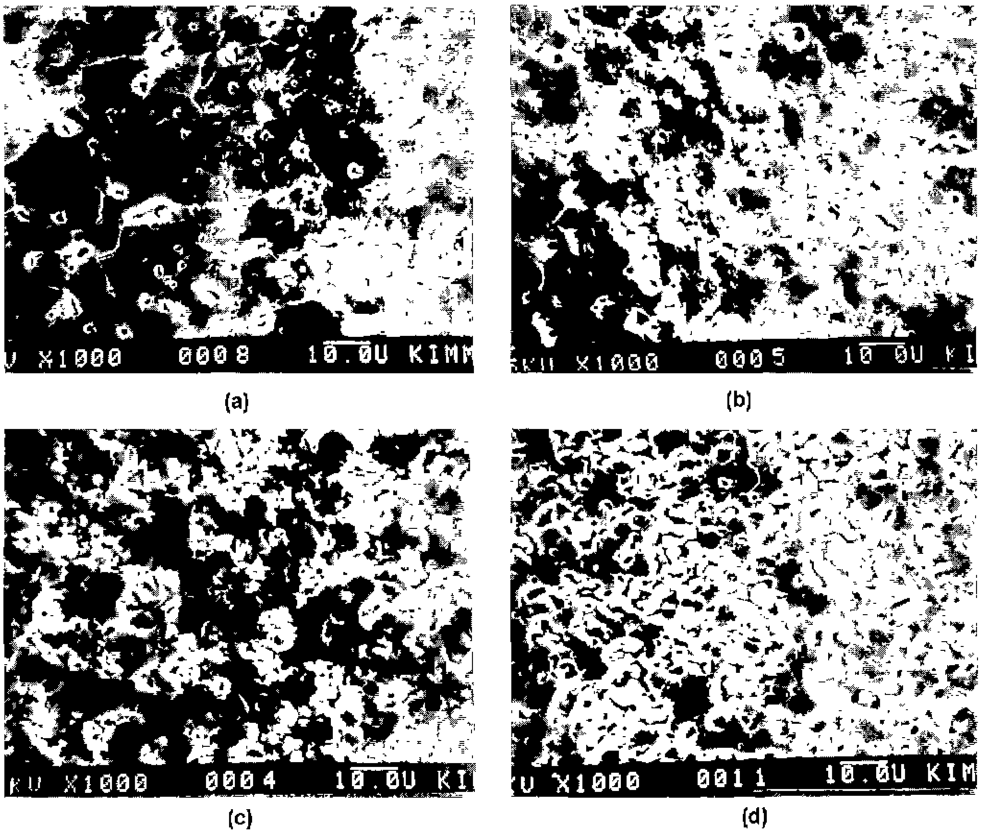

Fig. 8. SEM micrographs of the samples after etching in molten KOH; (a) TBA30, (b) TBA60, (c) TBA100 and (d) the comparison sample.

powders. TiB_2 particles in the SHS product were much finer than those of the commercial powder, and inhibited growth of Al_2O_3 grains, which was contributed to higher flexural strength of the composite.

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