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Preparation of Titanium Carbide Fiber-Reinforced Alumina Ceramic Matrix Composites by Self-Propagating High-Temperature Synthesis

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Al_2O_3-TiC composites were prepared from aluminum, titanium oxide, and carbon fibers by self-propagating high-temperature synthesis (SHS). After the SHS reaction, the TiC phase in the sample was found either fibrous or non-fibrous shape. The fraction of the fibrous TiC phase varied with the amount of Al_2O_3 diluent addition. The optimum amount of diluent to make fibrous carbide was determined to be 30%. The fibers were hollow inside and made of multiple grains with a composition of titanium carbide. The hollow fiber formation mechanism was suggested and discussed. The synthesized powders were consolidated to dense composites by hot pressing at 1750°C under 30 MPa.

Key words : Self-propagating high-temperature synthesis (SHS), Ceramic matrix composites (CMC), TiC fibers, Morphology, Fiber forming mechanism, Hot pressing

I. Introduction

Self-propagating high-temperature synthesis (SHS) is a simple method for the synthesis of carbides, borides, oxides, nitrides, or intermetallic materials from a mixture of constituent powders. The synthetic reaction is activated and propagated by the heat generated from the self-reaction.[1] Origin of SHS was the discovery of thermite reaction by H. Goldschmidt 100 years ago, but the method was fully developed by Merzhanov and Borovinskaya three decades ago.[2] SHS has several advantages over other methods for synthesis because it is simple, capable of giving high purity products, cost-effective, highly productive and can produce powders in the pseudo-equilibrium state that are highly sinterable.[3]

Recent industrial development requires advanced materials with high performances such as ceramic matrix composites (CMCs). CMCs have fibers, whiskers, or particulate materials as second phases, and thus have good mechanical and thermal properties. Al_2O_3-TiC particulate composites, for example, have good strength and hardness and are used for cutting tool inserts. If the TiC phase in the composites has a fibrous shape, the toughness of the composites would increase due to its high aspect ratio. However, non-oxide fibers are not easy to produce or obtain.

The SHS method has been used to produce non-oxide materials. While most materials synthesized by the SHS method have a particulate or equiaxed shape, synthesis of fibers by SHS has been reported in just a few papers.[4-8] Mullins *et al.*[5] found that the morphology of SHSed TiC changed with the shape of carbon, used for a raw material. Choi *et al.*[6,7] prepared fibrous TiC by SHS and also Al matrix composites containing TiC fibers by SHS. However, SHS of CMCs with TiC fibers has not been studied and the mechanism of TiC fiber formation is not clearly understood.

In the present study, Al_2O_3 matrix composites containing TiC fibers were prepared by the thermite reaction of aluminum, titanium oxide and carbon fibers. Mechanism of TiC fiber formation was suggested and discussed.

II. Experimental Procedure

Aluminum powders, titanium oxide powders and carbon fibers were ground and mixed with an agate mortar and pestle with 0, 20, 30, or 40% addition of aluminum oxide for diluent as indicated in equation (1). The percentages of alumina addition were determined based on the weight of TiC. They correspond to 0, 0.353, 0.529, and 0.705 in x values in equation (1).

$$3TiO_2 + 4Al + 3C_{fiber} + xAl_2O_3 = 3TiC + (2 + x)Al_2O_3 \quad (1)$$

Al and TiO_2 powders used were of 99% purity. Carbon fibers (Taekwang Ind. Co., Korea) were of 6.8 μm diameter and of 1 mm length (Fig. 1). The mixtures were pressed under 30 MPa to make disks of 2 cm diameter. The disk-shaped sample was ignited with an electric arc. SHS reaction was triggered and lasted for about 10 seconds. After synthesis, samples were ground with an

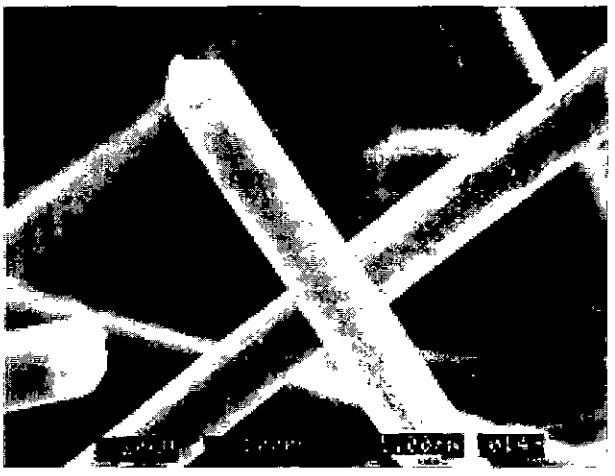

Fig. 1. Shape of the carbon fibers used for the SHS experiment.

agate mortar and pestle. Ground powders were consolidated by hot pressing under 30 MPa at 1650°C or 1750°C for an hour. Powders and samples were examined by an optical microscopy, x-ray diffractometer (XRD), scanning electron microscopy (SEM), and energy dispersive x-ray spectrometry (EDS).

III. Results and Discussion

1. Preparation of Al_2O_3-TiC composites powders by SHS

After the SHS reaction, the phase analysis by XRD revealed that alumina and titanium carbide were the main phases with very small amount of graphite, showing that the SHS reaction was almost completed (Fig. 2). Fig. 3 shows the fracture surfaces of SHSed samples with and without diluent alumina addition. In the sample with diluent additions, TiC fibers were observed all around the

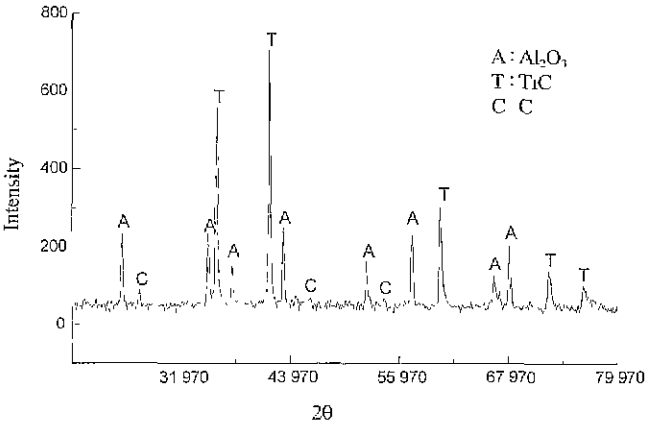

Fig. 2. Result of x-ray diffractometer (XRD) analysis of Al_2O_3-TiC sample after SHS reaction.

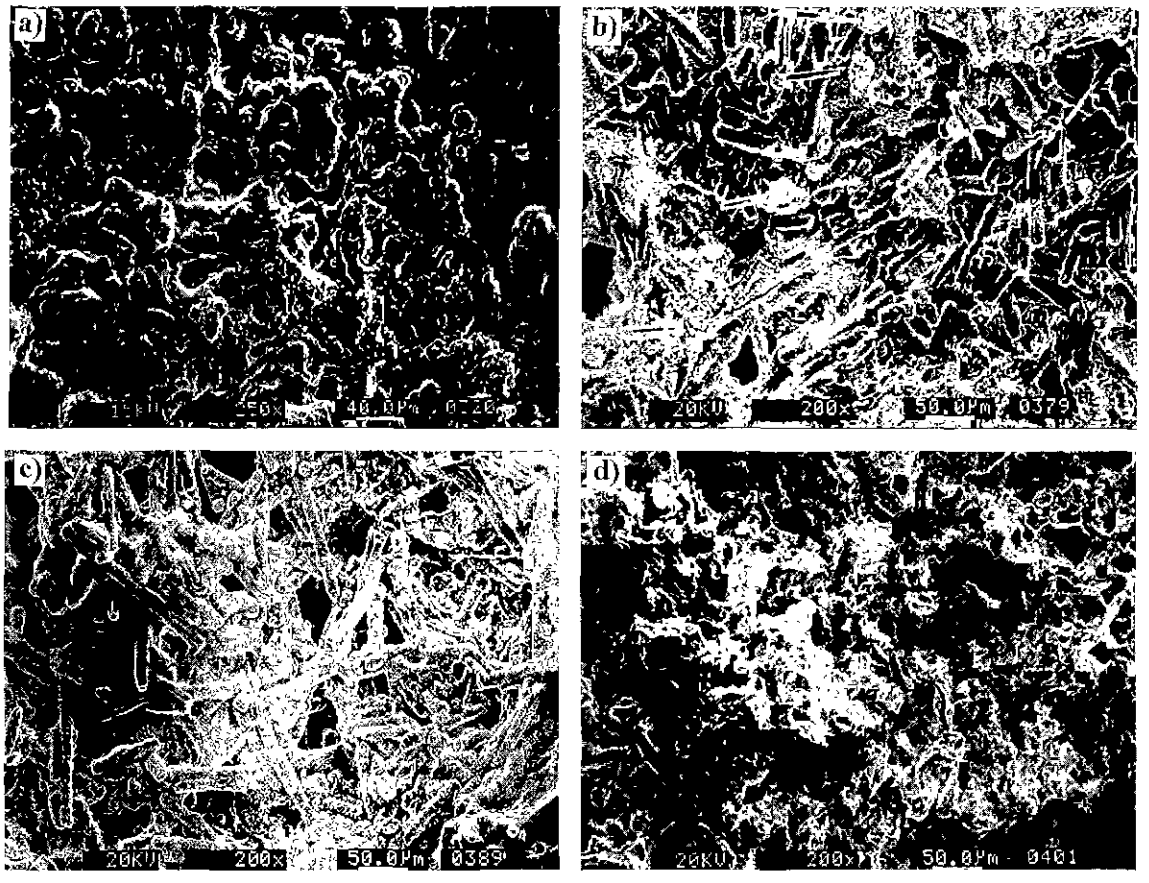

Fig. 3. Fracture surface of SHSed Al_2O_3-TiC sample with additions of Al_2O_3 diluent of a) 0%, b) 20%, c) 30% and d) 40%.

sample. Without addition, it was found that the fiber was not formed uniformly around the sample. Higher fiber content was observed near the surface of the sample. The reason for the morphological variation would be related to the change in the reaction temperature with diluent addition.[9] When the reaction temperature is higher than the eutectic reaction temperature, T_E=2776°C, of TiC and C, the TiC phase would not be directly formed on the surface of the carbon fiber, which is not in local equilibrium with solid TiC phase, but with Ti-C melt. Then, synthesized TiC phase would not follow the morphology of the carbon fiber. When the temperature is lower than T_E with the diluent addition, TiC phase can be formed directly on the surface of the carbon fiber, which is not in local equilibrium with Ti-C melt, but with solid TiC. The suggested explanation is in consistent with the observation of fibrous TiC on and near the surface of the SHSed sample without diluent addition, where the reaction temperature is lower than inside of the sample due to the dissipation of heat, while no fibers are observed inside of the sample. The optimum amount of diluent for the fiber formation was determined to be 30%.

The surface of TiC fiber was not smooth and was covered with small grains. It was quite different from the morphology of fibers synthesized by the reaction of Ti and C fibers in the absence of additional materials[8] (Fig. 4). The reaction sequence is suggested as follows. At the initial stage, aluminum, which is melted by the ignition, surrounds the titanium oxide powders and reduces TiO_2 to Ti. Reduced titanium reacts with carbon, forming titanium carbide. As a result of the excessive heat generated from both reactions, titanium with a melting point of 1670°C and alumina with a melting point of 2050°C melt. When two liquids surround the fibers, the TiC phase is formed on the fiber surface by the reaction between Ti and C. Whether two liquid phases would homogeneously mix or be separated is not known, but other experimental results suggest that two phases would mix.[10] When the carbon fiber is partly covered with titanium in the presence of alumina melt, the reaction of C and Ti would be limited by the physical blocking of alumina melt on the carbon fiber surface. Then TiC would not be formed uniformly on the surface as in the case of pure reaction between Ti and C. Rather in separate regions where the titanium contact the surface, TiC phase would be formed discretely on the fiber surface. Then the carbide grains would grow larger and make contacts with each other. Finally carbide fibers would be formed by the connected grains. The suggested mechanism is consistent with the experimental results. The scanning electron microscopic observation in the cross-sectional view showed that most fibers were made of many small grains as shown in Fig. 5. The fiber composition was determined by energy dispersive x-ray spectromety (EDS) to be mainly titanium and carbon with small amount of aluminum and oxygen. Probably some aluminum oxide was captured between growing TiC grains and formed a grain boundary second phase, while most liquid alumina was pushed away from the fiber surface as carbide grains grew.

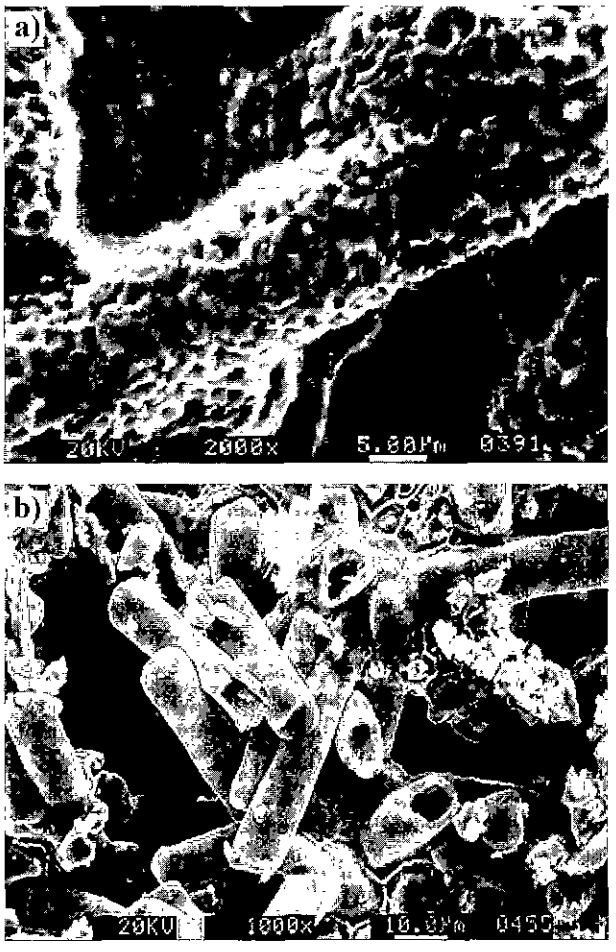

Fig. 4. Morphology of TiC fibers synthesized by SHS reaction between Ti and carbon fibers a) in the presence and b) in the absence of aluminum or alumina.[8]

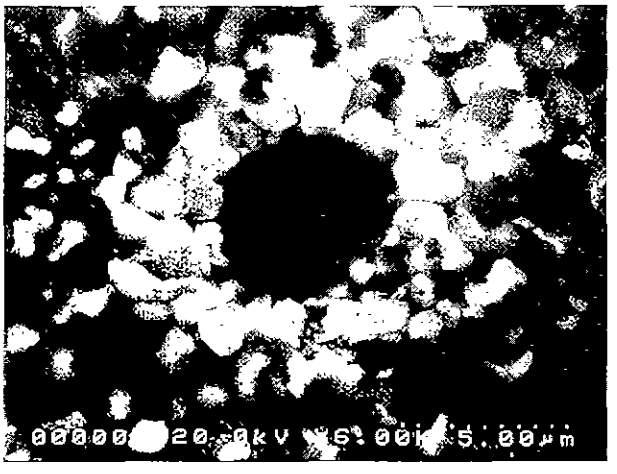

Fig. 5. SEM micrograph of the cross-section of Al_2O_3-TiC sample prepared by SHS reaction. Note the tube-like shape of TiC fibers having brighter contrasts.

The fibers produced were hollow inside and hence were tube-like as was the case of TiC fibers produced by SHS in the absence of aluminum or alumina. The formation mechanism of hollow carbide fibers would be similar to the former case in the absence of aluminum or alumina.[8,9] After the first formation of TiC phase at the C-Ti boundary on the surface of the carbon fibers, the carbide phase would further grow by the reaction between C and Ti at two growing fronts : C-TiC or inner boundary, and TiC-Ti or outer boundary. Titanium and carbon diffusion through TiC were required for the growth of TiC at inner and outer boundaries, respectively. Since carbon diffuses much faster than titanium does in TiC,[11,12] the rate of TiC growth at the outer boundary in the outward direction would be much faster than that at the inner boundary in the inward direction. Then most carbon would diffuse out, forming hollow fibers with TiC shell and empty core.

2. *Consolidation of Al_2O_3-TiC by hot pressing*

SHSed samples with 30% diluent addition were consolidated by hot pressing. Before hot pressing, the SHSed samples were ground to powders to increase sintering capability. When the sample was hot pressed under 30 MPa at 1650°C for an hour, the density was 95.5%. When the sample was hot pressed at 1750°C for an hour, the density increased to 99.3%. The XRD analysis showed that the major phase was alumina and TiC with very small amount of graphite and TiO_2. TiC phase appeared to have non-fibrous shape, but some TiC phase formed a closed circuit, like a deformed ring shape, as shown in Fig. 6a. Some fibers would have been broken during grinding after SHS, and some fibers would have been deformed during hot-pressing. TiC fibers could have been deformed due to their hollow microstructure and enhanced diffusion under high temperature and pressure during hot pressing. Deformation would have been enhanced also by the presence of aluminum oxide at the grain boundaries which had a relatively low melting point.

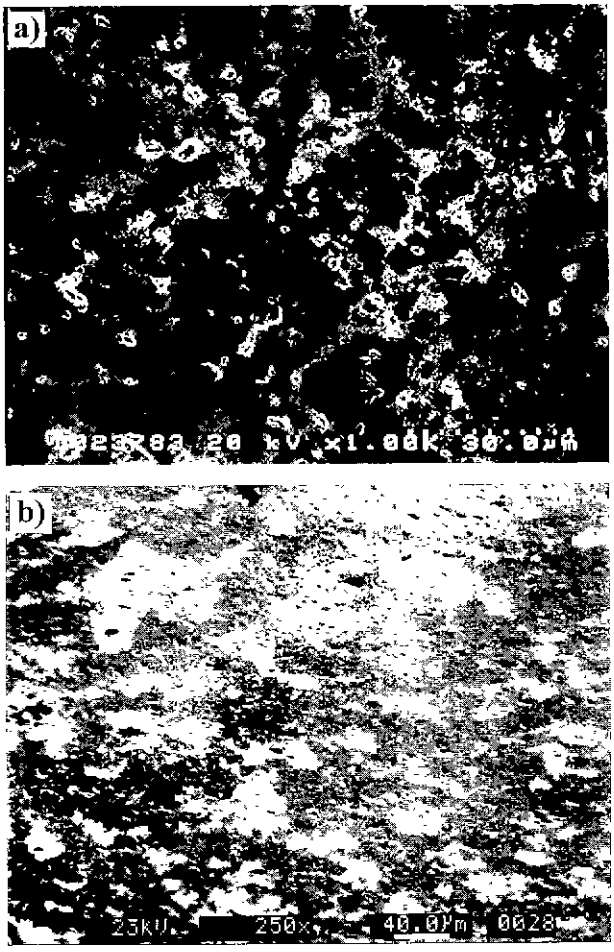

Fig. 6. SEM micrograph of Al_2O_3-TiC sample prepared a) by hot pressing of SHSed Al_2O_3-TiC powders after grinding and b) by hot-pressing of the mixture of SHSed and ground TiC fibers and commercial Al_2O_3 powders.

Other consolidation method was attempted for the comparison. TiC fibers prepared by SHS were mixed and ground with Al_2O_3 commercial fine powders, and the mixture was hot pressed under the same condition. The similar result was obtained: TiC phase had partly fibrous shape (Fig. 6b).

Two solutions are suggested: 1) Control grinding conditions to minimize the breakage of fibers, and to maximize the grinding effect. 2) Consolidate the powders during SHS in situ, using e.g., high pressure self-combustion sintering method.[13] Since constituents are in the liquid state, the fibers would not be broken. If the fibers were aligned in a direction by uniaxial pressing, improvement of mechanical properties would be additionally achieved. Suggested experiments are under progress in the authors' laboratory.

IV. Conclusions

The Al_2O_3 composites with fibrous TiC were prepared by the SHS method and hot pressing. Conclusions were drawn as follows:

(1) Al_2O_3-TiC composite powders were synthesized from aluminum, titanium oxide, and carbon fibers by the SHS method. The morphology of TiC phase varied with the amount of alumina added as a diluent. The TiC phase had a fibrous shape with an addition of diluent, while it did not have without an addition. The optimum amount of diluent addition for the fibrous TiC formation was determined to be 30%.

(2) The synthesized TiC fibers had a hollow tube-like shape and had many small grains on their surfaces. Mechanism of hollow fiber formation was suggested and discussed. The experimental results were consistent with the suggested mechanism.

(3) Highly dense Al_2O_3-TiC composites were prepared by hot pressing of the SHSed powders. The TiC phase

was found to have a partially fibrous shape.

Acknowledgment

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