# **Reactive Hot Pressing of Alumina-Silicon Carbide Nanocomposites**

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A dense alumina-silicon carbide (Al<sub>2</sub>O<sub>3</sub>-SiC) nanocomposite was synthesized in situ from the reaction of mullite, aluminum, and carbon by reactive hot pressing (RHP). Transmission electron microscopy investigation showed that in situ-formed. nanometer-sized SiC particles were mainly entrapped in the matrix grains, whereas submicrometer-sized particles were located at the grain boundaries or triple points of the Al<sub>2</sub>O<sub>3</sub>. In addition, no amorphous phase was observed at the interfaces of the Al<sub>2</sub>O<sub>3</sub> and SiC grains, which indicated strong direct bonding. Fracture-surface analysis by scanning electron microscopy revealed an intrafracture mode. The bending strength of the nanocomposite RHP-treated at 1800°C was  $795 \pm 160$  MPa, and the fracture toughness, measured by the indentation method, was 3.1 MPa·m<sup>1/2</sup>.

## I. Introduction

**R**EACTION synthesis is a promising process for directly fabricat-ing nanomaterials, which are difficult to obtain by the normal sintering of nanometer-sized starting powder compacts because of Oswald ripening at high temperatures. Alumina-silicon carbide (Al<sub>2</sub>O<sub>3</sub>–SiC) composites have received significant attention in the past decades because of their outstanding properties, including high bending strength,<sup>1-6</sup> excellent creep behavior,<sup>7-11</sup> and wear resistance.<sup>12,13</sup> Al<sub>2</sub>O<sub>3</sub>–SiC composites are produced conventionally by hot pressing mechanically mixed Al<sub>2</sub>O<sub>3</sub> and SiC powders (or whiskers) in a nonactive atmosphere. Submicrometer- or nanometer-sized SiC particles are needed to produce Al2O3-SiC nanocomposites. Such SiC powders usually contain oxide scale on the particle surfaces, because of the easy oxidation of fine particles. This oxide scale is believed to degrade the hightemperature mechanical properties of the obtained composites. In the case of  $Al_2O_3$ -SiC<sub>(w)</sub> composites,<sup>14</sup> problems are toxicity during whisker handling and the high cost of whisker production. On the other hand, *in situ* synthesis of composites can eliminate the above-mentioned problems and has been attracting the attention of investigators.

Al<sub>2</sub>O<sub>3</sub>-SiC composites were produced from mixtures of aluminosilicates and carbon by Chaklader et al.<sup>15</sup> Those researchers reported that high temperature, >1500°C, was needed to complete the reactions. Ultimately, a dense Al<sub>2</sub>O<sub>3</sub>-SiC composite with nanometer-sized SiC particles homogeneously distributed in an Al<sub>2</sub>O<sub>3</sub> matrix was obtained by hot pressing the synthesized

composite powders. Borsa et al.<sup>16</sup> and Amroune et al.<sup>17,18</sup> recently studied the reaction conditions for obtaining SiC whiskers in an Al<sub>2</sub>O<sub>3</sub> matrix from kaolin, andalusite, or kyanite (Al<sub>2</sub>O<sub>3</sub>·SiO<sub>2</sub>) and carbon in an argon atmosphere.

However, because CO gas is emitted during the abovementioned reaction process, only Al2O3-SiC composite powders can be prepared; subsequent hot pressing or pressureless sintering is needed to obtain dense composite materials.

Very recently, Al<sub>2</sub>O<sub>3</sub>-SiC composites were prepared from the reaction of SiO<sub>2</sub>-Al-C by the self-propagating high-temperature synthesis (SHS) technique.<sup>19,20</sup> The reaction synthesis of  $Al_2O_3$ -SiC composites without CO release during the process was accomplished by aluminum addition. Dense Al<sub>2</sub>O<sub>3</sub>-SiC composites also can be fabricated by subsequent hot pressing or pressureless sintering of the composite powders obtained from the SHS technique.

The use of aluminosilicates with a high Al<sub>2</sub>O<sub>3</sub> content is beneficial for obtaining Al<sub>2</sub>O<sub>3</sub>-SiC composites with a relatively low SiC content, which is especially common for nanocomposites.<sup>1</sup> In addition, composites with an even lower content and homogeneous distribution of SiC in the Al<sub>2</sub>O<sub>3</sub> matrix are easily obtainable by adding a small amount of Al<sub>2</sub>O<sub>3</sub>. This paper reports a method of preparing Al2O3-SiC nanocomposites based on the reaction of mullite, aluminum, and carbon, as follows:

$$3(3Al_2O_3 \cdot 2SiO_2) + 8Al + 6C \rightarrow 13Al_2O_3 + 6SiC$$
(1)

The calculated content of SiC phase in the obtained composite was 18.25 vol%. Reactive hot pressing (RHP) was used to fabricate the material, and the microstructure and properties of the obtained product were briefly characterized.

### **II. Experimental Procedures**

The preinvestigation revealed that starting materials with too coarse a particle size, e.g., 50-100 µm aluminum powder or  $10-15 \ \mu m$  graphite powder, were unfavorable for preparing dense and homogeneous composites. Accordingly, starting powders with a fine particle size were selected for the present study. The starting powders were mullite, aluminum, and carbon. The characteristics of the raw powders, as provided by the suppliers, are listed in Table I. The stoichiometric powders obtained according to reaction (1) were mixed in ethanol with  $Al_2O_3$  balls for 72 h, in a plastic bottle, and then dried. The obtained mixed powders were RHPtreated in a BN-coated graphite die under a pressure of 30 MPa for 60 min in an argon atmosphere. Material with a relative density of >95% of the theoretical density (TD) was impossible to obtain when the RHP temperature was <1700°C. Accordingly, an RHP temperature of 1800°C was used in the present study. The heating rate was 10°C/min. At temperatures <500°C, a vacuum of  $\sim$ 1.3  $\times$  $10^{-2}$  Pa was maintained in the furnace. Up to 1.3 atm of argon gas was then added to the chamber, and the pressure used for hot pressing was gradually increased to 30 MPa. The obtained product measured 45 mm  $\times$  42 mm  $\times$  6 mm.

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Table I. Characteristics of the Starting Powders

Starting powder	Mean particle size	Chemical composition	Manufacturer
Mullite	0.74 µm	KM102 grade, SiO <sub>2</sub> 28.1 wt%, Al <sub>2</sub> O <sub>3</sub> 71.4 wt%, impurities include (wt%) Fe <sub>2</sub> O <sub>3</sub> 0.017, TiO <sub>2</sub> 0.003, CaO 0.011, MgO 0.013, Na <sub>2</sub> O 0.01, K <sub>2</sub> O 0.003, and ZrO <sub>2</sub> 0.167	KCM Corp. (Nagoya, Japan)
Aluminum	3 µm	99.9% pure; impurities include Fe 0.1%, Ši 60 ppm, Cu 20 ppm	High Purity Chemicals Laboratory (Saitama, Japan)
Carbon	13 nm	2600# grade, volatile 1.8%, impurities include Al $<$ 100 ppm; Na and Fe $<$ 30 ppm; Si $<$ 10 ppm, Ca, Ni and Mo $<$ 3 ppm	Mitsubishi Chemical (Tokyo, Japan)

Specimens for property evaluation were cut from the RHP product and then ground with a 600-grit diamond wheel. The density was measured by the water-displacement method. TD values of 3.97 g/cm<sup>3</sup> for Al<sub>2</sub>O<sub>3</sub> and 3.22 g/cm<sup>3</sup> for SiC were used for calculating the TD of the composite. The phase composition was determined by X-ray diffractometry (XRD), using CuK $\alpha$  radiation. The three-point bend strength was measured on bars measuring 3 mm × 4 mm × 42 mm after the four edges had been beveled using 1000-grit SiC abrasive paper; the span was 30 mm, and the crosshead speed was 0.5 mm/min. The strength data were based on an average of five measurements. The fracture toughness was measured by the indentation method, using a 5 kg load, as in previous studies.<sup>21</sup>

The equation used for calculating fracture toughness,  $K_{IC}$ , was

$$K_{\rm IC} = 0.026 E^{0.5} P^{0.5} a C^{-1.5} \tag{1}$$

where *P* is the indentation load, *a* the half-length of the indent, *C* the half-length of the crack, and *E* the elastic modulus of the composite. The value of *E* is calculated from the elastic moduli of the components ( $E_{A12O3} = 380$  GPa and  $E_{SiC} = 414$  GPa), according to the rule of mixtures for particulate composite with random phase distribution ( $E = \Sigma E_i V_i = 386$  GPa, here  $E_i$  and  $V_i$  stand, respectively, for the elastic modulus and the volume fraction of the components Al<sub>2</sub>O<sub>3</sub> and SiC). The data for hardness and toughness were based on an average of 10 measurements. Scanning electron microscopy (SEM; Model JSM-5600, JEOL, Tokyo, Japan) observation of the fracture surfaces was conducted at 20 kV, and transmission electron microscopy (TEM; Model H-9000UHR III, Hitachi Ltd., Tokyo, Japan) analysis of the microstructure was conducted at 300 kV.

#### **III. Results and Discussion**

### (1) Thermodynamic Considerations

According to the thermodynamic data,<sup>22</sup> we can calculate the enthalpy of reaction (1) under standard conditions to be  $\Delta H^{\circ}_{298} = -1871$  kJ, indicating that the reaction is exothermic. The free enthalpy function,  $\Delta G^{\circ}(T)$ , in the temperature range of 298-2000 K is as follows:

$$\Delta G^{\circ}(T) = \Delta H^{\circ}_{298} - T\Delta S^{\circ} = -1871 + 336 \times 10^{-3} T (\text{kJ})$$
(2)

The value of  $\Delta G^{\circ}$  is highly negative in the experimental temperature range, demonstrating the thermodynamic possibility of reaction. On the other hand, the calculation method used in the theoretical analysis of the SHS process<sup>23</sup> gives an adiabatic temperature ( $T_{\rm ad}$ ) of 1070°C for this exothermic reaction if the reaction is conducted at 25°C. Empirically, a  $T_{\rm ad} \geq 1800$ °C is necessary for an SHS process.<sup>23</sup> This means that no SHS

Table II. Characteristics of the Al<sub>2</sub>O<sub>3</sub>–SiC Nanocomposite Reactive Hot Pressed at 1800°C

Phase composition	Relative	Bending	Vickers	Fracture
	density	strength	hardness	toughness
	(%TD)	(MPa)	(GPa)	(MPa•m <sup>1/2</sup> )
$Al_2O_3$ , β-SiC	99.9	$795 \pm 160$	17.7	3.1

process will occur for reaction (1). Thus, a normal heating program was adopted for RHP treatment of the system in the present investigation.

### (2) Characterization of the Composite

The XRD results for mixed-powder compacts heat-treated at different temperatures showed that the  $\beta$ -SiC phase appeared after  $\sim 1200^{\circ}$ C and that the reactant mullite disappeared at  $\sim 1600^{\circ}$ C. The XRD patterns of the obtained composites RHP-treated at 1600°, 1700°, and 1800°C indicated that the detectable phases were Al<sub>2</sub>O<sub>3</sub> and  $\beta$ -SiC. However, if the RHP temperature was  $< 1700^{\circ}$ C, composites with >95% TD could not be obtained. The properties of the composite RHP-treated at 1800°C are listed in Table II. This table shows that a fully densified material was produced.

The mean bending strength of the composites was 795 MPa, although the standard deviation was large. The highest value of bending strength was 1004 MPa. These results indicate that better mechanical properties probably are obtainable by more carefully machining and polishing the specimens and by optimizing such manufacturing parameters as the particle size of the raw materials, the mixing method, and the RHP program. On the other hand, the fracture toughness, measured by the indentation method, was as low as that of monolithic  $Al_2O_3$  and SiC, which suggests that the toughening effect caused by the *in situ*-formed SiC was insignificant.

Figure 1 shows a TEM photograph of the obtained nanocomposite. The grain size of the matrix  $Al_2O_3$  ranges from 0.5 to 3  $\mu$ m in this image. The *in situ*-formed, nanometer-sized SiC particles are mainly entrapped inside the  $Al_2O_3$  grains, whereas the submicrometer-sized particles are located at the grain boundaries or triple points of the  $Al_2O_3$ . This different location of the SiC particles of different sizes agrees with the grain growth dynamics in ceramic materials.<sup>24</sup> Such a type of SiC particle distribution is



**Fig. 1.** TEM photograph of the obtained nanocomposite by reactive hot pressing at  $1800^{\circ}$ C showing the distribution of the *in situ* formed SiC particles, i.e., nanometer-sized ones entrapped into the Al<sub>2</sub>O<sub>3</sub> grains and the submicrometer-sized ones located at the grain boundaries or triple points of Al<sub>2</sub>O<sub>3</sub>.



Fig. 2. High-resolution TEM image of the grain boundary between an  $Al_2O_3$  grain and a grain-boundary-located SiC particle indicating no obvious amorphous phase existed at the grain boundary.

beneficial for improving the strength of nanocomposites, according to the model developed by Ohji *et al.*<sup>2</sup>

Figure 2 shows a high-resolution TEM image of the grain boundary between an  $Al_2O_3$  grain and a grain-boundary-located SiC particle. No obvious amorphous phase exists at the grain boundary. Similar grain boundaries are also observed between  $Al_2O_3$  and intra-SiC particles. This feature of the grain boundaries indicates a strong bonding between  $Al_2O_3$  and SiC particles and the possibility of good high-temperature behavior, such as strength and creep resistance.

The fracture surface of the nanocomposite is shown in Fig. 3. The intrafracture mode is dominant here, which also indicates strong bonding of grain boundaries. Residual tensile stress existing in the  $Al_2O_3$  grains as a result of mismatch of the thermal expansion coefficients between  $Al_2O_3$  and SiC should have enhanced this intrafracture process. On the other hand, this fracture mode also relates to the high bending strength and low fracture toughness of the nanocomposite.

#### **IV.** Summary

A simple approach was used to prepare  $Al_2O_3$ -SiC nanocomposites by the *in situ* reaction of mullite, aluminum, and carbon by



Fig. 3. SEM photograph of the fracture surface of the nanocomposite showing intrafracture mode.

reactive hot pressing. *In situ*-formed nanometer-sized SiC particles were mainly entrapped in the Al<sub>2</sub>O<sub>3</sub> matrix grains, whereas submicrometer-sized particles were located at the grain boundaries or triple points of the Al<sub>2</sub>O<sub>3</sub>. The grain boundaries between Al<sub>2</sub>O<sub>3</sub> and SiC bonded directly, with no amorphous phase. The intrafracture mode dominated the fracture process, because of the strongly bonded interfaces and residual tensile stress in the Al<sub>2</sub>O<sub>3</sub> grains. The bending strength of the nanocomposite RHP-treated at 1800°C was 795  $\pm$  160 MPa, and the fracture toughness, measured by the indentation method, was 3.1 MPa·m<sup>1/2</sup>.

#### References

<sup>1</sup>K. Niihara, "New Design Concept of Structural Ceramics-Ceramic Nanocomposite," *J. Ceram. Soc. Jpn.*, **99**, 974–82 (1991).

<sup>2</sup>T. Ohji, Y. K. Jeong, Y. H. Choa, and K. Niihara, "Strengthening and Toughening Mechanisms of Ceramic Nanocomposites," *J. Am. Ceram. Soc.*, **81** [6] 1453–60 (1998).

<sup>3</sup>J. Zhao, L. C. Stearns, M. P. Harmer, H. M. Chan, G. A. Miller, and R. E. Cook, "Mechanical Behavior of Alumina-Silicon Carbide Nanocomposites," *J. Am. Ceram. Soc.*, **76** [2] 503–10 (1993).

<sup>4</sup>H. Z. Wu, C. W. Lawrence, S. G. Roberts, and B. Derby, "The Strength of Al<sub>2</sub>O<sub>3</sub>/SiC Nanocomposites after Grinding and Annealing," *Acta Mater.*, **46**, 3839–48 (1998).

<sup>5</sup>L. Carroll, M. Sternitzke, and B. Derby, "Silicon Carbide Particle Size Effects in Alumina-Based Nanocomposites," *Acta Mater.*, **44**, 4543–52 (1996).

<sup>6</sup>A. Nakahira, K. Niihara, and T. Hirai, "Microstructure and Mechanical Properties of Al<sub>2</sub>O<sub>3</sub>–SiC Composites," *J. Ceram. Soc. Jpn.*, **94**, 767–72 (1986).

<sup>7</sup>T. Ohji, A. Nakahira, T. Hirano, and K. Niihara, "Tensile Creep Behavior of Alumina/Silicon Carbide Nanocomposite," *J. Am. Ceram. Soc.*, **77** [12] 3259–62 (1994).

<sup>8</sup>A. M. Thompson, H. M. Chan, and M. P. Harmer, "Tensile Creep of Alumina-Silicon Carbide 'Nanocomposites," *J. Am. Ceram. Soc.*, **80** [9] 2221–28 (1997).

<sup>9</sup>T. Ohji, T. Kusunose, and K. Niihara, "Threshold Stress in Creep of Alumina-Silicon Carbide Nanocomposites," *J. Am. Ceram. Soc.*, **81** [10] 2713–16 (1998).

<sup>10</sup>T. Ohji, T. Hirano, A. Nakahira, and K. Niihara, "Particle/Matrix Interface and Its Role in Creep Inhibition in Alumina/Silicon Carbide Nanocomposites," *J. Am. Ceram. Soc.*, **79** [1] 33–45 (1996).

<sup>11</sup>Z. Y. Deng, J. L. Shi, Y. F. Zhang, T. R. Lai, and J. K. Guo, "Creep and Creep-Recovery Behavior in Silicon-Carbide-Particle-Reinforced Alumina," *J. Am. Ceram. Soc.*, **82** [4] 944–52 (1999).

<sup>12</sup>R. W. Davidge, P. C. Twigg, and F. L. Riley, "Effects of Silicon Carbide Nano-Phase on the Wet Erosive Wear of Polycrystalline Alumina," *J. Eur. Ceram. Soc.*, **16**, 799–802 (1996).

<sup>13</sup>J. Rodriguez, A. Martin, J. Y. Pastor, J. Llorca, J. F. Bartolome, and J. S. Moya, "Sliding Wear of Alumina/Silicon Carbide Nanocomposites," *J. Am. Ceram. Soc.*, 82 [8] 2252–54 (1999).

 [8] 2252–54 (1999).
<sup>14</sup>P. F. Becher, C. H. Hsueh, P. Angelini, and T. N. Tiegs, "Toughening Behavior in Whisker-Reinforced Ceramic Matrix Composites," *J. Am. Ceram. Soc.*, **71** [12] 1050–61 (1988).

<sup>15</sup>A. C. D. Chaklader, S. D. Gupta, E. C. Y. Lin, and B. Gutowski, "Al<sub>2</sub>O<sub>3</sub>–SiC Composites from Aluminosilicate Precursors," *J. Am. Ceram. Soc.*, **75** [8] 2283–85 (1992).

<sup>16</sup>C. E. Borsa, F. M. Spiandorello, and R. H. G. A. Kiminami, "Synthesis and Characterization of Al<sub>2</sub>O<sub>3</sub>/SiC Powders from Natural Aluminosilicates," *Mater. Sci. Forum*, **299–300**, 57–62 (1999).

<sup>17</sup>A. Amroune, G. Fantozzi, J. Dubois, J. P. Deloume, B. Durand, and R. Halimi, "Formation of Al<sub>2</sub>O<sub>3</sub>–SiC Powder from Andalusite and Carbon," *Mater. Sci. Eng. A.*, **290**, 11–15 (2000).

<sup>18</sup>A. Amroune and G. Fantozzi, "Synthesis of Al<sub>2</sub>O<sub>3</sub>–SiC from Kyanite Precursor," J. Mater. Res., 16, 1609–13 (2001).

<sup>19</sup>J. H. Lee, C. Y. An, C. W. Won, S. S. Cho, and B. S. Chun, "Characteristics of Al<sub>2</sub>O<sub>3</sub>–SiC Composites Powder Prepared by the Self-Propagating High-Temperature Synthesis Process and Its Sintering Behavior," *Mater. Res. Bull.*, **35**, 945–54 (2000).

<sup>20</sup>L. C. Pathak, D. Bandyopadhyay, S. Srikanth, S. K. Das, and P. Ramachandrarao, "Effect of Heating Rates on the Synthesis of Al<sub>2</sub>O<sub>3</sub>–SiC Composites by the Self-Propagating High-Temperature Synthesis (SHS) Technique," *J. Am. Ceram. Soc.*, **84** [5] 915–20 (2001).

<sup>21</sup>G. J. Zhang, Z. Y. Deng, N. Kondo, J. F. Yang, and T. Ohji, "Reactive Hot Pressing of ZrB<sub>2</sub>–SiC Composites," *J. Am. Ceram. Soc.*, **83** [9] 2330–32 (2000).

<sup>22</sup>I. Barin and O. Knacke, *Thermochemical Properties of Inorganic Substances*. Spinger-Verlag, Berlin/Heidelberg and Verlag Stahleisen m. b. H., Dusseldorf, Germany, 1973.

<sup>23</sup>Z. A. Munir, "Synthesis of High Temperature Materials by Self-Propagating Combustion Methods," *Am. Ceram. Soc. Bull.*, **67** [2] 342–49 (1988).

<sup>24</sup>A. Piciacchio, S. H. Lee, and G. L. Messing, "Processing and Microstructure Development in Alumina–Silicon Carbide Intragranular Particulate Composites," *J. Am. Ceram. Soc.*, **77** [8] 2157–64 (1994).