Fabrication of Boron Nitride Dispersed Nanocomposites by Chemical Processing and Their Mechanical Properties

Takafumi KUSUNOSE

The Institute of Scientific and Industrial Research (ISIR), Osaka University, 8-1, Mihogaoka, Ibaraki-shi 567-0047

化学プロセスを用いた窒化ホウ素分散ナノ複合材料の作製とその特性

楠瀬尚史

大阪大学産業科学研究所, 567-0047 大阪府茨木市美穂ヶ丘 8-1

Hexagonal boron nitride (h-BN) dispersed nanocomposites were fabricated through a chemical process involving sintering of matrix ceramic powders covered partly with turbostratic BN (t-BN), which was synthesized by the reduction of a mixture of boric acid and urea precipitating on the matrix ceramic powder during drying after wet-ball milling. Silicon carbide (SiC), silicon nitride (Si_3N_4), alumina (Al_2O_3) and aluminum nitride (AlN) were employed as matrix for h-BN dispersed nanocomposites. The nano-sized h-BN particles were found to be homogeneously dispersed within the matrix grains as well as at grain boundaries, which is typical of nanocomposite structures. As a result, the present nanocomposites showed unique and excellent properties such as high strength, low Young's modulus, high thermal shock resistance, and good machinability.

[Received December 1, 2005]

Key-words : BN, SiC, Nanocomposite, Thermal shock resistance, Machinability

1. Introduction

Ceramic materials have been recognized as having such disadvantages as low thermal shock resistance and hard machinability compared with metals, but several recent investigations have attempted to improve these properties in high-strength structural ceramics.^{(1)–(7)} Engineering ceramics like SiC, Si_3N_4 , Al_2O_3 , and AlN are viewed as prime candidates for structural materials in the 21st century owing to their high strength, high wear resistance, high refractoriness, and chemical inertness.^{(8)–(10)} Moreover, in recent years, these ceramics have received considerable attention as materials for semiconductor manufacturing equipment owing to their high thermal conductivity and high corrosion resistance to plasma and halogen atmosphere.⁽¹¹⁾ However, their thermal shock resistance and machinability is still not sufficient for wider applications. In order to improve these properties, a number of researchers have looked into the possibility of adding h-BN as a second phase.^{(12), (13)} However, while h-BN has high thermal shock resistance and good machinability, it has low fracture strength and Young's modulus. It has been reported that the fracture strength of the composites decreased remarkably with increased addition of h-BN due to the inhomogeneous dispersion of large, micron-sized BN particles and their agglomeration, even though thermal shock resistance and machinability were somewhat improved.⁽¹⁴⁾ In the conventional fabrication of h-BN dispersed composites, commercially available h-BN powders with grain sizes of several micrometers are ball-milled with the matrix powders.^{(12)–(16)} It is difficult to disperse fine h-BN particles in the matrix homogeneously by conventional mixing of commercial h-BN powders. Thus, the large h-BN particles and their agglomerates are thought to initiate fracture and decrease fracture strength of the composites because of their low Young's modulus and cleavage fracture. Hence, the fabrication of strong machinable ceramics with high thermal shock resistance was thought to be impossible. However, if it were possible to decrease the size of the h-BN particles and prevent their agglomeration, h-BN dispersed com-

sites could retain strengths matching those of monoliths. Thus, for h-BN dispersed ceramic composites, a nanocomposite structure,^{(17)–(20)} i.e., the homogeneous dispersion of nano-sized h-BN particles in a matrix, would presumably be effective in enhancing the fracture strength. Also, thermal shock resistance can potentially be further improved by increasing fracture strength, in addition to preparing h-BN dispersion with low Young's modulus.

As mentioned above, it is difficult to disperse fine h-BN particles in a matrix powder homogeneously by using a conventional powder mixing method like ball-milling. Besides, a pure and fine h-BN powder is not commercially available. To solve these problems and obtain a nanocomposite structure, various processes based on precursors for nanocomposites have been developed.^{(20)–(22)} We sought a new synthetic method capable of yielding a microstructure with a homogeneous dispersion of h-BN within a matrix. Thus, we proposed a simple chemical process for precipitating an h-BN precursor, which is soluble in any ball-milling solvent and can readily transform into h-BN on matrix particles.^{(23)–(25)} Boric acid and urea are very suitable as boron and nitrogen sources for h-BN, respectively. **Figure 1** shows a conceptual schematic of the chemical process. It has been reported that h-BN can be synthesized by reducing a mixture of boric acid and a nitrogen compound in hydrogen gas.⁽²³⁾

Fig. 1. Conceptual schematic of the chemical process for BN dispersed nanocomposites.

The present paper reports the fabrication of BN dispersed nanocomposites, with SiC, Si₃N₄, Al₂O₃, or AlN used as matrix, by chemical processing, and their mechanical properties, such as strength, thermal shock resistance, and machinability.

2. Experimental

2.1 Sample preparation

The starting powders used as a matrix for h-BN dispersed composites were the commercially available β -SiC (Ultra Fine grade, Ibiden Co., Ltd., Gifu), α -Si₃N₄ (SNE-10 grade, Ube Industries, Yamaguchi), α -Al₂O₃ (AKP53 grade, Sumitomo Chemicals, Co., Ltd., Tokyo), or AlN (F grade, Tokuyama Corporation, Tokyo). This section will describe the chemical process used to fabricate the SiC/BN composite as a typical example. Boric acid (Reagent grade, Wako Pure Chemical Industries, Tokyo) and urea (Reagent grade, Wako Pure Chemical Industries, Tokyo) were used as raw materials for the BN precursor. The BN content was adjusted to 5, 10, 15, 20 and 30 vol%. SiC powder, boric acid, and urea were mixed by the conventional wet ball milling method with Si₃N₄ balls and ethanol in a plastic bottle for 24 h to ensure homogeneity of the powder mixture. Before drying, a small amount of ion-exchanged water was added to the slurry to dissolve the boric acid and urea completely and also to prevent boric acid from evaporating. The dried mixtures were reduced at 350°C for 3 h and at 1100°C for 8 h in hydrogen gas, and then heated at 1500°C for 5 h and 1650°C for 5 h in nitrogen gas to produce a SiC-BN composite powder. The composite powders were ball-milled with the sintering aid (7 wt% Al₂O₃ + 2 wt% Y₂O₃) for 72 h. After a second ball-milling run, the slurries were dried, and the powders were dry ball milled for 6 h to eliminate hard agglomerates. The composite powders were hot-pressed at 1850°C for 1 h in nitrogen atmosphere under an applied pressure of 30 MPa to fabricate SiC/BN nanocomposites. For comparison, a commercially available h-BN powder with an average grain size of 9 μ m (GP grade, Denki Kagaku Kogyo Kabushiki Kaisha, Tokyo) was used to produce microcomposites.

2.2 Characterization

The crystalline phase of the reduced composite powders and the hot-pressed samples were determined by X-ray diffractometry, using Cu K α radiation (Rigaku RAD-B, Tokyo). The microstructure was characterized by scanning electron microscopy (SEM, Model S-5000, Hitachi, Tokyo) and transmission electron microscopy (TEM, Model H-8100, Hitachi, Tokyo). The grain size distribution was estimated from SEM photographs of chemically-etched surfaces by using an image analysis technique. At least 1000 grains of SiC were measured for each sample.

Fracture strength was evaluated by three-point bending tests at room temperature. The tensile surfaces of specimens were perpendicular to the hot-pressing direction. The span length and crosshead speed were 30 mm and 0.5 mm/min, respectively. Young's modulus was determined by the resonance vibration method with first-mode resonance. Thermal shock fracture resistance was determined by measuring the bending strength of water-quenched samples. The samples were soaked for 10 min at a selected temperature in a vertical tube furnace and then dropped into a water bath at 20°C.

Machinability of each composite was tested using a tungsten carbide (WC/Co) drill bit 1 mm in diameter. The drilling test was performed using a standard drill press operating at 660 rpm. The composite specimens were mounted on a load cell and tested by manually applying a constant normal force on

Fig. 2. Hertzian test geometry for bonded-interface specimen. Sphere, radius r , delivers load P over contact radius a . Specimen consists of two polished halves bonded across the interface.

the drill under a load of 50 N.

Ball indentations for the Hertzian contact test were made using WC/Co spheres of radii $r = 1, 1.5$ and 2 mm, with a load range from $P = 0$ to 1960 N using a universal testing machine (Autograph, AG-10TC, Shimadzu Co., Ltd.), as shown in Fig. 2. Contact radius (a) at each applied load was determined by measuring the residual traces in the gold layer formed by ball indentation. Then, contact pressure (p_0) was plotted as a function of indentation strain (a/r) (see Fig. 12). Sub-surface contact damage induced by ball-indentation was examined using a bonded-interface technique, consisting of two polished half blocks joined by an adhesive. Indentations were made symmetrically across the traces of the interface at loads from 1470 to 1960 N with a tungsten carbide (WC) sphere of radius 1.5 mm. After testing, the bonded materials were separated and the surfaces and sections cleaned with acetone. The polished specimens were viewed in an optical microscope using Nomarski interference contrast to reveal the macroscopic damage patterns, as represented in Fig. 2.

3. Results and discussion

3.1 Fabrication of SiC/BN nanocomposites

Figure 3 illustrates the transformation of crystalline phases in the SiC/BN composite fabricated by the chemical process using boric acid and urea as h-BN source. Since the starting powder before reduction in H₂ consisted of SiC, boric acid, and urea, it is thought that the boric acid and urea that precipitated onto SiC powders did not react during drying of the ball milled slurry. The reduced powder of Fig. 3(b) showed almost the same XRD pattern as the starting powder except for the disappearance of the peaks of boric acid and urea and the appearance of the extremely broad peak arising from turbostratic-BN (t-BN). This agrees with the XRD data for mixtures consisting of only boric acid and urea reduced by H₂ under the same conditions.²³⁾

Figure 4 shows the representative TEM pictures of the reduced powder corresponding to (b) in Fig. 3. It can be seen that the SiC particles are surrounded with a low contrast phase. On the basis of observation of the disordered layer using higher resolution TEM in Fig. 4(b) and the identification of boron using EDX, the reduced powder was found to be SiC partly covered with t-BN. It is well known that t-BN is transformed into h-BN,^{26)–28)} analogous to the structural

Fig. 3. XRD profiles of the powder mixture and sintered body of SiC/10 vol% BN composite: (■) SiC, (▲) boric acid, (△) urea, (○) t-BN, and (●) h-BN; (a) dried mixture before reduction, (b) powder mixture reduced at 350°C for 3 h and at 1100°C for 8 h in hydrogen gas, and then heated at 1500°C for 5 h and 1650°C for 5 h in nitrogen gas, and (c) composite hot-pressed at 1850°C for 1 h.

Fig. 4. TEM images of t-BN formed on the surface of SiC powder reduced at 350°C for 3 h and at 1100°C for 8 h in hydrogen gas, and then heated at 1500°C for 5 h and 1650°C for 5 h in nitrogen gas: (a) low magnification and (b) higher magnification.

change of graphite at 2000°C in nitrogen. Indeed, the broad peak of t-BN at around 25° (2θ) in Fig. 3(b) evolved into the (002) peak of h-BN at 26° (2θ) in Fig. 3(c) during hot-pressing of the reduced powder at 1850°C for 1 h in nitrogen gas.

The sample studied could be identified as a composite consisting of SiC and h-BN in Fig. 3(c). **Figure 5** shows a TEM image of the hot-pressed SiC/10 vol%BN composite produced via the chemical route. The nano-sized BN particles were homogeneously dispersed within the SiC grains as well as at grain boundaries. No apparent impurity phases were observed at the interface between SiC and intragranular BN, which attained a graphite-like structure, as shown in Fig. 5(b). Thus, it is concluded that SiC/BN nanocomposites were successfully fabricated through the chemical process, followed by reduction and hot-pressing.

3.2 Microstructure of SiC/BN nanocomposites

Figure 6 shows the fractured surface of monolithic SiC and SiC/10 vol%BN composites. The microstructure of the large BN grains of the microcomposite were dispersed at grain boundaries of the SiC grains, whereas the nanocomposite exhibited a finer microstructure consisting of fine BN particles

Fig. 5. TEM images of the hot-pressed SiC/10 vol%BN composite processed through the chemical route: (a) low magnification, and (b) interface structure between SiC matrix and intragranular h-BN particulate.

Fig. 6. SEM micrographs of fractured surfaces for monolithic SiC and SiC/10 vol%BN composites: (a) monolithic SiC, (b) nanocomposite, and (c) microcomposite.

Fig. 7. Grain-diameter distribution for monolithic SiC and SiC/10 vol%BN composites: (a) monolithic SiC, (b) nanocomposite, and (c) microcomposite.

and micro-sized SiC matrix grains. The grain size distributions of SiC for monolithic SiC, the SiC/10 vol%BN microcomposite, and the nanocomposite are shown in **Fig. 7**. The monolithic SiC and the microcomposite have a wide grain size distribution, in which large SiC grains (diameter > 2 μm) were observed, but the nanocomposites exhibited a narrow size distribution in the fine grain end of the spectrum. These results agreed well with the SEM observations in Fig. 6. On the basis of these findings, we conclude that the finer BN particles markedly inhibited grain growth of the SiC matrix. This result can be supported by Zener's pinning effect,^{29),30)} which suggests that, when the volume fraction of second phase particles is constant, the restraining force on grain boundary migration is inversely proportional to the radius of second phase particles. The inhibition of grain growth of matrix ceramics was observed not just in the case of SiC/BN nanocomposites, but in other h-BN dispersed nanocomposites as well.^{23),24)}

Fig. 10. Machining of the nanocomposites using WC/Co bits: (a) turning of $\text{Al}_2\text{O}_3/30 \text{ vol}\% \text{BN}$, (b) turning of $\text{Si}_3\text{N}_4/30 \text{ vol}\% \text{BN}$, (c) drilling of $\text{Si}_3\text{N}_4/20 \text{ vol}\% \text{BN}$, and (d) drilling of $\text{SiC}/30 \text{ vol}\% \text{BN}$.

Considering the physical properties related to Eq. (1), the improvement in thermal shock resistance for the nanocomposites is mainly attributed to the higher strength and lower Young's modulus caused by the dispersion of soft BN. As shown in Table 1, the thermal shock resistance of the $\text{Al}_2\text{O}_3/\text{BN}$ nanocomposite was improved only slightly, while those of the $\text{Si}_3\text{N}_4/\text{BN}$ and SiC/BN nanocomposites were improved significantly.

3.5 Machinability of h-BN dispersed nanocomposites

It was difficult to machine h-BN dispersed composites containing less than 15 vol% BN by using a WC/Co drill. However, as shown in Fig. 10, good machinability was observed in both h-BN dispersed microcomposites and nanocomposites containing more than 20 vol% BN. The nanocomposites, in particular, exhibited an excellent machinability comparable to that of metals, and retained their high strength. The difference in machinability between 15 and 20 vol% BN content is attributed to h-BN particles dispersed at grain boundaries. Intergranular, rather than intragranular, BN particles, are conducive to good machinability because intergranular fractures were frequently observed in the drilled surface of composites containing over 20 vol% of BN. It has been reported that machinability is the result of the weak interface between matrix grains and second phases at grain boundaries. Morgan et al. and Hikichi et al. reported that even the considerably hard ZrO_2 exhibited machinability owing to the easy grain detachment enabled by the incorporation of rare-earth phosphate into the microstructure, i.e., the weak interface between ZrO_2 and rare-earth phosphate. The machinability observed in nanocomposites with high strength was probably achieved by grain detachment promoted by the weak interface between the hard matrix grains and fine intergranular h-BN particles with cleavage properties.

Figure 11 shows SEM micrographs of the drilled surfaces of $\text{Al}_2\text{O}_3/\text{BN}$ microcomposite and nanocomposite materials containing a 30 vol% BN dispersion as typical examples of h-BN dispersed composites. It appears that, in all samples, the intergranular fracture of Al_2O_3 grains was dominant, and the surface was partly covered with the debris of h-BN. These SEM micrographs reveal a significantly different micro-mechanism of material removal for the micro- and nanocomposites. In the microcomposite, the damage caused by drilling was very severe because of the larger crack path along micro-sized BN grains and their aggregates. As shown in Fig. 11 (d), large chippings of drilling track were observed in the drilled surface of the microcomposites. In contrast, the damage in the nanocomposites, characterized by the finer h-BN dispersion, was relatively minor. Furthermore, as can be seen from Figs. 3 (a) and (b), the drilling tracks in the nanocomposite were clearly visible, shallow, continuous grooves. These grooves

Fig. 11. SEM micrographs from surfaces of drilled holes in (a) (c) $\text{Al}_2\text{O}_3/30 \text{ vol}\% \text{BN}$ nanocomposite ($\downarrow$: direction of grooves by drilling) and (b) (d) $\text{Al}_2\text{O}_3/30 \text{ vol}\% \text{BN}$ microcomposite. (a) (b): Low magnification, (c) (d): high magnification.

formed by the sharp edge of the drill bit demonstrate good machinability that would presumably enable the nanocomposites to be formed into complex shapes. In the microcomposites, such sharp grooves were not evident because of the heavy damage in the drilled surface. The superior damage properties and machinability of the nanocomposites presumably result from the homogeneous dispersion of finer h-BN particles, which is expected to absorb and distribute the damage force during the machining operations by the many finer cracks formed along the grain boundaries.

3.6 Contact damage of h-BN dispersed nanocomposites

Investigation of the contact damage of this nanocomposite is also interesting because of the unique microstructure in which extremely soft and weak second phase particles are homogeneously dispersed in a hard ceramic matrix. The Hertzian contact test developed by Lawn et al. is a simple experiment to determine the potential for absorbing a mechanical shock. In the present work, this test was performed in order to demonstrate the damage mechanism of each sample. Figure 12 shows indentation stress-strain curves for monolithic Al_2O_3 and $\text{Al}_2\text{O}_3/\text{BN}$ nanocomposites containing 20 and 30 vol% BN dispersions. The responses were obtained by monitoring the mean contact pressure (p_0)

$$p_0 = P / \pi \cdot a^2 \quad (2)$$

as a function of the geometrical ratio a/r , where P , a and r are the indentation load, the radius of contact and the sphere radius, respectively. The monolithic Al_2O_3 behaved as an ideal brittle material, with a near linear response up to $p_0 = 8.5 \text{ GPa}$. However, above that stress, the curve slightly deviated below the Hertzian line due to deformation of the WC/Co spherical indenter. In contrast, the curves of the $\text{Al}_2\text{O}_3/\text{BN}$ nanocomposites containing 20 and 30 vol% BN dispersions dramatically deviated from the linear response at $p_0 = 6$ and 5 GPa . On the basis of these responses of the monolith and nanocomposites, it was presumed that some deformation occurred at lower indentation stresses with increasing BN content. These results suggested that the deformation can be promoted by homogeneous dispersion of nano-sized BN.

Figure 13 shows the half-surface (upper) and side section (lower) of the Hertzian contact damage for an Al_2O_3 monolith and $\text{Al}_2\text{O}_3/\text{BN}$ microcomposite and nanocomposite con-

Fig. 12

Fig. 13

Fig. 12. Indentation stress-strain curves for monolithic Al_2O_3 and $\text{Al}_2\text{O}_3/\text{BN}$ nanocomposites, from Hertzian contact test. Data plotted for range of sphere radius $r = 1\text{--}3$ mm. Solid curves are empirical fits to the data. Horizontal dashed lines indicate Vickers hardness for monolithic Al_2O_3 and $\text{Al}_2\text{O}_3/\text{BN}$ nanocomposites.

Fig. 13. Optical micrographs of Hertzian contact damage in (a) monolithic Al_2O_3 , (b) $\text{Al}_2\text{O}_3/20$ vol%BN microcomposite and (c) nanocomposite, showing half-surface (top) and section (bottom) views of subsurface deformation zone in bonded-interface specimens [see Fig. 1], at indentation loads (a) $P = 1960$ N, (b) 1470 N, and (c) 1960 N. WC sphere radius $r = 3$ mm.

taining 20 vol% BN dispersion, respectively. The damage in the monolithic Al_2O_3 showed typical Hertzian cone fracture, in which the cone cracks propagate downwards and outwards into the specimen (Fig. 13(a)), and no detectable deformation besides the cone crack could be observed beneath the contact. This fracture pattern is indicative of a highly brittle solid. By contrast, there were many large cracks in the subsurface deformation zone of the $\text{Al}_2\text{O}_3/20$ vol%BN microcomposite (Fig. 13(b)). These large cracks, which obviously differed from the classical Hertzian cone crack observed in the monolithic Al_2O_3 , were formed by the propagation of cracks between large BN particles or agglomerates thereof.

In contrast to the above two materials, in the nanocomposite, the damage observed in subsurface deformation zone appeared to be quasi-plastic deformation, similar to the plastic deformation zone in ductile metals. This deformation accompanied the residual surface depression instead of a surface ring crack, which indicates the transition from brittle to ductile induced by the finer h-BN dispersion. The nanocomposite had a microstructure in which fine h-BN particles were homogeneously dispersed within Al_2O_3 grains as well as along grain boundaries. Thus, it is thought to be possible to distribute and absorb the stresses due to the ball-indentation through deformation and/or large cracks originating from soft h-BN particles dispersed along the grain boundaries.

Figures 14(a) and (b) show SEM micrographs of the non-deformed surface and quasi-plastic deformation zone of the ball-indented nanocomposite specimen. Significant grain boundary detachment was often observed in the damage zone. These observations suggested that the nano-sized intergranular BN particles weakened the bonding strength of the grain boundary. The quasi-plastic deformation zone, in which the microcracks were concentrated, was driven by a strong shear component at the grain boundary. It is thought that the quasi-plastic deformation observed in the nanocomposites played an important role in their machinability. Quasi-plastic deformation by Hertzian contact test was observed in other h-BN dispersed nanocomposites such as $\text{Si}_3\text{N}_4/\text{BN}$, SiC/BN , and AlN/BN .

4. Conclusion

The h-BN dispersed nanocomposites of SiC/BN , $\text{Al}_2\text{O}_3/$

Fig. 14. SEM observation of subsurface damage in $\text{Al}_2\text{O}_3/30$ vol% BN nanocomposite: (a) quasi-plastic deformation zone [location A in Fig. 13(c)], and (b) interface crackings of grain boundaries [location B in Fig. 13(c)].

BN , $\text{Si}_3\text{N}_4/\text{BN}$, and AlN/BN were fabricated by sintering of nanocomposite powders, which are matrix powders coated partly with nano-sized t-BN. The matrix powders was coated with t-BN via a chemical process, in which boric acid and urea as BN sources were precipitated onto matrix powders and heated in hydrogen atmosphere. The microstructure of the resultant composites showed a homogeneous distribution of nano-sized h-BN particles within the matrix grains as well as along the grain boundaries. Also, h-BN dispersed nanocomposites had finer and more homogeneous microstructures due to the inhibition of grain growth, compared with the monolith and the microcomposites. As a result, the Young's moduli of both micro- and nanocomposites decreased with increasing h-BN content according to the rule of mixtures, but the strength of the nanocomposites was much higher than that of microcomposites. Additionally, owing to their high strength and low Young's modulus, the thermal shock resistance of h-BN nanocomposites was significantly improved compared with the monolith and the microcomposites. Moreover, nanocomposites containing more than 20 vol% BN dispersion simultaneously attained high strength and good machinability. The damage caused by drilling in the nanocomposites was minor compared to that observed in the microcomposites. Although the contact damage of the monoliths was classical Hertzian cone crack, indicative of a highly brittle material, the

nanocomposites showed quasi-plastic deformation, which is expected to absorb and dissipate the damage. This deformation zone was formed by microfractures that were caused by the weak interface between matrix grains and the nano-sized h-BN particles along the grain boundaries.

Acknowledgments This study was supported by Industrial Technology Research Grant Program in '01 from New Energy and Industrial Technology Development Organization (NEDO) of Japan. The author would like to gratefully thank Prof. Koichi Niihara and Prof. Tohru Sekino for useful discussion, and Mr. Norikazu Tachibana, Mr. Takeshi Kawase, and Mr. Hideaki Fujiwara for experimental support.

References

- Padture, N. P., Evans, C. J., Xu, H. K. and Lawn, B. R., *J. Am. Ceram. Soc.*, Vol. 78, pp. 215–217 (1995).
- Davis, J. B., Marshall, D. B., Housley, R. M. and Morgan, P. E. D., *J. Am. Ceram. Soc.*, Vol. 81, pp. 2169–2175 (1998).
- Kawai, C. and Yamakawa, A., *J. Am. Ceram. Soc.*, Vol. 80, pp. 2705–2708 (1997).
- Saraswati, V. and Raoot, S., *J. Mater. Sci.*, Vol. 27, pp. 429–432 (1992).
- Uno, T., Kasuga, T. and Nakayama, S., *J. Ceram. Soc. Japan*, Vol. 100, pp. 315–319 (1992).
- Uno, T., Kasuga, T., Nakayama, S. and Ikushima, A. J., *J. Am. Ceram. Soc.*, Vol. 76, pp. 539–541 (1993).
- Uno, T., Kasuga, T. and Niihara, K., *J. Am. Ceram. Soc.*, Vol. 74, pp. 3139–3141 (1991).
- Mitomo, M., "Proceedings of the 1st International Symposium on the Science of Engineering Ceramics," Ed. by Kimura, S. and Niihara, K., Ceramic Society of Japan (1991) pp. 101–107.
- Hirosaki, N., Akimune, Y. and Mitomo, M., *J. Am. Ceram. Soc.*, Vol. 76, pp. 1892–1894 (1993).
- Ohji, T., Hirano, T., Nakahira, A. and Niihara, K., *J. Am. Ceram. Soc.*, Vol. 79, pp. 33–45 (1996).
- Kusunose, T., Semiconductor Equipment Association of Japan, No. 98, pp. 50–51 (2005) [in Japanese].
- Funabashi, T., Isomura, K., Harita, A. and Uchimura, R., "Ceramic Materials and Components for Engines," Ed. by Tenney, V. J., Am. Ceram. Soc. (1986) pp. 968–976.
- Mazdiyasn, K. S. and Ruh, R., *J. Am. Ceram. Soc.*, Vol. 64, pp. 415–418 (1981).
- Goeuriot-Launay, D., Brayet, G. and Thevenot, F., *J. Mater. Sci. Lett.*, Vol. 5, pp. 940–942 (1986).
- Lutz, E. H. and Swain, M. V., *J. Am. Ceram. Soc.*, Vol. 75, pp. 67–70 (1992).
- Liu, H. and Hsu, S. M., *J. Am. Ceram. Soc.*, Vol. 79, pp. 2452–2457 (1996).
- Niihara, K., *J. Ceram. Soc. Japan*, Vol. 99, pp. 974–982 (1991).
- Ohji, T., Jeong, Y. -K., Choa, Y. -H. and Niihara, K., *J. Am. Ceram. Soc.*, Vol. 81, pp. 1453–1460 (1998).
- Zhao, J., Stearns, L. C., Harmer, M. P., Chan, H. M., Miller, G. A. and Cook, R. E., *J. Am. Ceram. Soc.*, Vol. 76, pp. 503–510 (1993).
- Dusza, J., Sajgalik, P. and Steen, M., *J. Am. Ceram. Soc.*, Vol. 82, pp. 3613–3615 (1999).
- Herrmann, M., Schuber, C., Rendtel, A. and Hübner, H., *J. Am. Ceram. Soc.*, Vol. 81, pp. 1095–1108 (1998).
- Sternitzke, M., Derby, B. and Brook, R. J., *J. Am. Ceram. Soc.*, Vol. 81, pp. 41–48 (1998).
- Kusunose, T., Sekino, T., Choa, Y. -H. and Niihara, K., *J. Am. Ceram. Soc.*, Vol. 85, pp. 2678–2688 (2002).
- Kusunose, T., Kim, Y. -H., Sekino, T., Matsumoto, T., Tanaka, N., Nakayama, T. and Niihara, K., *J. Mater. Res.*, Vol. 20, pp. 183–190 (2005).
- Kusunose, T., Sekino, T., Kim, B. -S., Choa, Y. -H., Nomoto, T., Yamamoto, Y. and Niihara, K., *Mater Science Forum*, Vol. 439, pp. 131–136 (2003).
- Brozek, V. and Hubaacek, M., *J. Solid State Chem.*, Vol. 100, pp. 120–129 (1992).
- Alkoy, S., Toy, C., Gonul, T. and Tekin, A., *J. Eur. Ceram. Soc.*, Vol. 17, pp. 1415–1422 (1997).
- Hagio, T., Nonaka, K. and Sato, T., *J. Mater. Sci. Lett.*, Vol. 16, pp. 795–798 (1997).
- Zener, C., quoted by C. S. Smith: Grains, phase, and Interfaces: an interpretation of microstructure. *Trans. Am. Inst. Min. Metall. Soc.*, Vol. 175, pp. 15–15 (1948).
- Steans, L. C. and Harmer, M. P., *J. Am. Ceram. Soc.* Vol. 79, pp. 3020–3028 (1996).
- Kingery, K. D., Bowen, H. K. and Uhlmann, D. R., Introduction to Ceramics, 2nd ed., John Wiley & Sons (1976) pp. 783–787.
- Kusunose, T., Sekino, T., Choa, Y. -H. and Niihara, K., *J. Am. Ceram. Soc.*, Vol. 85, pp. 2689–2695 (2002).
- Kusunose, T., Nomoto, T., Sekino, T., Kim, B. -S., Yamamoto, Y. and Niihara, K., *J. Ceram. Soc. Japan*, Vol. 111, pp. 821–825 (2003).
- Kusunose, T., Choa, Y. -H., Sekino, T. and Niihara, K., *Key Engineering Materials*, Vols. 161–163, pp. 475–480 (1999).
- Hasselmann, D. P. H., *Am. Ceram. Soc. Bull.*, Vol. 49, pp. 1033–1037 (1970).

Takafumi KUSUNOSE is a research associate of The Institute of Scientific and Industrial Research (ISIR), Osaka University. He graduated from the Faculty of Science at Kochi University in 1994 and received his Master and Doctor degrees of Engineering from Osaka University in 1996 and 1999, respectively. He was JSPS Research Fellow in 1996 to 1999, a research associate of ISIR since 1999. His research interest is in nonoxide ceramic nanocomposite including powder processing, sintering, and properties.