Microstructural control for ultrafine-grained non-oxide structural ceramics

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Ultrafine-grained non-oxide ceramics were prepared by combining the synthesis technology for fine-grained starting powders and the rapid sintering technology for spark plasma sintering (SPS); the two technologies were combined for obtaining ceramics with improved heat and corrosion resistance and improved mechanical properties. Hollow spherical Ca- α SiAlON powders composed of nanosized particles were synthesized by carbothermal reduction-nitridation of a SiO_2 - Al_2O_3 - CaCO_3 powder mixture. Using the Ca- α SiAlON powder, dense Ca- α SiAlON nanoceramics and porous Ca- α SiAlON ceramics with excellent mechanical properties and high heat and corrosion resistance were fabricated by the SPS technique. Ultrafine-grained Si_3N_4 and SiC ceramics were prepared from fine-grained Si_3N_4 and SiC powders by SPS. The densification of cubic-BN-dispersed ceramics composites was achieved without the phase transformation of cubic BN to low-hardness hexagonal BN, at a moderate pressure by the SPS technique.

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1. Introduction

Structural ceramics are expected have uses in various fields such as manufacturing, energy, and environmental sciences and to contribute to energy saving and a reduction of the environmental load. Accordingly, the author considers it necessary to further improve the thermal, mechanical, and chemical properties of structural ceramics by means of microstructural development by using ultrafine grains. Among the structural ceramics, non-oxide ceramics have high hardness, high elastic modulus, and excellent heat resistance. In the present work, using a combination of a synthesis technology for fine-grained raw powders and a rapid sintering technology, ultrafine-grained non-oxide ceramics were developed.

1.1 SiAlON

SiAlON ceramics have high hardness, and excellent corrosion and oxidation resistance at high temperatures, which makes them useful for engineering applications. α -SiAlON is a solid solution with the α - Si_3N_4 crystal structure in which some Si and N atoms are replaced by Al and O atoms, and some metal cations M, such as those of Li, Mg, Ca, Y or most rare-earth elements, are incorporated as a stabilizer.¹⁾ α -SiAlON ceramics are generally produced through liquid-phase sintering of Si_3N_4 - AlN - M_xO_y powder mixtures.²⁾ The high-temperature strength and corrosion resistance of α -SiAlON ceramics are degraded by a residual glass phase at the grain boundary resulting from the liquid-phase sintering.³⁾ Furthermore, it is difficult to achieve a uniform composition, and form homogeneous and fine-grained microstructure from the powder mixtures of Si_3N_4 - AlN - M_xO_y . Consequently, the development of high-purity and fine-grained α -SiAlON powders is necessary to improve the reliability of α -SiAlON

ceramics. α -SiAlON powders have been synthesized through carbothermal reduction-nitridation (CRN) of SiO_2 - Al_2O_3 - M_xO_y system. There are reports that α -SiAlON powder can be made by heating powder mixtures of SiO_2 - Al_2O_3 -(Ca- or Y-) oxide,^{4,5)} talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$)-halloysite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) clay minerals,^{6,7)} clay-metal compounds,⁸⁾ slag-clay mixtures,^{9,10)} or zeolite¹¹⁾ with carbon in flowing N_2 gas. Among α -SiAlON ceramics, Ca- α SiAlON has received considerable attention because of the low cost of the raw material (a Ca compound), high cation (Ca) solubility in the α -SiAlON lattice, thus a low residual glass phase, and good thermal stability.¹²⁾ However, rare-earth doped α -SiAlON has largely fabricated to enhance oxidation and corrosion resistance of α -SiAlON.¹³⁻¹⁸⁾

1.2 Silicon nitride

Silicon nitride (Si_3N_4) ceramics are one of the most promising materials for structural applications at high temperatures. However, Si_3N_4 is very difficult to densify by solid-phase sintering because of its strong covalent bonding and the low self-diffusion coefficients of Si and N. The conventional method for the densification of Si_3N_4 ceramics generally involves liquid-phase sintering with metal oxide additives. In contrast, the grain boundary phase derived from the sintering additives degrades the mechanical properties and oxidation and corrosion resistance at high temperatures.¹⁹⁾ Therefore, for improving these properties, the amount of sintering additives used for the fabrication of dense Si_3N_4 ceramics should be minimized.

1.3 Silicon carbide

Silicon carbide (SiC) ceramics have many attractive properties such as relatively low density, high hardness, excellent mechanical strength at high temperatures, and good thermal stability. However, it is difficult to densify a SiC powder without using sintering additives because of its strong covalent bonding; the same is true for Si_3N_4 . The typical densification technique for

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SiC is solid-phase sintering with B-C additives,²⁰⁾ or liquid-phase sintering with metal oxide additives such as Al_2O_3 and Y_2O_3 .²¹⁾ The merit of using liquid-phase sintering for SiC ceramics is that homogeneous and fine-grained microstructures can be formed, unlike solid-phase sintering, because of the lower sintering temperature and the presence of the liquid phase.²²⁾ The residual glass phase significantly affects the high-temperature mechanical properties of SiC ceramics.²³⁾

1.4 Cubic boron nitride

Cubic boron nitride (cBN) has the highest hardness and thermal conductivity next to diamond, and it is more thermally stable and less reactive with iron than diamond. Because of these properties, cBN is used for fabricating cutting tools for machining hardened steel and cast iron.²⁴⁾ However, it is difficult to obtain fully dense cBN materials because of the strong covalent bonding and the low self-diffusion coefficients of B and N. Moreover, cBN transforms into low-hardness hexagonal BN (hBN) at high temperatures.^{25)–27)} Hence, high-density cBN bodies for cutting tools have usually been produced by sintering under an ultrahigh pressure (greater than 5 GPa) with various types of additives, such as Al, Ti, TiN, and TiC.^{28)–31)} However, an economical sintering process involving a moderate pressure of less than 100 MPa is required for preparing cBN-based materials that can be used for fabricating cutting tools for a wide range of applications.³²⁾ While cBN and common ceramics such as Al_2O_3 , TiN, Si_3N_4 , and SiAlON possess high hardness and excellent thermal stability, their fracture toughness is lower than that of high-speed steels, hard metals, and cermets. Therefore, a combination of ceramics and cBN would be a promising material for cutting tools with high hardness and fracture toughness.

1.5 Spark plasma sintering

The spark plasma sintering (SPS) technique can be used for heating specimens rapidly because a pulsed direct current can pass through a graphite die and punch rod.³³⁾ The advantage of the technique is grain growth can be inhibited during sintering since the total sintering process can be completed in a short time owing to the rapid heating. Moreover, hardly sinterable ceramics such as Si_3N_4 , SiAlON, and SiC, which are difficult to densify by using conventional sintering techniques, have been produced as fully dense ceramics using the SPS technique.^{34)–39)} The SPS technique is also called pulse electric current sintering (PECS),^{34)–36)} field-assisted sintering technique (FAST),³⁷⁾ and plasma-assisted sintering (PAS)³⁸⁾ because the generation of spark discharge and/or plasma during the process has not been verified. Many researchers have reported that fine-grained and fully dense ceramics can be produced by the SPS technique.^{35),38),39)} Moreover, the phase transformation of cBN to low-hardness hBN might be suppressed because of the short sintering time of the SPS process.

2. Hollow spherical SiAlON powders composed of nanosized particles^{40),41)}

A Ca- α SiAlON powder was synthesized by carbothermal reduction-nitridation (CRN) of SiO_2 - Al_2O_3 - CaCO_3 and carbon powder mixtures.^{40),41)} The proportions of the starting powders were calculated to obtain nominal Ca- α SiAlON compositions of $\text{Ca}_x\text{Si}_{12-3x}\text{Al}_{3x}\text{O}_x\text{N}_{16-x}$ (i.e., $x = n = m/2$ in $\text{M}_x\text{Si}_{12-(m+n)}\text{Al}_{m+n}\text{O}_n\text{N}_{16-n}$) with x varying from 0.3 to 1.4. The mixture of the starting powders was heated in a N_2 gas flow using a horizontal electrical furnace. The residual carbon was removed by firing the powders at 700°C in air.

Fig. 1. SEM micrograph of Ca- α SiAlON powder prepared at 1450°C for 120 min for $x = 1.0$.⁴⁰⁾

Fig. 2. TEM micrograph of Ca- α SiAlON powder prepared at 1450°C for 120 min for $x = 1.0$.⁴⁰⁾

The crystalline phases appearing in the final specimens after heating at 1450°C for 120 min were Ca- α SiAlON, β -SiAlON, and AlN for all the compositions. The amount of the crystalline phases depended on the starting composition. The maximum amount of α -SiAlON was greater than 85 mass % for $x = 1.0$ with AlN as a minor phase. The synthesized Ca- α SiAlON powders showed a unique morphology of hollow spheres with diameters of 200–500 nm (Fig. 1).⁴⁰⁾ This morphology was basically observed for $x = 0.5$ to 1.2. Further observations indicated that the Ca- α SiAlON hollow spheres were composed of large numbers of nanosized particles having diameters of 10–30 nm and submicron-sized particles with a diameter of approximately 100 nm (Fig. 2).⁴⁰⁾ The thickness of the shells of the Ca- α SiAlON hollow spheres was around 50 nm; therefore, these nanosized particles had very high surface areas. Moreover, the bonding between the nanosized particles in the Ca- α SiAlON hollow spheres did not appear to be very strong because the hollow spheres could be broken down into nanosized particles by ultrasonic vibration. This particle morphology was significantly different from Ca- α SiAlON powders synthesized by CRN under similar conditions but using different starting powders.^{4),5)}

3. Investigation of formation mechanism of the SiAlON hollow spheres composed of nanosized particles^{42)–44)}

The formation mechanism of the Ca- α SiAlON hollow spheres composed of nanosized particles during the CRN process of the

$\text{SiO-Al}_2\text{O}_3\text{-CaCO}_3$ powder mixtures was analyzed by investigating specimens obtained at various heating temperatures and various holding times.⁴²⁾ A large number of solid spherical particles consisting of a Si-Al-Ca-O amorphous phase were formed at the initial stage of CRN. Very fine particles were subsequently generated on the surface of these solid spheres, and the solid spheres gradually changed into hollow spheres with the progress of nitridation. When heating temperature was increased to 1450°C, the XRD intensity of Al_2O_3 and the amorphous hump decreased, with oxynitride phases such as $\text{Si}_2\text{N}_2\text{O}$ and $\text{SiAl}_7\text{O}_{12}\text{N}_7$ now being detected. The intermediate phases were not observed in previous study when Ca- α SiAlON was synthesized through CRN, where SiO_2 and mullite were the only crystalline phases detected below 1250°C.^{4),5)} The formation of the Ca- α SiAlON hollow spheres depends on the formation of the solid spherical particles from the Si-Al-Ca-O liquid phase at the initial stage of the CRN. I guessed that an increase in the density and a decrease in the mass were the results of the conversion from the amorphous to crystalline α -SiAlON, and that these results contributed to the formation of Ca- α SiAlON hollow spheres composed of nanosized particles.

Ca- α SiAlON powders were also prepared using SiO_2 starting powders with different characteristics in terms of particle size, shape, and crystalline state in order to investigate the formation process of the Ca- α SiAlON hollow spheres.⁴³⁾ Ca- α SiAlON hollow spheres composed of a large number of nanosized particles were formed through an intermediate Si-Al-Ca-O liquid phase through a similar formation process, irrespective of the characteristics of the SiO_2 starting powders used.

Furthermore, Ca- α SiAlON powders were prepared using $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$ glass in order to find evidence for the Ca- α SiAlON hollow spheres being derived from the Si-Al-Ca-O liquid phase.⁴⁴⁾ The particle morphology of the powders was the same as that of the Ca- α SiAlON hollow spheres obtained from the CRN of $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaCO}_3$ powder mixtures.

4. Dense SiAlON nanoceramics from nanosized Ca- α SiAlON powder⁴⁵⁾

The prepared Ca- α SiAlON hollow spheres composed of nanosized particles were ground to obtain a nanosized Ca- α SiAlON starting powder.⁴⁵⁾ The powder was then sintered without using any sintering additive by spark plasma sintering (SPS) at 1700°C for 20 min in N_2 under a uniaxial pressure of 30 MPa at a heating rate of 100°C/min.

The phase content of the specimen sintered by SPS was almost the same as that in the starting powder. The sintered body had a full density of 99.2% in SPS, while no densification or significant grain growth occurred upon gas pressure sintering (GPS) of the nanosized Ca- α SiAlON powder. Crystallite sizes of the Ca- α SiAlON starting powder and the body sintered by SPS were 27 and 34 nm, respectively, as calculated by Scherrer's equation. The specimen had a bimodal microstructure composed of fine grains with diameters lesser than 50 nm and submicron-sized grains with diameters of 100–200 nm, as shown in Fig. 3.⁴⁵⁾ The grain sizes were approximately the same as that of the starting powder, indicating that significant grain growth did not occur during the SPS process. Moreover, no residual glass phase was observed at the grain boundary of the Ca- α SiAlON nanoceramics by high-resolution TEM. The Vickers hardness of the Ca- α SiAlON nanoceramics was around 18 GPa, which was higher than that of typical Si_3N_4 ceramics fabricated by GPS. The fracture toughness, approximately $3.2 \text{ MPa}\cdot\text{m}^{1/2}$, was slightly lower than that of the Si_3N_4 ceramics. The flexural strength

Fig. 3. TEM micrograph of dense Ca- α SiAlON nanoceramics prepared at 1700°C for 20 min at 30 MPa.⁴⁵⁾

at room temperature was 680 MPa on average. Jones et al.¹⁵⁾⁻¹⁷⁾ reported that room-temperature strength of Y- and Lu- α SiAlON with grain size of 1–2 μm was approximately 400 MPa. The flexural strength at the high temperature of 1200°C had the high value of 700 MPa, which was similar to that the value at room temperature. Liu et al.¹³⁾ reported that the flexural strength of ScLu- α SiAlON at test temperature of 1200°C reached 601 MPa, which retained 92% of strength at room temperature. These results indicated that the excellent strength at both room and high temperatures could be achieved by adding Ca not rare-earth elements. The corrosion resistance of the Ca- α SiAlON nanoceramics in H_2SO_4 solution was superior to that of commercial Si_3N_4 ceramics for bearing grade. The residual glass phase in the commercial Si_3N_4 ceramics would be easily corroded because the Si_3N_4 ceramics are fabricated using sintering additives such as Y_2O_3 and Al_2O_3 . The excellent strength at high temperature and corrosion resistance of the Ca- α SiAlON nanoceramics would be caused by the absence of a glass phase at the grain boundary.

5. Porous SiAlON ceramics from hollow spherical Ca- α SiAlON powder⁴⁶⁾

Porous Ca- α SiAlON ceramics were fabricated by using the hollow spherical Ca- α SiAlON powder and by maintaining their unique shape.⁴⁶⁾ The hollow spherical powder was sintered without using any sintering additive by SPS at 1700°C for 1–20 min in N_2 under a uniaxial pressure of 5 MPa at a heating rate of 100°C/min.

The open and closed porosities of the sample fabricated for 1 min by SPS were 44 and 2%, respectively. The open porosity decreased with an increase in the holding time. In all samples, the phase content was almost the same as that of the Ca- α SiAlON starting powder. In the porous Ca- α SiAlON ceramics fabricated for 1 min, hollow spheres with a morphology similar to that of the starting powder were observed, as shown in Fig. 4.⁴⁶⁾ As the holding time increased, the hollow spheres gradually disappeared and the total porosity decreased. Pore-size-distribution measurements showed that the porous Ca- α SiAlON ceramics had a large number of pores with diameters of 200–500 nm and a small number of pores with a diameter of approximately 10 nm. This suggested that the morphology of the hollow spheres in the starting powder was maintained in the porous Ca- α SiAlON ceramics with high porosity. The flexural

Fig. 4. SEM micrograph of the fracture surface of porous Ca- α SiAlON ceramics prepared at 1700°C for 1 min at 5 MPa.⁴⁶⁾

strength of the porous Ca- α SiAlON ceramics decreased with an increase in the porosity. The strength of the porous Ca- α SiAlON ceramics was higher than that of typical porous ceramics such as Al_2O_3 reported by Coble.⁴⁷⁾ The Vickers hardness of the porous Ca- α SiAlON ceramics decreased with increasing porosity. The hardness was higher than that of dense mullite and cordierite ceramics, and was similar to that of reaction-bonded Si_3N_4 and porous Si_3N_4 ceramics prepared using starch.⁴⁸⁾ The corrosion resistance of the porous Ca- α SiAlON ceramics in H_2SO_4 solution was better than that of commercial dense Si_3N_4 ceramics, although the weight loss of the porous Ca- α SiAlON ceramics in the H_2SO_4 solution was higher than that of the prepared dense Ca- α SiAlON nanoceramics because of its high surface area.

6. Fine-grained Si_3N_4 ceramics with small amount of sintering additives^{49),50)}

The use of a nanosized Si_3N_4 starting powder is expected to give fine-grained Si_3N_4 ceramics that reduce the amount of sintering additives, leading to the improvement of the mechanical properties at high temperatures and to the improvement of the corrosion and oxidation resistance. In this work, a nanosized amorphous Si_3N_4 powder (average particle size: 80 nm; total oxygen content: 4.8 mass %) was first prepared by a vapor phase reaction involving SiCl_4 and NH_3 gases. As a reference, a submicron-sized α - Si_3N_4 powder (β -phase: <5%; average particle size: 170 nm; total oxygen content: 1.2 mass %) was used. The Si_3N_4 powders were then sintered with a relatively small amount of sintering additives, 1.5 mass % Y_2O_3 and 0.5 mass % Al_2O_3 , by SPS at 1500–1700°C for 30 min and at 1800°C for 1 min at a uniaxial pressure of 30 MPa under N_2 .⁴⁹⁾

The densification of the nanosized amorphous Si_3N_4 powder and the phase transformation to a β -phase were completed at a relatively lower temperature, i.e., 1500°C, as compared to that in the case of the submicron-sized α - Si_3N_4 powder (Fig. 5).⁴⁹⁾ In the case of the submicron-sized α - Si_3N_4 powder, the relative density of the sample fabricated at 1500°C was approximately 60%. As the temperature increased to 1800°C, the sample had a high density of >98%. In the nanosized amorphous Si_3N_4 powder, the density of the sample reached 95% even at 1500°C, although the densification of the submicron-sized α - Si_3N_4 powder required a high temperature of 1800°C. α - Si_3N_4 transformed into β - Si_3N_4 with an increase in the density of the sample

Fig. 5. Effect of sintering temperature on the relative density and α -phase ratio of Si_3N_4 ceramics prepared at 1500–1700°C for 30 min and at 1800°C for 1 min at 150°C/min.⁴⁹⁾

when the submicron-sized α - Si_3N_4 powder was used, and only the β -phase formed at 1800°C. In the nanosized amorphous Si_3N_4 powder, the amorphous phase directly transformed into the crystalline β -phase, and only the β -phase existed even at 1500°C. The high sinterability of the nanosized amorphous Si_3N_4 powder could result from the small particle size and the high total oxygen content of the nanosized amorphous Si_3N_4 powder. The phase transformation from α - to β - Si_3N_4 is mainly dependent on the densification.⁵¹⁾ Consequently, because the densification of the nanosized amorphous Si_3N_4 powder was achieved at a temperature lower than that for the submicron-sized α - Si_3N_4 powder, the transformation to the β -phase would be completed at a low temperature.

The Si_3N_4 body obtained from the nanosized amorphous Si_3N_4 powder was composed of finer equiaxed and elongated grains, compared to that obtained from the submicron-sized α - Si_3N_4 powder, at 1700°C for 30 min at 150°C/min (Fig. 6).⁴⁹⁾ In addition, residual pores were observed in the Si_3N_4 body obtained from the submicron-sized α - Si_3N_4 powder. Therefore, the grain growth was inhibited during sintering, leading to the production of fine-grained Si_3N_4 ceramics. The densification of liquid-phase sintered Si_3N_4 using conventional sintering techniques such as gas-pressure sintering and hot-pressing generally required the amount of sintering additives of 5–10 mass %.^{51),52)}

$\text{Si}_2\text{N}_2\text{O}$ formed as a secondary phase for a long sintering time at 150°C/min at 1500–1700°C for a holding time of 30 min when the nanosized amorphous Si_3N_4 powder was used. When rapid sintering was performed at 300°C/min at 1800°C for 1 min, dense β - Si_3N_4 ceramics consisting of equiaxed grains with an average size of 300 nm were fabricated without the formation of $\text{Si}_2\text{N}_2\text{O}$.

7. Fine-grained SiC ceramics with AlN sintering additive^{53)–55)}

The SiC ceramics prepared through liquid-phase sintering with AlN and rare-earth oxides have showed an improvement in the high-temperature strength and oxidation resistance.^{56),57)} Some researchers have reported that the improvement of these properties is due to a decrease in the amount of glass phase in the grain boundary; the decrease results from the formation of a SiC–AlN solid solution and an increase in the heat resistance of

Fig. 6. SEM micrographs of the etched surfaces of Si_3N_4 ceramics prepared at 1700°C for 30 min at $150^\circ\text{C}/\text{min}$ using nanosized amorphous Si_3N_4 (a) and submicron-sized $\alpha\text{-Si}_3\text{N}_4$ powders (b).⁴⁹⁾

the glass phase because of the addition of AlN and rare-earth oxide additives.^{58),59)} In this work, SiC ceramics were prepared from submicron- and nano-sized $\beta\text{-SiC}$ powders with 10 vol % AlN and Y_2O_3 sintering additives by SPS.

In the case of the submicron-sized $\beta\text{-SiC}$ starting powder, the relative density of SiC sintered bodies was greater than 95% at 1900°C for 10 min in N_2 at a pressure of 30 MPa. The density increased with increasing AlN additive content for 10 vol % AlN– Y_2O_3 additives. The crystalline phase of the SiC bodies was mainly 3C ($\beta\text{-SiC}$). A 2H phase, which is assigned to AlN or one of $\alpha\text{-SiC}$ phases, was detected when a large amount of AlN additive was used. In contrast, a 4H–SiC ($\alpha\text{-SiC}$) phase was identified when Al_2O_3 was used as the sintering additive. Because AlN has hexagonal crystal system and is soluble in 2H–SiC, AlN can form a solid solution with 2H–SiC.⁶⁰⁾ Hence, the peak of the 2H phase observed in this work may suggest the existence of a SiC–AlN solid solution and/or AlN remaining in the SiC bodies sintered with the AlN additive. The size of the SiC grains decreased with an increase in the amount of the AlN additive (Fig. 7).⁵³⁾ The grain morphology changed from globular to angular when the amount of AlN additive was increased. The size and morphology of the SiC grains prepared at an additive composition of 95 mol % AlN and 5 mol % Y_2O_3 were almost the same as those of the SiC starting powder, suggesting that the grain growth was inhibited during the liquid-phase sintering. On the other hand, in a dense SiC body sintered with 2 mass % Al_2O_3 additive, grain growth and elongated grains were observed. The flexural strength of the SiC sintered bodies increased with the AlN additive amount. The strength of the sample obtained at 95 mol % AlN and 5 mol % Y_2O_3 reached a high value of 1150 MPa. In the sample sintered with 2 mass % Al_2O_3 additive, the strength was 780 MPa.

Fig. 7. SEM micrographs of the etched surfaces of SiC ceramics prepared with different compositions of AlN– Y_2O_3 additives and with 2 mass % Al_2O_3 additive at 1900°C for 10 min.⁵³⁾

By using nanosized $\beta\text{-SiC}$ starting powder with a particle diameter of 40 nm, SiC ceramics were prepared by SPS; AlN– Y_2O_3 additives were used in the preparation.⁵⁴⁾ As a result, the behaviors of the densification, phase transformation, and grain morphology were similar to those of SiC ceramics prepared using the submicron-sized $\beta\text{-SiC}$ powder. Fully dense SiC ceramics prepared with 10 vol % additives consisting of 90 mol % AlN and 10 mol % Y_2O_3 had the smallest grain size of 150 nm. Furthermore, nanostructured SiC ceramics consisting of equiaxed grains (diameter: 70 nm) were fabricated by using AlN-rich additives with a 10 vol % additive containing 95 mol % AlN and 5 mol % Y_2O_3 and by short-time sintering by SPS at 1900°C for 5 min at the heating rate of $100^\circ\text{C}/\text{min}$.⁵⁵⁾

8. Cubic-BN-dispersed ceramic composites^{61)–66)}

Cubic-BN (cBN)-dispersed ceramic composites were fabricated at a moderate pressure of 100 MPa at various sintering temperatures by SPS, and the densification, phase transformation, microstructure, and mechanical properties of the composites were investigated.

Al_2O_3 –cBN composites were prepared from Al_2O_3 and cBN powders by SPS at $1200\text{--}1600^\circ\text{C}$ for 10 min at a pressure of 100 MPa.⁶¹⁾ Al_2O_3 –cBN composites originally containing 10–20 vol % cBN with a relative density greater than 98% were obtained at 1300°C without a phase transformation of cBN to hexagonal BN (hBN) (Fig. 8).⁶¹⁾ The phase transformation of cBN in the Al_2O_3 –cBN composites was more likely than in the cBN body. The addition of cBN to Al_2O_3 inhibited the grain growth of Al_2O_3 in the Al_2O_3 –cBN composites. The Vickers hardness of the dense Al_2O_3 –cBN composites originally containing 10–20 vol % cBN prepared at 1300°C reached a maximum value of 26 GPa. In cBN–TiN–Al composites, the hardness increased with an increase in cBN content and the hardness of the composite containing 75 vol % cBN was 30 GPa.⁶⁷⁾ In WC–Co–cBN composites prepared by hot isostatic pressing, the hardness of the composites reached 25 GPa.⁶⁸⁾ Moreover, in WC–

Fig. 8. Effect of cBN content on the relative density of Al_2O_3 bodies and Al_2O_3 -BN composites prepared at 1200–1400°C for 10 min.⁽⁶¹⁾

Fig. 9. Effect of cBN content on the relative density of βSiAlON bodies and βSiAlON -BN composites prepared at 1650 and 1700°C without a holding time.⁽⁶³⁾

Co-cBN composites prepared by SPS, the addition of cBN to WC-Co increased the hardness from 19 to 21 GPa.⁽⁶⁹⁾ The Al_2O_3 -cBN composite originally containing 20 vol% cBN prepared at 1300°C had the highest fracture toughness, $4.1 \text{ MPa}\cdot\text{m}^{1/2}$. In addition, the Vickers hardness of the Al_2O_3 -cBN composites was characterized at indentation loads from 0.098 to 19.6 N.⁽⁶²⁾ The hardness of the BN grains in the Al_2O_3 -BN composite prepared at 1300°C without the transformation of the cBN to the hBN phase was 59 GPa at the indentation load of 0.098 N. The hardness of the Al_2O_3 matrix in the Al_2O_3 -BN composites originally containing 10–30 vol% cBN prepared at 1300–1400°C was approximately 25 GPa at 0.098 N, which was higher than that of the monolithic Al_2O_3 bodies prepared at the same temperatures. The hardness of the Al_2O_3 matrix in the Al_2O_3 -BN composites decreased with increasing sintering temperature.

βSiAlON -cBN composites were prepared from βSiAlON and cBN powders at 1600–1900°C without a holding time.⁽⁶³⁾ The finishing temperature of shrinkage of the βSiAlON -BN composites originally containing 10–30 vol% cBN was lower than that of monolithic βSiAlON . The relative density of the βSiAlON -BN composites increased when 10–30 vol% cBN was added to βSiAlON (Fig. 9),⁽⁶³⁾ although the addition of cBN to Al_2O_3 led to a decrease in relative density of the Al_2O_3 -cBN composites. The densification of the βSiAlON -BN composite originally containing more than 40 vol% cBN was inhibited. Martínez and Echeberria⁽⁶⁸⁾ studied the densification behavior of WC-Co-cBN composites with the addition of cBN up to 50 vol% and found the densification of WC-Co was significantly prevented by the

addition of cBN. Martín et al.⁽⁷⁰⁾ also reported the reduction of densification of cBN-Cu-Ti composites with an increase in the cBN content. The phase transformation of cBN to hBN in the βSiAlON -BN composite was suppressed to a greater extent than in the cBN body. When 10 vol% cBN was added to βSiAlON , the Vickers hardness of the βSiAlON -BN composite prepared at 1650 and 1700°C increased from 9 to 14 GPa and 13 to 16 GPa, respectively. The cBN phase transformed into hBN, and the hardness decreased with increasing holding time.⁽⁶⁴⁾ The phase transformation of cBN was retarded by increasing the heating rate, resulting in increased hardness of the βSiAlON -BN composite.

Dense TiN-cBN and mullite-cBN composites without the phase transformation from cBN to low-hardness hBN were also obtained under a moderate pressure of 100 MPa by SPS.^{(65), (66)}

9. Summary

Hollow spherical Ca- α SiAlON powders composed of nano-sized particles were successfully synthesized from a relatively inexpensive starting material such as a SiO_2 - Al_2O_3 - CaCO_3 powder mixture by using a convenient production process involving carbothermal reduction-nitridation. Using the nano-sized Ca- α SiAlON powder, dense Ca- α SiAlON nanoceramics with high hardness, high corrosion resistance, and excellent strength at high temperatures were obtained by using the SPS technique; no sintering additive was used. Porous Ca- α SiAlON ceramics were also obtained, without using a sintering additive, from the hollow spherical Ca- α SiAlON powders by SPS. Ultrafine-grained Si_3N_4 and SiC ceramics were prepared from fine-grained starting powders by rapid sintering using the SPS technique. The densification of cBN-dispersed ceramic composites, such as Al_2O_3 -cBN, βSiAlON -cBN, TiN-cBN, and mullite-cBN, was achieved without the phase transformation of cBN to low-hardness hBN, at a moderate pressure by SPS.

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