Fabrication of silicon nitride nanoceramics—Powder preparation and sintering: A review

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Abstract

Fine-grained silicon nitride ceramics were investigated mainly for their high-strain-rate plasticity. The preparation and densification of fine silicon nitride powder were reviewed. Commercial sub-micrometer powder was used as raw powder in the "as-received" state and then used after being ground and undergoing classification operation. Chemical vapor deposition and plasma processes were used for fabricating nanopowder because a further reduction in grain size caused by grinding had limitations. More recently, nanopowder has also been obtained by high-energy milling. This process in principle is the same as conventional planetary milling. For densification, primarily hot pressing was performed, although a similar process known as spark plasma sintering (SPS) has also recently been used. One of the advantages of SPS is its high heating rate. The high heating rate is advantageous because it reduces sintering time, achieving densification without grain growth. We prepared silicon nitride nanopowder by high-energy milling and then obtained nanoceramics by densifying the nanopowder by SPS.

Keywords: Silicon nitride; Nanopowder; Nanoceramics; High-energy milling; Spark plasma sintering

1. Introduction

Silicon nitride ceramics have been developed mainly as structural materials for high-temperature applications.
They exhibit unique properties because of their high fracture toughness due to a composite microstructure and a high creep resistance controlled by grain boundary chemistry. The high-strain-rate plasticity of a silicon nitride ceramic, known as superplasticity, was first reported by Wakai et al. [1] in 1990. This ceramic is a composite of silicon carbide and silicon nitride with a small grain. Their report indicated that silicon nitride with a small grain could exhibit plastic behavior even if it is typically tough and strong. Since 1990, many fine-grained silicon nitride ceramics have been developed. Table 1 shows a summary of fine-grained silicon nitride ceramics that have thus far been reported [1–28]. Most of the materials reported exhibited high-strain-rate plastic deformation; however, in later years, a material for tribological use [18] with fine-grained but low-strain-rate plastic sialon [28] was reported. The preparation of fine raw powder starts from an “as-received” material as commercial powder, followed by its grinding and sedimentation, resulting in the formation of nanopowder by chemical reaction. In recent days, a high-energy milling technique for commercial powder has also been used. A conventional hot pressing technique has been used for sintering. A recent technique of obtaining fine-grained ceramics is pulsed electric current sintering (PECS), also known as spark plasma sintering (SPS). Here, in this paper, powder preparation and densification techniques for fabricating fine-grained silicon nitride ceramics are reviewed, and then, the fabrication of silicon nitride nanoceramics, which are mostly composed of grains <100 nm, by a combination of high-energy milling and SPS is described.

2. Preparation of fine powder

Fine-grained silicon nitride ceramics, which are mostly composed of grains in the order of 100 nm, were developed mainly to confer plasticity to ceramics. The plastic deformation of silicon nitride ceramics is analyzed using the following constitutive equation:

\[ \dot{\varepsilon} = A\sigma^n d^{-p} \exp \left( \frac{-Q}{kT} \right), \]

where \( \dot{\varepsilon} \) is strain rate, \( \sigma \) is applied stress, \( d \) is grain size, \( Q \) is activation energy, \( R \) is gas constant, and \( T \) is temperature. \( A, n \), and \( p \) in this equation are constants [2–4,8,11,13,17,27,28]. According to the above-mentioned creep equation, the applied stress, the grain size of the deformed material, and the temperature affect the strain rate; namely, a fine grain is favorable for plastic deformation at a high strain rate under constant stress and temperature conditions. The fine grain is also favorable for plastic deformation at a low temperature under constant stress and strain rate conditions. Fine raw powder is necessary for fabricating fine-grained silicon nitride ceramics. The raw powder is densified by sintering. During sintering, grain growth and densification occur simultaneously [29]. When the particle size distribution is wide, large particles tend to grow by absorbing small particles even when the average grain size of the overall distribution is small. Therefore, for suppressing grain growth, a narrow particle size distribution is preferred.

2.1. Commercial fine powders

Commercial z-type silicon nitride powders (average particle size: 0.5–0.6 μm) have widely been used as raw powders. These powders in some cases were used without grinding. For processes involving grinding, a process known as attrition milling was employed; however, the results of grinding, e.g., particle size or particle size distribution, were not reported [2,4,6,12,13]. Another process employed for grinding is known as mechanochemical grinding [18]. This process is similar to high-energy milling and will be addressed later in this paper.

During sintering, phase transformation from low-temperature α-type to high-temperature β-type occurs and induces grain growth. Hence, α-powder is not considered a suitable starting material for fabricating fine-grained ceramics. For this reason, Mitomo et al.[7] used β-powder as raw powder. They removed coarse particles from the powder by centrifugal sedimentation to control the particle size distribution. Using this technique, the average grain size changed from 510 to 280 nm and the distribution became narrower than that of the original powder; i.e., the value of 90% particle size reduced from 1110 to 450 nm. The sintering temperature of complete densification was reduced by the control of the particle size distribution, indicating that grain growth during sintering could be suppressed [7].

2.2. Formation of fine powders

Several original fine powders were developed for fabricating fine-grained ceramics. Amorphous Si-C-N powder was fabricated from [Si(CH3)3]2NH/NH3/N2 by vapor-phase reaction. A Si3N4/SiC composite was fabricated from the powder [1]. Belloli et al.[22] used the Si3N4 nanopowder produced by a plasma process. This powder was already doped with Y2O3 and Al2O3. About 30% of the powder was crystalline; the remaining 70% was amorphous. According to transmission electron microscope (TEM) studies, the mean particle size of the powder was 32 nm, whereas the size of most particles ranged from 10 to 40 nm and that of the rest ranged from 50 to 200 nm [22]. z-Sialon nanoceramics were formed from the Ca-z-sialon nanopowder synthesized by the carbothermal reduction and nitridation of a powder mixture of SiO2, Al2O3, CaCO3, and carbon [28]. The synthesized powders were an agglomerate of fine particles 10–30 nm in diameter [30]. A study on the synthesis of nanopowder for sintering bulk nanoceramics is in progress; however, the control of the distribution and agglomeration of particles is still not satisfactory. The preparation of nanopowder by grinding that involves the breaking down of particles has been found...
| Powder sintering additives                  | Grinding condition       | Particle size (nm) | Sintering condition | Grain size (nm) | Deformation condition | Ref.  |
|--------------------------------------------|--------------------------|--------------------|---------------------|-----------------|------------------------|-------|
| SiC–N amorphous powder (Si<sub>3</sub>N<sub>4</sub>/ SiC) 6 wt% Y<sub>2</sub>O<sub>3</sub> + 2 wt% Al<sub>2</sub>O<sub>3</sub> | Attrition mill, 900 rpm, 2 h | >200               | HP, 1650 °C, 0.7 h, 34 MPa | Spherical <200 nm, elongated <500 nm | 1600 °C, 8 × 10<sup>-5</sup>–4 × 10<sup>-5</sup>/s | [1]   |
| zAlN + Al<sub>2</sub>O<sub>3</sub> + Y<sub>2</sub>O<sub>3</sub> (sialon) | Attrition mill, 900 rpm, 2 h | HP, 1550 °C, 20 min, 28 MPa | HP, 1650–1800 °C, 1–4 h, 34 MPa | 1500–1575 °C, 10<sup>-6</sup>–10<sup>-3</sup>/s | 114% | [2]   |
| SiC–N amorphous powder (Si<sub>3</sub>N<sub>4</sub>/ SiC) Y<sub>2</sub>O<sub>3</sub> + Al<sub>2</sub>O<sub>3</sub> | Attrition mill, 900 rpm, 2 h | HP, 1550 °C, 30 min, 35 MPa, 15 K/min to 1000 °C | HP, 25 K/min to 1000 °C, 15 K/min to 1550 °C, 17–30 min, 27 MPa | 350 | Tension, 1535–1580 °C, 3 × 10<sup>-3</sup>–1 × 10<sup>-3</sup>/s | [4]   |
| zAlN + Al<sub>2</sub>O<sub>3</sub> + Y<sub>2</sub>O<sub>3</sub> (sialon) | Attrition mill, 900 rpm, 2 h | HP, 25 K/min to 1000 °C, 15 K/min to 1550 °C, 17–30 min, 27 MPa | 200 | 1550 °C, 1 × 10<sup>-4</sup>–1 × 10<sup>-3</sup>/s | [5]   |
| zAlN + Al<sub>2</sub>O<sub>3</sub> + Y<sub>2</sub>O<sub>3</sub> (sialon) | Attrition mill, 900 rpm, 2 h | HP, 1550 °C, 30 min, 35 MPa, 15 K/min to 1000 °C | HP, 25 K/min to 1000 °C, 15 K/min to 1550 °C, 17–30 min, 27 MPa | 350 | Tension, 1535–1580 °C, 3 × 10<sup>-3</sup>–1 × 10<sup>-3</sup>/s | [4]   |
| β5 wt% Y<sub>2</sub>O<sub>3</sub> + 2 wt% Al<sub>2</sub>O<sub>3</sub> | Sedimentation            | 280                | HP, 1700 °C, 0 min, 20 MPa | 210 | 1450–1650 °C, 7 × 10<sup>-4</sup>/s, 100 MPa | [7.8] |
| β5 wt% Y<sub>2</sub>O<sub>3</sub> + 2 wt% Al<sub>2</sub>O<sub>3</sub> | Sedimentation            | 280                | SPS, 1550 °C, 8.5 min, 49 MPa | 1450–1500 °C, 5 × 10<sup>-6</sup>–5 × 10<sup>-5</sup>/s, 10–50 MPa | [9]   |
| z + 5 wt% Y<sub>2</sub>O<sub>3</sub> | Attrition mill           | 500                | SPS, 1550 °C, 8.5 min, 49 MPa | 1450–1500 °C, 5 × 10<sup>-6</sup>–5 × 10<sup>-5</sup>/s, 10–50 MPa | [10,11] |
| zY<sub>2</sub>O<sub>3</sub> + Al<sub>2</sub>O<sub>3</sub> | Attrition mill           | 500                | SPS, 1550 °C, 8.5 min, 49 MPa | 1450–1500 °C, 5 × 10<sup>-6</sup>–5 × 10<sup>-5</sup>/s, 10–50 MPa | [10,11] |
| zAlN + Al<sub>2</sub>O<sub>3</sub> + Li<sub>2</sub>O + Y<sub>2</sub>O<sub>3</sub> | Sedimentation            | 280                | SPS, 1550 °C, 8.5 min, 49 MPa | 1450–1500 °C, 5 × 10<sup>-6</sup>–5 × 10<sup>-5</sup>/s, 10–50 MPa | [10,11] |
| zSi<sub>3</sub>N<sub>4</sub> doped with 6.1 wt% Y<sub>2</sub>O<sub>3</sub> and 3.2 wt% Al<sub>2</sub>O<sub>3</sub>, plasma synthesis | High-energy milling, 4 h | 32                 | SPS, 1550 °C, 5 min, 30 MPa | 1500 C, 1 × 10<sup>-3</sup>/s, 34 MPa | [20]  |
| zβ 5 mol% Y<sub>2</sub>O<sub>3</sub> + 2 mol% Al<sub>2</sub>O<sub>3</sub> | High-energy milling, 4 h | 32                 | SPS, 1550 °C, 5 min, 30 MPa | 1500 C, 1 × 10<sup>-3</sup>/s, 34 MPa | [20]  |
| zβ 5 mol% Y<sub>2</sub>O<sub>3</sub> + 2 mol% Al<sub>2</sub>O<sub>3</sub> | High-energy milling, 4 h | 32                 | SPS, 1550 °C, 5 min, 30 MPa | 1500 C, 1 × 10<sup>-3</sup>/s, 34 MPa | [20]  |

z: commercial z-Si<sub>3</sub>N<sub>4</sub> powder; β: commercial β-Si<sub>3</sub>N<sub>4</sub> powder.
to be difficult. Hence, the fabrication process for nanoparticles must be improved further.

2.3. High-energy milling

A mechanical alloying technique, which involves mixing and alloying raw powders using high energy, has been widely used in the field of metallurgy; this technique is now being applied to ceramics. z-Silicon nitride powder mixed with Y2O3 and Al2O3 as sintering additives was ground with metallic titanium and Si3N4 balls in a Si3N4 pot in a N2 atmosphere. An important factor in the process is a high rotation speed, at which the angular acceleration is 150g, which is about 10 times the value of conventional planetary milling. A decrease in the particle size of Si3N4 and the formation of TiN were revealed by XRD analysis. The particle size of Si3N4 was 5–20 nm, and that of TiN was a few nm. The process was performed by “mechanochemical grinding” [18]. An important point to note is that silicon nitride nanopowder could be obtained by grinding, namely, the breaking down of particles. In this study, metallic titanium acts as a grinding additive that promotes the grinding of silicon nitride particles. Xu et al. [20] showed that commercial silicon nitride submicrometer powder could be ground to <100 nm by high-energy milling without using a grinding additive. The result will be cited later in Section 4 of this paper.

3. Densification

Hot pressing has been mainly used for fabricating fine-grained silicon nitride before the year 2000, as shown in Table 1. The sintering temperature of monolithic fine-grained silicon nitride or sialon has been low (1550–1700 °C), and the soaking time has been short (0–30 min) to suppress grain growth. For hot pressing, a high heating rate of 30 K/min was used [7].

The SPS technique was used in most of the studies performed after 2000 [18–21, 23–25–28]. This technique is similar to hot pressing; however, it is different from hot pressing in terms of the heating process. The powder to be compacted is in a metal or carbon die and is pressed by the upper and lower punches of the same material as the die. A pulsed direct electric current is applied between the upper and lower punches. The electric current goes through the die and the die generates heat. In this method, heating at a considerably high rate (>300 K/min) can be performed. Another technique similar to SPS is plasma-assisted sintering (PAS) [10, 11]. The difference between the two techniques lies in their time factors; the entire heating time for SPS, and in the case of PAS, the initial short period (30 s) of conducting the electric current. A continuous direct current is conducted after 30 s for PAS. A difference between the “measured” temperature and the temperature of powder in SPS was pointed out by Wada et al. [31]. Here, the measured temperature refers to the temperature of a hole on the surface of a die. This temperature is used to represent the sintering temperature of the powder since the temperature of powder in the die cannot be measured directly. Wada et al. measured the temperature of the silicon nitride powder in a die with a thermocouple and compared the temperature of the hole with the temperature inside the die. The obtained results indicated that the temperature inside the die was about 150 °C higher than the temperature of the hole [31]. The sintering temperature of SPS was found to be lower than that of conventional hot pressing, although this temperature difference was accounted for.

The use of the hot isostatic pressing technique was indicated in Refs. [12, 24]. The sintering time of this technique was long, 60–90 min.

The nanopowder doped with Y2O3 and Al2O3 prepared by a plasma process was densified up to 99% in relative density by pressureless sintering at 1750 °C for 30 min [22]. The complete densification of conventional sub-micrometer powder with sintering additives by pressureless sintering was difficult. The complete densification of the nanopowder is attributed to a high surface energy originating from nanometer-size particles. The microstructure of the ceramic is bimodal and is composed of fine and elongated grains. A nanoceramic can be obtained from the nanopowder by reducing sintering temperature and suppressing grain growth, if the sintering method used is pressure sintering, i.e., hot pressing, hot isostatic pressing or SPS.

4. Combination of high-energy milling and SPS

We have investigated the fabrication of silicon nitride nanoceramics for realizing monolithic silicon nitride ceramics with microstructures on the nanometer scale and making a breakthrough in the mechanical properties of nanoceramics. The preparation of the nanopowder by high-energy milling has been attempted because grinding could be successfully applied to many types of ceramic powder. The SPS technique was used for sintering, because high-speed heating could be possible by this technique.

4.1. High-energy milling

Sub-micrometer β-Si3N4 powder (NP500 grade, average grain size: 0.5 μm, Denki Kagaku Kogyo Co., Tokyo, Japan) was used mainly as raw powder to avoid the grain growth induced by phase transformation. Sub-micrometer z-Si3N4 powder (SN-E10, average grain size: 0.5 μm, Ube Industries, Ltd., Tokyo, Japan) was used for some of the experiments. After mixing silicon nitride powder with sintering additives by conventional planetary milling under wet conditions, the powder mixture was dried and milled by high-energy milling. Planetary milling (PM1200, Seishin Enterprise Co., Ltd.) was carried out at 475 rpm for 4 h. A pot lined with silicon nitride was employed for this purpose. It contained silicon nitride balls that were mainly used as milling media for minimizing contamination. The
introduction of the powder mixture into the pot and the extraction of the milled powder were performed in a glove box filled with nitrogen gas to avoid oxidation. The high-energy-milled powder mixture of $\beta$-Si$_3$N$_4$, 5 mol% Y$_2$O$_3$ (99.9% pure, Shin-etsu Chemical Co., Tokyo, Japan) and 2 mol% Al$_2$O$_3$ (99.9% pure, Sumitomo Chemical Co., Tokyo, Japan) was observed using a TEM (JEM-3000F, JEOL, Tokyo, Japan). Typical images from these experiments are shown in Fig. 1. It is very difficult to distinguish individual particles from agglomerates in Fig. 1(a) because the particles overlapped each other. Particles smaller than 100 nm can be observed near a micron bar. Selected area diffraction patterns (SADP) revealed not only diffraction spots but also diffuse diffraction rings; the latter indicates vitrification by milling (Fig. 1(b)). We can observe crystalline areas in the glassy part surrounded by dotted lines and pointed by arrows in Fig. 1(c). The size of the crystalline area was about 10 nm. The particle size of the original Si$_3$N$_4$ sample was about 500 nm. A decrease in particle size and vitrification occurred during high-energy milling.

A powder mixture of $\beta$-Si$_3$N$_4$, AlN (Grade F, Tokuyama Corp., Tokyo, Japan) and Al$_2$O$_3$ in Si$_5$AlON$_7$ composition was analyzed by XRD (PW1700, Philips) before and after milling. XRD patterns of the powder mixture of $\beta$-sialon composition before and after high-energy milling are shown in Fig. 2. The XRD patterns indicate the presence of crystalline phases before milling, while the diffuse diffraction rings after milling indicate vitrification.

Fig. 1. TEM observation of high-energy-milled Si$_3$N$_4$ particles. (a) Typical low-magnification image, (b) selected area diffraction patterns (SADP), and (c) high-magnification image [20].

Fig. 2. XRD patterns of powder mixture of $\beta$-sialon composition before and after high-energy milling [21].

Fig. 3. Effect of metallic aluminum on high-energy milling.
The peak height of $\beta$-Si$_3$N$_4$ decreased and the peaks of AlN and Al$_2$O$_3$ disappeared in the XRD pattern of the milled powder. Another point to note is the increase in background height. These results indicate the vitrification of $\beta$-Si$_3$N$_4$, AlN, and Al$_2$O$_3$, and the decrease in the particle size of $\beta$-Si$_3$N$_4$ [21]. The result of XRD analysis supports the TEM observation in Fig. 1. The silicon nitride balls used as the milling media collided with the particles of the powder mixture during milling. The crystal structure of the surface of a particle might be destroyed by such collisions when the entire particle is broken into small pieces. The collision energy in high-energy milling was significantly high, because the grinding speed was three times higher than that in conventional planetary milling and because the ball/powder ratio (weight ratio of the balls to the milled powder) was more than 10 times the value of conventional setups. These are some of the probable reasons for the vitrification and decrease in the grain size of the high-energy-milled powder.

Metallic Al was added as a grinding additive. Fig. 3 shows the effects of the metallic Al addition and ball/powder weight ratio on the relative intensity in the XRD
chart. The relative intensity is the peak height after high-energy milling relative to that before the milling. A low relative intensity indicates a high impact of high-energy milling. The average relative intensity of the (2 0 0), (1 0 1), (2 1 0), (2 0 1), and (3 0 1) peaks of $\beta$-Si$_3$N$_4$ is plotted in Fig. 3. When high-energy milling was performed without metallic Al, the relative intensity decreased with the increase in the ball/powder ratio. When metallic Al was added, a higher amount of Al became more effective for reducing the relative intensity. When 10.9% of Al was added and the ball/powder ratio was 1.6, the relative intensity was 44.0%; this value corresponded to the intensity of 42.2% obtained without Al addition at a ball/powder ratio of 5. This result suggests that metallic Al makes Si$_3$N$_4$ milling more effective.

The milled powder was analyzed using a TEM (Hitachi, HF-3000) operated at an acceleration voltage of 300 kV. The elemental maps of Si, Al, N, and O shown in Fig. 4 were obtained using an energy filter (Gatan, GIF2002) attached to the electron microscope [32]. The distributions of Si and N are similar, confirming that most of the grains are Si$_3$N$_4$. Al exists at the edge of the grains and also in the entire area of some large grains. O exists only at the edge of the grains. The discrepancy between the observed distributions of Al and O indicates that large grains containing Al are metallic Al and that Al$_2$O$_3$ exists around the Si$_3$N$_4$ grains, probably with Y$_2$O$_3$.

4.2. Sintering

SPS (SPS-1030, SPS Syntax Inc., Kanagawa, Japan) was carried out in nitrogen at a compressive stress of 30 MPa for 5 min. The heating rate was about 300 °C/min. Filling the milled powder into a die was also performed in the glove box to minimize oxidation.

The high-energy-milled powder of $\beta$-Si$_3$N$_4$, Y$_2$O$_3$, and AlN with Y$_{0.45}$Si$_{0.975}$Al$_{2.025}$O$_{0.675}$N$_{15.325}$ composition sintered at 1500 °C was almost fully densified. A typical microstructure on a fractured surface of the obtained $\alpha$-sialon nanoceramics is shown in Fig. 5. The shape of the grain is nearly equiaxial. The grain diameter is about 60–90 nm [25].

Fig. 6 shows typical apparent shrinkage during SPS sintering. The shrinkage of the “as-mixed” powder starts at a temperature lower than the temperature at which the high-energy-milled powder starts shrinking. After the start of shrinkage, degree and rate in the shrinkage of milled powder became much higher than those of as-mixed powder. This difference in densification manner may be caused by the small grain size of Si$_3$N$_4$ and the vitrification of Si$_3$N$_4$, Y$_2$O$_3$, and Al$_2$O$_3$ [20].

The final density is plotted as a function of sintering temperature in Fig. 7. The high-energy-milled powder is almost completely densified at 1500 °C and the as-mixed powder at 1650 °C [21].

The fractured surfaces of ceramics from the high-energy-milled Si$_3$N$_4$ powder with Y$_2$O$_3$, Al$_2$O$_3$, and metallic Al
were observed by SEM (Fig. 8). The size of the grain on the observed surface from a ceramic sintered at 1550 °C is about 100 nm. The microstructure of a ceramic sintered at 1600 °C appears coarser and sub-micrometer grains also appear to exist. Grain growth is enhanced by increasing the sintering temperature up to 1500 °C. This suggests that sintering temperature must be controlled precisely [23]. The typical plastic deformation data of silicon nitride nanoceramics fabricated by the combination of high-energy milling and SPS are shown in Fig. 9. Compression tests were carried out at 1450–1600 °C for β-Si₃N₄ sintered with 5 mol% Y₂O₃ and 2 mol% Al₂O₃. A high plastic deformation of ε > 0.4 was attained even at 1450 °C [33]. The precise analysis of material deformation [33], the effect of sintering additives [26], the amount of sintering additives [27], and the deformation analysis of z-sialon [34] have been reported elsewhere.

5. Conclusion

The fabrication of fine-grained silicon nitride ceramics was reviewed. Commercial sub-micrometer powders were used as raw powders in the “as-received” state, ground or classified. A process for fabricating nanopowder involving high-energy milling is being developed but the breaking down of particles to a nanometer scale continues to be a difficult task until now. The fabrication of nanopowder with chemical processing and a plasma process has been recently reported and should be investigated further as a new powder preparation method. Hot pressing has been used for densification. SPS that enables heating at a high rate has also been used; it is expected that this process will densify the powder without grain growth. The fabrication of silicon nitride nanoceramics by a combination of high-energy milling and SPS was explained. Commercial sub-micrometer Si₃N₄ was high-energy-milled with oxide additives. A decrease in the particle size of Si₃N₄ and the vitrification of Si₃N₄ and oxides occurred. The milled powder was densified by SPS. A Si₃N₄ nanoceramic with a grain size of about 70 nm was obtained. The nanoceramic exhibited plasticity at 1450 °C.

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References

[1] F. Wakai, Y. Kodama, S. Sakaguchi, N. Murayama, K. Izaki, K. Niihara, Nature 344 (1990) 421.
[2] I. Chen, S. Hwang, J. Am. Ceram. Soc. 75 (1992) 1073.
[3] T. Rouxel, F. Wakai, K. Izaki, J. Am. Ceram. Soc. 75 (1992) 2363.
[4] X. Wu, I. Chen, J. Am. Ceram. Soc. 75 (1992) 2733.
[5] S. Hwang, I. Chen, J. Am. Ceram. Soc. 77 (1994) 165.
[6] S. Hwang, I. Chen, J. Am. Ceram. Soc. 77 (1994) 2575.
[7] M. Mitomo, H. Hirotsumi, H. Suehata, T. Nishimura, J. Am. Ceram. Soc. 78 (1995) 211.
[8] G. Zhan, M. Mitomo, T. Nishimura, R. Xie, T. Sakuma, Y. Ikuhara, J. Am. Ceram. Soc. 78 (2000) 841.
[9] T. Nishimura, M. Mitomo, H. Hirotsumi, M. Kawahara, J. Mater. Sci. Lett. 14 (1995) 1046.
[10] J.A. Schneider, S.H. Risbud, A.K. Mukherjee, J. Mater. Res. 11 (1996) 358.
[11] J.A. Schneider, A.K. Mukherjee, J. Am. Ceram. Soc. 82 (1999) 761.
[12] P. Burger, T. Duclos, J. Crampon, J. Am. Ceram. Soc. 80 (1997) 879.
[13] A. Rosenflanz, I. Chen, J. Am. Ceram. Soc. 80 (1997) 1341.
[14] T. Rouxel, F. Rossignol, J. Besson, P. Goursat, J. Mater. Res. 12 (1997) 480.
[15] P. Descamps, D. Beugnies, F. Cambier, J. Euro. Ceram. Soc. 17 (1997) 433.
[16] P. Burger, R. Duclos, J. Crampon, Key Eng. Mater. 132–136 (1997) 555.
[17] R. Xie, M. Mitomo, G. Zhan, H. Emoto, J. Am. Ceram. Soc. 83 (2000) 2529.
[18] M. Yoshimura, O. Komura, A. Yamakawa, Scr. Mater. 44 (2001) 1517.
[19] Z. Shen, H. Peng, M. Nygren, Adv. Mater. 15 (2003) 1066.
[20] X. Xu, T. Nishimura, N. Hirosaki, R. Xie, Y. Zhu, Y. Yamamoto, H. Tanaka, J. Am. Ceram. Soc. 88 (2005) 934.
[21] X. Xu, T. Nishimura, N. Hirosaki, R. Xie, Y. Yamamoto, H. Tanaka, Nanotechnology 16 (2005) 1569.
[22] A. Bellosi, J. Vicens, V. Medri, S. Guicciardi, Appl. Phys. A 81 (2005) 1045.
[23] T. Nishimura, X. Xu, N. Hirosaki, K. Kimoto, Y. Yamamoto, H. Tanaka, Key Eng. Mater. 287 (2005) 156.
[24] E. Narimatsu, Y. Shinoda, T. Akatsu, F. Wakai, J. Euro. Ceram. Soc. 26 (2006) 1069.
[25] X. Xu, T. Nishimura, N. Hirosaki, R. Xie, Y. Yamamoto, H. Tanaka, Key Eng. Mater. 317–318 (2006) 629.
[26] X. Xu, T. Nishimura, N. Hirosaki, R. Xie, Y. Yamamoto, H. Tanaka, J. Am. Ceram. Soc. 89 (2006) 1745.
[27] X. Xu, T. Nishimura, N. Hirosaki, R. Xie, Y. Yamamoto, H. Tanaka, Scr. Mater. 55 (2006) 215.
[28] K. Chihara, D. Hiratsu, J. Tatami, F. Wakai, K. Komeya, Scr. Mater. 56 (2007) 871.
[29] M. Mitomo, N. Hirosaki, T. Nishimura, R.-J. Xie, J. Ceram. Soc. Jpn. 114 (2006) 867.
[30] K. Komeya, C. Zhang, M. Hotta, J. Tatami, T. Meguro, Y. Cheng, J. Am. Ceram. Soc. 83 (2000) 995.
[31] S. Wada, M. Suganuma, Y. Kitagawa, N. Murayama, J. Ceram. Soc. Jpn. 107 (1999) 887.
[32] C.C. Ann, Transmission Electron Energy Loss Spectrometry in Materials Science and the EELS Atlas, Wiley, New York, 2004.
[33] X. Xu, T. Nishimura, N. Hirosaki, R. Xie, Y. Yamamoto, H. Tanaka, Acta Mater. 54 (2006) 255.
[34] X. Xu, T. Nishimura, N. Hirosaki, R. Xie, Y. Yamamoto, H. Tanaka, Key Eng. Mater. 336–338 (2007) 1001.