We are IntechOpen, the world’s leading publisher of Open Access books
Built by scientists, for scientists

5,100
Open access books available

126,000
International authors and editors

145M
Downloads

154
Countries delivered to

TOP 1%
Our authors are among the most cited scientists

12.2%
Contributors from top 500 universities

WEB OF SCIENCE™
Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com
Chapter 16

Effect of Nano-TiN on Mechanical Behavior of Si$_3$N$_4$ Based Nanocomposites by Spark Plasma Sintering (SPS)

Jow-Lay Huang and Pramoda K. Nayak

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/50547

1. Introduction

Ceramic nanocomposites are often defined as a ceramic matrix reinforced with submicron/ nano sized particles of a secondary phase. The advantages of these nanocomposites include: improved mechanical properties, surface properties, high thermal stability and superior thermal conductivity. It is very fascinating/interesting for the researchers to synthesize these composites as the incorporation of few percent nanosized particles changes the materials property substantially. Niihara et al.,[35], [36] have reported that the mechanical properties of ceramics can be improved significantly by dispersing nanometer-sized ceramic particles into ceramic matrix grains or grain boundaries. According to their observation, 5 vol% of silicon carbide nanoparticles into alumina matrix increases the room temperature strength from 350 MPa to approximately 1 GPa. Other strength improvements through similar approaches have been observed in alumina-silicon nitride, magnesia-silicon carbide, and silicon nitride-silicon carbide composite systems. Apart from the basic mechanical properties such as micro hardness, fracture strength, and fracture toughness [9; 23; 44], nanocomposites also exhibit electro conductive, wear resistance, creep resistance and high temperature performance [10; 24; 37; 38, 39] However, the degree of improvement in these properties is dependent on the type of composite system involved.

1.1. Novel Synthesis of Ceramic nanocomposite

Chemical Vapor Deposition (CVD) is a very preferable method to disperse the nano-sized second phases into the matrix grains or at the grain boundaries [33]. However, the CVD process is not applicable to fabricate the large and complex shaped component for the mass produc-
tion and also it is very expensive. Processing route is another technique to prepare ceramic nanocomposites. Following the initial work of [34], several research groups have tried to synthesize the nanocomposites using different processing route such as conventional powder processing [6; 8], hot press sintering [25; 47] sol-gel processing [30; 50] and polymer processing [5; 16]. The ceramic nanocomposites can be synthesized using microwave plasma [48; 49]. The main advantage of this technique is that the reaction product does not form hard agglomerates because of the specific conditions during synthesis.

Figure 1. Schematics of Spark Plasma Synthesis (SPS) process

Recently developed Spark plasma sintering (SPS) is a novel sintering technique that uses the idea of pressure driven powder consolidation under pulsed direct electric current passing through a sample compressed in a graphite matrix. It is also known as the field assisted sintering technique or pulse electric current sintering. This newly developed sintering technique is regarded as an energy-saving technology due to the short process time and fewer processing steps. This technique was first described by Raichenko, 1987 and the key characteristics of this SPS are given as follows:

i. The generation of local electric discharge plasma and its effect on the material.

ii. The combined effect of external fields, such as a force field and electric field, on the densification and phase formation in a particulate system.

iii. The influence of electric current in the near surface layers of conductors and semiconductors (the so-called “skin-effect”).

iv. The rapid and nonuniform heating/cooling throughout the sample, causing large temperature gradients.
The schematic of SPS process is shown in Fig.1 [41].

1.2. Advantages of SPS over other synthesis method

The most impressive advantage of SPS is its applicability to sinter materials of various types of chemical bonding and electric conductivity. Novel materials have been prepared from powders of ceramic dielectrics, conductors, semiconductors, amorphous alloys, and, sometimes, polymers. The traditional driving force involved in commonly used consolidation techniques such as solid state sintering and hot press sintering are: surface tension, external pressure, chemical potential due to the gradient of surface curvature, concentration gradient in multicomponent system etc. In SPS technique, the additional driving forces include electromechanical stress, high local temperature gradients creating thermal stresses intensifying thermal diffusion, and dislocation creep. These additional driving forces are responsible for much faster transport mechanism, that accelerates rapid sintering, which is observed in SPS.

1.3. TiN/Si$_3$N$_4$ Ceramic Nanocomposites

Si$_3$N$_4$ ceramics are regarded as one of the important high temperature structural materials. These ceramics have attracted much attention due to their good mechanical and chemical properties and due to their reliability at room and elevated temperatures [14; 19]. High strength and high-toughness Si$_3$N$_4$ matrix composites such as whisker-reinforced of particulate-reinforced ceramics, have been developed to improve the mechanical reliability of Si$_3$N$_4$ ceramics [2; 13]. However, these composites are extremely hard and machining using conventional tools is difficult, which limits the widespread application of these materials in many fields. If, sintered Si$_3$N$_4$ bodies can be made electro conductive, electrical discharge machining (EDM) technique can be applied to manufacture complex components [32]. It has been reported that introduction of electro conductive second phase can improve the mechanical properties and electroconductivity of Si$_3$N$_4$ ceramics [14; 18; 43].

TiN exhibits a number of desirable properties, including high hardness, good chemical durability, high electrical conductivity and is a popular second phase additive due to its good compatibility with Si$_3$N$_4$. It often incorporated into the β-Si$_3$N$_4$ matrix as cutting-tool materials [4; 14; 17; 28]. There are two advantages to the Si$_3$N$_4$ based composites. First of all, the good physical properties of TiN, such as high melting point, hardness, strength and chemical stability, as well as its good erosion and corrosion resistance, enable it to be an excellent toughening material [7; 28; 51]. Secondly, the electrical resistance of Si$_3$N$_4$ can be substantially decreased, which consequently makes electric-discharge machining possible [17; 21].

2. Spark Plasma Sintering of TiN/Si$_3$N$_4$ nanocomposite

As described in the previous section, SPS is a newly developed sintering technique and it is beneficial to consolidate Si$_3$N$_4$ based nanocomposites in a short time. Some researchers have already reported that TiN/Si$_3$N$_4$ based nanocomposites with excellent mechanical properties and conductivity can be processed through a chemical route and sintered by SPS [1; 22].
However, due to the complexity of these processing techniques, they are not suitable for large scale production. The planetary milling process has been introduced in their study. Moreover, the details of microstructural development of Si$_3$N$_4$ and TiN have not described, especially in the presence of a pulse direct current through the sintering compact during a sintering cycle.

In the present study, we have prepared TiN/Si$_3$N$_4$ nanocomposite using SPS from Si$_3$N$_4$ and TiN nano powders. The Si$_3$N$_4$ and TiN nano powders were applied because they are sensitive to the microstructural changes during the sintering process. The relationship between microstructure and performance, like mechanical properties and electrical conductivity, of these TiN/Si$_3$N$_4$ nanocomposites are discussed. Finally, the effect of nano-TiN on the mechanical behavior of Si$_3$N$_4$ based nanocomposite has been investigated in sufficient details.

### 2.1 Experimental Details

#### 2.1.1. Preparation of TiN/Si$_3$N$_4$ nanocomposite powder

Commercially available Si$_3$N$_4$ nano powder (SM131, Fraunhofer-Institut fur Keramische Technologien and Sinterwerkstoffe, Dresden, Germany) doped with sintering additives of 6 wt% Y$_2$O$_3$ and 8 wt% Al$_2$O$_3$ was taken as raw material for the matrix phase. It contains 90 wt% β-phase and 10 wt% α-phase, with a manufacturer-determined average particle size of 70nm by the Rietveld method. Nanosized TiN with size of ∼30nm (Hefei Kiln Nanometer Technology Development, Hefei, China) was used as secondary phase and it was mixed with Si$_3$N$_4$ nano powders. The composition was chosen to yield a TiN content of 5, 10, 15, 20, and 30 wt % in the final product. The specimen designations and corresponding TiN/Si$_3$N$_4$ ratios in volume percentage (vol.%) for each composite are shown in Table 1. The mixing powders were ultrasonically dispersed in ethanol for 15 min, and then mixed by planetary milling at a rotation speed of 300rpm for 6 h using a 375 ml nylon bottle with Si$_3$N$_4$ balls. The powder mixture was dried in a rotary evaporator, iso-statically cold-pressed into round ingots at a pressure of 200 MPa, crushed and then passed through a #200 sieve for granulation.

| TiN/Si$_3$N$_4$ content ratio (wt%) | Designation | TiN/Si$_3$N$_4$ content ratio (vol%) |
|------------------------------------|-------------|-------------------------------------|
| 5                                  | 5TN         | 3.31                                |
| 10                                 | 10TN        | 6.75                                |
| 15                                 | 15TN        | 10.06                               |
| 20                                 | 20TN        | 14.00                               |
| 30                                 | 30TN        | 21.81                               |

Table 1. Specimen designation of composites for different TiN content.
2.1.2. Preparation of sintered bodies by SPS

The granulated powders were loaded into a graphite mold with a length of 50 mm and inner and outer diameters of 20 and 50 mm, respectively. A graphite sheet was inserted into the small gap between the punches and mold to improve the temperature uniformity effectively. The graphite mold was also covered with carbon heat insulation to avoid heat dissipation from the external surface of the die. After the chamber was evacuated to a pressure of 10 Pa, the sample was heated to 1600°C under a uniaxial pressure of 30 MPa by SPS (Dr. Sinter 1050, Sumitomo Coal Mining, Kawasaki, Japan). All the SPS measurements were carried out with a heating rate of 200°C/min and holding time of 3 min. A 12 ms-on and 2 ms-off pulse sequence was used. The heating process was controlled using a monochromatic optical pyrometer that was focused on the surface of the graphite mold.

2.1.3. Characterization of sintered bodies

The effective densities of the sintered composites were measured by the Archimedes principle. Phase identification was performed by an X-ray diffractometer (XRD; Model D-MAX/IIB, Rigaku, Tokyo, Japan). Cell dimensions were determined from XRD peak data using UNITCELL with a Si standard. A semiconductor parameter analyzer (HEWLETT PACKARD 4140B, USA) was used to determine the electrical resistivity of the samples. The upper surfaces of the sintered samples were polished down to 1μm. Hardness was measured with a Vickers hardness tester (AKASHI AVK-A, Japan) and by applying a micro-hardness indent at 196N for 15 s. Fracture toughness was measured by the Vickers surface indentation technique [12]. The polished and plasma etched surfaces were used for microstructural characterization by field emission scanning electron microscope (FESEM, XL-40FEG, Philips, The Netherlands). A thin specimen was prepared with a focused ion beam system (FIB, SEIKO, SM3050, Japan). Transmission electron microscopy (FEGTEM, Tecnai G2 F20, Philips, Eindhoven, Netherlands) was used to characterize the TiN grain of the sintered sample.

2.2. Results and Discussion

2.2.1. Phase Identification of nanocomposite powders by XRD

Fig.2 shows the typical X-ray diffraction patterns of sintered TiN/Si₃N₄ composites with varying TiN content. These composites consist of the β-Si₃N₄ phase as a major phase along with coexistence of secondary TiN phase. The intensity of TiN peaks continues to increase with increasing TiN content. The value of the lattice constant for TiN is 4.25Å, approaching that of pure TiN. On the other hand, the values for a₀ and c₀ for the β-Si₃N₄ phase are 7.61 and 2.91Å, respectively, which are somewhat deviated from those for pure β-Si₃N₄ (+0.01Å). This result suggests that a tiny amount of Si–N may be replaced by Al–O in the particle dissolution and coarsening stages of liquid phase sintering and form the β-SiAlON phase [45].
2.2.2. Densification Behavior

The apparent density of samples containing up to 30 wt% TiN is presented in Fig.3. The apparent density is found to increase with the increase of TiN content. The increase in density is as predicted, because the theoretical density of TiN (5.39 g/cm$^3$) is substantially greater than that of monolithic Si$_3$N$_4$ (3.19 g/cm$^3$) (Lide, 2002). No obvious pores are also observed on the polished surfaces of the samples (Fig.4), which suggest the TiN/Si$_3$N$_4$ composites are near full densification.

Figure 2. X-ray diffraction patterns of composites with different TiN content.

Figure 3. Variation of apparent density of the composites with TiN content.
Figure 4. Backscattered SEM images of polished TiN/Si$_3$N$_4$ composites with varying TiN content. The brighter phase is TiN phase and the darker phase is β-SiAlON matrix.

2.2.3. Microstructure Observation of Nanocomposites

The backscattered electron images in SEM of the polished surface of composites with varying TiN content are shown in Fig. 4. As stated earlier, the samples were sintered at 1600°C for 3min with a heating rate of 200°C/min in a vacuum. The lighter and heavier atoms in the backscattered images show up as the gray and white regions corresponding to the β-SiAlON matrix (including glassy phase) and TiN particles. Therefore, the TiN particles are distributed homogeneously in the β-SiAlON matrix. However, most of the TiN appear as submicrosized grains, which are much larger than the size of the starting nano powders.

The typical bright field and dark field images of the TiN grain for the as-sintered composite containing 10 wt% TiN content are shown in Fig. 5(a) and (b), respectively. Fig. 5(c) presents the [0 1 1] selected area diffraction pattern (SAD) for the submicrosized TiN grain, and it shows the existence of a twin structure. The results suggest that grain growth and coalescence of TiN occurs in the composite during the spark plasma sintering process in a short time.
Figure 5. a) Bright field and (b) dark field micrographs, and (c) [0 1 1] selected area diffraction patterns of TiN in spark plasma sintered TiN/Si$_3$N$_4$ composite containing 10 wt% TiN.

The typical micrographs of β-SiAlON grains with different TiN content are presented in Fig. 6. In general, the TiN in TiN/Si$_3$N$_4$ based composite inhibits grain boundary diffusion and reduces the grain size of the Si$_3$N$_4$ matrix [20]. However, for the special case of 10TN among all these composites, the large, elongated grains can be obtained. The conductive phase of TiN might play an important role in the microstructural development of TiN/Si$_3$N$_4$ based composites. The electrical resistivity of TiN (3.34×10⁻⁷Ω.m) [14] is in the range of metallic materials. Although a tiny current appears as measured by a semiconductor parameter analyzer, it is reasonable that a large current might be induced in the presence of pulsed electrical field during sintering. A leakage current might go through the sintering compact during a heating process, and a similar phenomena is also proposed in ferroelectric ceramics [30; 45], and TiCxOyNz/Si$_3$N$_4$ based nanocomposites [31]. Therefore, it is expected that a direct current might hop across conductive TiN grains embedded in the insulating β-SiAlON matrix when applying a pulsecurrent. A temporary high temperature might occur in the specimen, and consequently accelerate the grain coarsening behavior of β-SiAlON during a sintering cycle.

Except for the case of the 10TN composite, most of the β-SiAlON grains for the composites have an equiaxial shape with a grain size of less than 200nm (as shown in Fig. 6), whereas a tiny amount of elongated grains with a grain width of 100nm were observed. For the composite of 5 TN, the percolation concentration is too low (i.e. the interparticle distance of TiN is large) to allow a pulse current to pass through the sintering body [52]. For the samples of 15 TN, 20 TN, and 30 TN, the TiN phase significantly inhibits the grain growth of the β-SiA-
ION matrix, even though it is possible for a pulse current to pass through the samples during sintering.

Figure 6. SEM micrographs showing the etching surface of TiN/Si$_3$N$_4$ composites with varying TiN content.

2.2.4. Electrical Properties

The change in electrical resistance for the above composites with varying TiN content is shown in Fig. 7. The electrical resistance substantially decreases from $2.43 \times 10^{10}$ (5 TN) to $1.93 \times 10^8$ (20 TN) (Ω.m) with the increase in TiN content, whereas it suddenly increases to a value of $4.19 \times 10^{10}$ (Ω.m) for composite 30 TN. It has been reported that if the fraction of conductive TiN phase in the composite is under the degree of percolation threshold, the insulating property of the composites is maintained as the electrical resistance of non-conductive Si$_3$N$_4$ matrix [52]. This suggests the TiN phase does not form a connective network. As it is evidenced from Fig. 4, the submicrosized TiN grains are nearly isolated from each other. Moreover, the change of electrical resistance possibly depends on the grain size of the conductive phase [11]. Compared with the special cases for 20TN and 30 TN, the larger particle size of TiN for 30TN increases the interparticle distance, leading to a higher magnitude of electrical resistance over composite 20 TN.
2.2.5. Mechanical Properties

The mechanical performance of the above nanocomposites has been studied from hardness and toughness measurements. Indentation hardness is a measure of resistance of a sample to permanent plastic deformation due to a constant compression load from a sharp object. This test works on the basic premise of measuring the critical dimensions of an indentation left by a specifically dimensioned and loaded indenter. Vickers hardness is a common indentation hardness scale, which was developed by Smith & Sandland [42]. Vickers test is often easier to use than other hardness tests since the required calculations are independent of the size of the indenter, and the indenter can be used for all materials irrespective of hardness. The influence of the TiN content of TiN/Si$_3$N$_4$ based nanocomposites on the Vickers hardness is shown in Fig. 8. The hardness value for these composites decreases with an increasing amount of TiN phase in the β-SiAlON matrix, and a similar trend was also observed by Lee et al., [31].
Fracture toughness describes the ability of a material containing a crack to resist fracture, and is one of the most important properties of any material for virtually all design applications. It is also a quantitative way of expressing a material’s resistance to brittle fracture when a crack is present. The fracture toughness of the composites containing various compositions of TiN measured by the indentation technique for composites is shown in Fig. 9. The monolithic Si₃N₄ ceramics have the highest value of 5.4 MPa.m¹/². Among the TiN/Si₃N₄ composites, the toughness reaches a maximum value of 4.9 MPa.m¹/² for the composite containing 10 wt% TiN, whereas the other composites have values lower than 4.2 MPa.m¹/². An equation derived by Buljan et al., 1988, which expresses the increase in toughness as function of grain size under the assumption that the grain shapes are the same, is given by

\[ dK = C K_c 0 \left( \frac{dD}{D_0} - 1 \right) \]  

Where C is a coefficient dependent on the mode of fracture; \( K_c 0 \) and \( D_0 \) are the initial toughness and grain size; \( dK \) and \( dD \) are the respective changes in toughness and diameter. Hence, the changes in grain size and shape are directly related to toughness. An increase in Si₃N₄ grain size results in increasing fracture toughness. Although the addition of TiN does not improve the mechanical properties of Si₃N₄ based composites, the special sintering behavior produced by pulse direct current (grain coarsening effect for Si₃N₄ based grain) may occur in a SPS process.

3. Conclusions

i. By utilizing Si₃N₄ and TiN nano powders as starting materials, a series of near-fully dense TiN/Si₃N₄ based nanocomposites containing varying TiN contents (5–30 wt %) have been fabricated successfully by a spark plasma sintering technique.
ii. A grain coalescence of the TiN phase has been demonstrated by TEM. The conductive TiN grains in the insulating Si₃N₄ matrix are observed to be isolated from each other. From the microstructural observations, the composites appear to be insulating materials.

iii. For the nanocomposite of 5 TN, 15 TN, 20 TN, and 30 TN, the TiN phase inhibits the grain growth of Si₃N₄ based grains during sintering. Hence, the nanosized Si₃N₄ based crystallites are maintained in size as the raw material.

iv. The spark plasma sintered TiN/Si₃N₄ based composite containing 10 wt% TiN achieves the largest grain size and the highest toughness of 4.9 MPa.m¹/² compared to the other composites. A possible pulse current sintering mechanism might occur, which causes a temporary high temperature in the sintering compact, and then accelerates the grain coarsening of Si₃N₄ based grains.

Acknowledgements

Authors are thankful to National Science Council of Taiwan for its financial support under the contract No: NSC 99-2923-E-006-002-MY3 to carry out the present work.

Author details

Jow-Lay Huang* and Pramoda K. Nayak

*Address all correspondence to: JLH888@mail.ncku.edu.tw

National Cheng Kung University, Taiwan

References

[1] Ayas, E., Kara, A., & Kara, F. (2008, July). A novel approach for preparing electrically conductive α/β SiAlON-TiN composites by spark plasma sintering. Journal of the Ceramic Society of Japan, 116(1355), 2008, 812-814, 0914-5400.

[2] Buljan, S. T., Baldoni, J. G., & Huckabee, M. L. (1987). Si₃N₄-SiC composite, American Ceramic Society Bulletin, 66(2), 347-352, 0002-7812.

[3] Buljan, S. T., Baldoni, J. G., Neil, J., & Zilberstein, G. (1988). Dispersoid-toughened silicon nitride composites., ORNL/Sub/8522011/1, GTE.

[4] Balakrishnan, S., Burnellgray, J. S., & Datta, P. K. (1995). in: S. Hampshire, M. Buggy, B. Meenan, N. Brown (eds.) Preliminary studies of TiN particulate-reinforced
Si(3)N(4) matrix composite (SYALON 501) following exposure in oxidizing and oxychloridising environments. Key Engineering Materials, 1013-9826, 99(1), 279-290.

[5] Borsa, C. E., & Brook, R. J. (1995). Fabrication of Al₂O₃/SiC nanocomposites using a polymeric precursor for SiC. In Ceramic Transactions Ceramic. Processing and Science, The American Ceramic Society, H. Hausner, G. L. Messing and S.-I. Hirano, (Ed.), Westerville, OH, 51, 653-657.

[6] Borsa, C. E., Ferreira, H. S., & Kiminami, R. H. G. A. (1999, May). Liquid Phase Sintering of Al₂O₃/SiC Nanocomposites. Journal of the European Ceramic Society, 19(5), 1999, 615-621, 0955-2219.

[7] Blugan, G., Hadad, M., Janczak-Rusch, J., Kuebler, J., & Graule, T. (2005, April). Fractography, mechanical properties, and microstructure of commercial silicon nitride-titanium nitride composites. Journal of the American Ceramic Society, 88(4), 2005, 926-933, 1551-2916.

[8] Carroll, L., Sternitzke, M., & Derby, B. (1996, November). Silicon carbide particle size effects in alumina based nanocomposites. Acta Materialia, 14(11), 1996, 4543-4552, 1259-6454.

[9] Dusza, J., Šajgalík, P., & Steen, M. (1999). Fracture Toughness of Silicon Nitride/Silicon Carbide Nanocomposite at 1350°C. Journal of the American Ceramic Society, 82(12), 3613-3615, 1551-2916.

[10] Dusza, J., Kovalčík, J., Hvizdoš, P., Šajgalík, P., Hnatko, M., & Reece, M. (2004). Creep Behavior of a Carbon-Derived Si₃N₄-SiC Nanocomposite. Journal of the European Ceramic Society, 24(12), 3307-3315, 0955-2219.

[11] Deepa, K. S., Kumari, Nisha. S., Parameswaran, P., Sebastian, M. T., & James, J. (2009). Effect of conductivity of filler on the percolation threshold of composites. Applied Physics Letters, 0003-6951, 94(14), 142902.

[12] Evans, A. G., & Charles, E. A. (1976, July). Fracture Toughness Determinations by Indentation. Journal of the American Ceramic Society, 59(7-8), 1976, 371-372, 1551-2916.

[13] Greil, P., Petzow, G., & Tanaka, H. (1987). Sintering and hipping of silicon nitride-silicon carbide composite materials, Ceramics International (September 1986) 0272-8842, 13(1), 19-25.

[14] Gogotsi, Y. G. (1994). Review: particulate silicon nitride based composite. Journal of Materials Science, January (1994). 1573-4803, 29(10), 2541-2556.

[15] Gao, L., Li, J. G., Kusunose, T., & Niihara, K. (2004, February). Preparation and properties of TiN-Si₃N₄ composites. Journal of the European Ceramic Society, 24(2), 2004, 381-386, 0955-2219.

[16] Galusek, D., Sedláček, J., Šváňárek, P., Riedel, R., Satet, R., & Hoffmann, M. (2007). The influence of post-sintering HIP on the microstructure, hardness, and indentation.
fracture toughness of polymer-derived Al$_2$O$_3$-SiC nanocomposites. *Journal of the European Ceramic Society*, 27(2-3), 1237-1245, 0955-2219.

[17] Guo, Z., Blugan, G., Kirchner, R., Reece, M., Graule, T., & Kuebler, J. (2007, September). Microstructure and electrical properties of Si$_3$N$_4$-TiN composites sintered by hot pressing and spark plasma sintering. *Ceramics International*, 33(7), 2007, 1223-1229, 0272-8842.

[18] Herrmann, M., Balzer, B., Schubert, C., & Hermel, W. (1993). Densification, microstructure and properties of Si$_3$N$_4$-Ti(C,N) composites. *Journal of the European Ceramic Society*, 12(3), 287-296, 0955-2219.

[19] Huang, J. L., Chen, S. Y., & Lee, M. T. (1994). Microstructure, chemical aspects and mechanical properties of TiB$_2$/Si$_3$N$_4$ and TiN/Si$_3$N$_4$ composites. *Journal of Materials Research*, 0884-2914, 9(9), 2349-2354.

[20] Huang, J. L., Lee, M. T., Lu, H. H., & Lii, D. F. (1996). Microstructure, fracture behavior and mechanical properties of TiN/Si$_3$N$_4$ composites, *Materials Chemistry and Physics*, 45(3), 203-210, 0254-0584.

[21] Kawano, S., Takahashi, J., & Shimada, S. (2002). Highly electroconductive TiN/Si$_3$N$_4$ composite ceramics fabricated by spark plasma sintering of Si$_3$N$_4$ particles with a nano-sized TiN coating, *Journal of Materials Chemistry*, 12(2), 361-365, 1364-5501.

[22] Kawano, S., Takahashi, J., & Shimada, S. (2003, April). Fabrication of TiN/Si$_3$N$_4$ ceramics by spark plasma sintering of Si$_3$N$_4$ particles coated with nanosized TiN prepared by controlled hydrolysis of Ti(O-i-C$_3$H$_7$)$_4$. *Journal of the American Ceramic Society*, 86(4), 2003, 701-705, 1551-2916.

[23] Kašiarová, M., Dusza, J., Hnatko, M., Lenčěš, Z., & Šajgalík, P. (2002). Mechanical Properties of Recently Developed Si$_3$N$_4$ + SiC Nanocomposites. *Key Engineering Materials*, 223, 233-236, 1013-9826.

[24] Kašiarová, M., Rudnayová, E., Kovalčík, J., Dusza, J., Hnatko, M., Šajgalík, P., & Merstallinger, A. (2003). Wear and creep characteristics of a carbon-derived Si$_3$N$_4$/SiC micro/nanocomposite. Materialwissenschaft und Werkstofftechnik, April (2003). 1521-4052, 34(4), 338-342.

[25] Kašiarová, M., Dusza, Ján., Hnatko, M., Šajgalík, P., & Reece, M. J. (2006). Fractographic Montage for a Si$_3$N$_4$/SiC Nanocomposite. *Journal of the American Ceramic Society* May (2006)., 1551-2916, 89(5), 1752-1755.

[26] Lee, B. T., Yoon, Y. J., & Lee, K. H. (2001, January). Microstructural characterization of electroconductive Si$_3$N$_4$-TiN composites, *Materials Letters*, 47(1-2), 2001, 71-76, 0016-777X.

[27] Lide, D. R. (2002). Experimental Data: Evaluation and Quality Control. CRC Hand- book of Chemistry and Physics 83rd ed. CRC Press Boca Raton April (2002).
[28] Liu, C. C., & Huang, J. L. (2003). Effect of the electrical discharge machining on strength and reliability of TiN/Si$_3$N$_4$ composites. *Ceramics International, 29*(6), 679-687, 0272-8842.

[29] Liu, X. K., Zhu, D. M., & Hou, W. C. (2006). Microwave permittivity of SiC-A1$_2$O$_3$ composite powder prepared by sol-gel and carbothermal reduction. *Transactions of Nonferrous Metals Society of China, 16*, s494-s497, 1003-6326.

[30] Liu, J., Shen, Z. J., Nygren, M., Kan, Y. M., & Wang, P. L. (2006). SPS processing of bismuth-layer structured ferroelectric ceramics yielding highly textured microstructures. *Journal of the European Ceramic Society, 26*(15), 3233-3239, 0955-2219.

[31] Lee, C. H., Lu, H. H., Wang, C. A., Nayak, P. K., & Huang, J. L. (2011, March). Influence of Conductive Nano-TiC on Microstructural Evolution of Si3N4-Based Nanocomposites in Spark Plasma Sintering. *Journal of the American Ceramic Society, 94*(3), 2011, 959-967, 1551-2916.

[32] Martin, C., Mathieu, P., & Cales, B. (1989). Electrical discharge machinable ceramic composite. *Materials Science and Engineering: A, 109*, 351-356, 0921-5093.

[33] Niihara, K., & Hirai, T. (1986). Super-Fine Microstructure and Toughness of Ceramics. *Bull. Cerum. Soc. Jpn., 21*(7), 598-604.

[34] Niihara, K., & Nakahira, A. (1988). Strengthening of oxide ceramics by SiC and Si$_3$N4 dispersions. In: Proceedings of the Third International Symposium on Ceramic Materials and Components for Engines, The American Ceramic Society, V. J. Tennery, (Ed.), Westerville, Ohio , 919-926.

[35] Niihara, K., & Nakahira, A. (1991). Strengthening and toughening mechanisms in nanocomposite ceramics. *Ann. Chim. (Paris), 16*, 479-486, 0151-9107.

[36] Niihara, K. (1991). New design concept for structural ceramics-Ceramic nanocomposites. *The Centennial Memorial Issue of The Ceramic Society of Japan, 99*(10), 974-982, 0914-5400.

[37] Nakahira, A., Sekino, T., Suzuki, Y., & Niihara, K. (1993). High-temperature creep and deformation behavior of Al$_2$O$_3$/SiC nanocomposites. *Ann. Chim. (Paris), 18*, 403-408, 0151-9107.

[38] Ohji, T., Nakahira, A., Hirano, T., & Niihara, K. (1994). Tensile creep behavior of Alumina/ Silicon carbide nanocomposite. *Journal of the American Ceramic Society, 77*(12), 3259-3262, 1551-2916.

[39] Ohji, T., Jeong-K, Y., Choa-H, Y., & Niihara, K. (1998, June). Strengthening and toughening mechanisms of ceramic nanocomposites. *Journal of the American Ceramic Society, 81*(6), 1998, 1453-1460, 1551-2916.

[40] Raichenko, A. I. (1985, January). Theory of metal powder sintering by an electric-pulse discharge. *Soviet Powder Metallurgy and Metal Ceramics, 24*(1), 1985, 26-30, 0038-5735.
[41] Ragulya, A. V. (2010). Fundamentals of Spark Plasma Sintering. Encyclopedia of Materials: Science and Technology, 978-0-08043-152-9, 1-5.

[42] Smith, R. L., & Sandland, G. E. (1922). An Accurate Method of Determining the Hardness of Metals, with Particular Reference to Those of a High Degree of Hardness. Proceedings of the Institution of Mechanical Engineers, LCCN 0801 8925, I, 623-641.

[43] Sinha, S. N., & Tiegs, T. N. (1995). Fabrication and properties of Si$_3$N$_4$-TiN composite. Ceramic Engineering and Science Proceedings July (1995), 0196-6219, 16(4), 489-496.

[44] Šajgalík, P., Dusza, J., & Hoffmann, M. J. (1995). Relationship Between Microstructure, Toughening Mechanisms and Fracture Toughness of Reinforced β-Si$_3$N$_4$ Ceramics. Journal of the American Ceramic Society, 78(10), 2619-2624, 1551-2916.

[45] Shen, Z., & Nygren, M. (2001). Kinetic aspects of superfast consolidation of silicon nitride based ceramics by spark plasma sintering. Journal of Materials Chemistry, 11(1), 204-207, 0959-9428.

[46] Shen, Z. J., Peng, H., Liu, J., & Nygren, M. (2004). Conversion from nano- to micron-sized structures: Experimental observations. Journal of the European Ceramic Society, 24(12), 3447-3452, 0955-2219.

[47] Šajgalík, P., Hnatko, M., Lojanová, Š., Lenčéš, Z., Pálková, H., & Dusza, J. (2006). Microstructure, hardness, and fracture toughness evolution of hot-pressed SiC/Si$_3$N$_4$ nano/micro composite after high-temperature treatment. International Journal of Materials Research, 1862-5282, 97(6), 772-777.

[48] Vollath, D., Szabó, D. V., & HauBelt, J. (1997). Synthesis and Properties of Ceramic Nanoparticles and Nanocomposites. Journal of the European Ceramic Society, 17(11), 1317-1324, 0955-2219.

[49] Vollath, D., & Szabó, D. V. (2006). Microwave Plasma Synthesis of Ceramic Powders. In: Advances in Microwave and Radio Frequency Processing Part-IX, Springer, 619-626.

[50] Xu, Y., Nakahira, A., & Niihara, K. (1994). Characteristics of Al$_2$O$_3$-SiC nanocomposite prepared by sol-gel processing. Journal of the Ceramic Society of Japan, 102(3), 312-315, 0914-5400.

[51] Yoshimura, M., Komura, O., & Yamakawa, A. (2001, May). Microstructure and tribological properties of nano-sized Si 3N4. Scripta Materialia, 44(8-9), 2001, 1517-1521, 1359-6462.

[52] Zivkovic, L., Nikolic, Z., Boskovic, S., & Miljkovic, M. (2004, June). Microstructural characterization and computer simulation of conductivity in Si3N4-TiN composites. Journal of Alloys and Compounds, 373(1-2), 2004, 231-236, 0925-8388.