

# Characterization of rare-earth doped Si<sub>3</sub>N<sub>4</sub>/SiC micro/nanocomposites<sup>#</sup>

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## Abstract

Influence of various rare-earth oxide additives  $(La_2O_3, Nd_2O_3, Sm_2O_3, Y_2O_3, Y_2O_3, and Lu_2O_3)$  on the mechanical properties of hot-pressed silicon nitride and silicon nitride/silicon carbide micro/nano-composites has been investigated. The bimodal character of microstructures was observed in all studied materials where elongated  $\beta$ -Si<sub>3</sub>N<sub>4</sub> grains were embedded in the matrix of much finer Si<sub>3</sub>N<sub>4</sub> grains. The fracture toughness values increased with decreasing ionic radius of rare-earth elements. The fracture toughness of composites was always lower than that of monoliths due to their finer Si<sub>3</sub>N<sub>4</sub>/SiC microstructures. Similarly, the hardness and bending strength values increased with decreasing ionic radius of frare-earth elements of rare-earth elements either in monoliths or composites. On the other hand, the positive influence of finer microstructure of the composites on strength was not observed due to the present defects in the form of SiC clusters and non-reacted carbon zones. Wear resistance at room temperature also increased with decreasing ionic radius of rare-earth elements of rare-earth element. Significantly improved creep resistance was observed in case either of composite materials or materials with smaller radius of RE<sup>3+</sup>.

Keywords: silicon nitride, composite, rare-earth element, mechanical properties

# I. Introduction

Silicon nitride  $(Si_3N_4)$  based ceramics are most often used as structural components especially for hightemperature applications. The high-temperature properties of  $Si_3N_4$  based ceramics strongly depend on the oxide additives used for the densification. The rareearth oxide additives are considered as the ideal additives for  $Si_3N_4$  ceramics due to their high melting point and because they control the  $\alpha \rightarrow \beta$  phase transformation rates of the  $Si_3N_4$ , the grain growth anisotropy and the aspect ratio of the  $\beta$ -Si<sub>3</sub>N<sub>4</sub> [1–4].

Satet et al. [1] reported the influence of different rare earth (RE)-MgO intergranular phase composition on the room temperature properties of  $Si_3N_4$  ceramics. The room temperature measurements showed that the fracture toughness of these materials increased with increasing ionic radius of RE<sup>3+</sup> and the bending strength decreased with increasing ionic radius. They found that weaker grain-boundary interface in the case of  $La^{3+}$  addition results in a higher toughness, but in lower strength of the bulk  $Si_3N_4$  material.

Silicon nitride-silicon carbide  $(Si_3N_4$ -SiC) nanocomposites have been developed recently in order to improve hardness, strength, as well as resistance to creep, oxidation and corrosion of  $Si_3N_4$  ceramics [5–7]. Significantly higher creep resistance of the  $Si_3N_4$ -SiC nanocomposite in comparison with monolithic  $Si_3N_4$ was observed by Dusza et al. [6]. On the other hand, the lower fracture toughness and lower strength of  $Si_3N_4$ -SiC composite compared to the  $Si_3N_4$  monolith were reported by Kašiarová et al. [7].

The influence of various rare-earth oxide additives on the microstructure evolution and mechanical properties of silicon nitride has been investigated by numerous authors [1–4] during the last decade. On the other hand, their influence in  $Si_3N_4$ -SiC nanomaterials has not been investigated in detail.

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The aim of the present work is to study the influence of various rare-earth additives on the microstructure and mechanical properties of the  $Si_3N_4/SiC$  micro/nano-composites. These results were subsequently compared to those obtained on the  $Si_3N_4$  monoliths sintered with the same rare-earth oxide additives ( $La_2O_3$ ,  $Nd_2O_3$ ,  $Sm_2O_3$ ,  $Y_2O_3$ ,  $Yb_2O_3$  and  $Lu_2O_3$ ).

## **II. Experimental procedure**

The starting mixtures of the set of six Si<sub>2</sub>N<sub>4</sub>/SiC micro/nano-composites consisted of the following powders: α-Si<sub>2</sub>N<sub>4</sub> (grade SN-E10, UBE Industries, Japan), amorphous SiO<sub>2</sub> (50 m<sup>2</sup>g<sup>-1</sup>, Aerosil OX–50, Degussa, Germany), carbon black (1000 m<sup>2</sup>g<sup>-1</sup>, Cabot) and different rareearth oxides  $RE_{2}O_{2}$  (RE = La, Nd, Sm, Y, Yb, or Lu): La<sub>2</sub>O<sub>3</sub>, Nd<sub>2</sub>O<sub>3</sub>, Sm<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub>, Yb<sub>2</sub>O<sub>3</sub> and Lu<sub>2</sub>O<sub>3</sub>. All compositions contained the same atomic amount of RE element. Amount of SiO<sub>2</sub> and C was calculated to achieve 5 vol% of SiC after "in situ" carbothermal reduction process. Simultaneously, the set of six reference monolithic Si<sub>2</sub>N<sub>4</sub> materials with the same composition of sintering additives were prepared in order to compare the microstructure and mechanical properties. Sieved (25 µm) starting powder was poured into a graphite rectangular die sprayed by thin hexagonal BN layer from inside. Bulk bodies of 65×65×5 mm<sup>3</sup> were then hot-pressed at 1750°C with a load of 30 MPa and 0.15 MPa pressure of nitrogen for 1 hour.

Microstructural characterization was carried out using a scanning electron microscopy (SEM) (JEOL JSM-7000F, Japan). X-ray diffraction (XRD) (CuK $\alpha$  radiation, STOE powder diffraction system, Germany) was used for the characterization of the crystalline phases of the materials.

Hardness was measured on polished cross-sections (perpendicular to the hot pressing direction) of bars using the standard Vickers indentation method at the load of 9.8 N (LECO LM-700, USA).

The fracture toughness was measured by Indentation Strength (IS) method [8]. Each of the IS bar specimens  $(3 \times 4 \times 45 \text{ mm}^3)$  was indented at the centre of the tensile surface using the Vickers indenter with indentation load (*P*) of 98 N in air. The samples were then broken in 4-point-bending mode with cross-head speed of 0.5 mm/min (Lloyd Instruments LR5K-Plus, United Kingdom). The fracture strength ( $\sigma_f$ ) value has been determined using the maximal applied load and the fracture toughness ( $K_{IC}$ ) was calculated using the following equation [8]:

$$K_{IC} = 0.88. (\sigma_f . P_i^{1/3})^{3/4}$$
(1)

Strength was determined by four-point bending test with inner and outer span 20 mm and 40 mm, respectively (Lloyd Instruments LR5K-Plus, United Kingdom). The specimens ( $3 \times 4 \times 45$  mm<sup>3</sup>) were ground in parallel to the axis of the specimen to a final 3 µm before testing. Tensile surface of the bars was always perpendicular to the hot pressed direction. The specimens were broken at a cross-head speed of 0.5 mm/min in air. For each material composition ten samples were tested and the mean value of strength was calculated after the test [9].

Wear behaviour of the materials was studied by a ballon-disc tribometer at room temperature without any lubricant (high temperature tribometer DTHT 70010, Switzerland). The tests were performed in air with a relative humidity about 60 %. The applied load was 5 N, sliding distance was 500 m and the sliding velocity was 0.1 m/s. The friction coefficients were continually recorded during the tests and wear volume on each specimen was calculated from the surface profile traces (usually 4) across the track and perpendicular to the sliding direction.

Creep experiments were performed in four-point bending mode with inner and outer span of 20 and 40 mm, respectively. The measurements were carried out in a creep machine with dead-weight loading system in air atmosphere at temperatures between 1250°C and 1400°C with outer fiber stresses in the range from 50 to 150 MPa. The deflection of sample was recorded continuously during the creep test.

# III. Results and discussion

#### 3.1. Microstructure evolution

Similar bimodal character of microstructures was observed for all Si<sub>3</sub>N<sub>4</sub> monoliths and all Si<sub>3</sub>N<sub>4</sub>-SiC micro/ nano-composites that consist of elongated  $\beta$ -Si<sub>3</sub>N<sub>4</sub> grains embedded in the matrix of much finer Si<sub>3</sub>N<sub>4</sub> grains. Fig. 1 and 2 show the microstructures of monoliths and composites doped with additive having the largest size of  $RE^{3+}(La_2O_3)$ , with the smallest size of  $RE^{3+}(Lu_2O_3)$  and with the middle-size of RE<sup>3+</sup> cation ( $Y_2O_2$ ), respectively. The composites additionally contain globular nano and submicron sized SiC particles, intragranularly located in the Si<sub>3</sub>N<sub>4</sub> grains or intergranularly between the grains. The microstructures of the composites were always finer compared to the microstructures of the monoliths because the SiC particles, formed at the grain boundaries of the Si<sub>3</sub>N<sub>4</sub> grains, hinder the growth of the  $\beta$ -Si<sub>3</sub>N<sub>4</sub> grains during the evolution of microstructure.

From the microstructural observations using SEM and TEM it seems that the SiC particles are situated at the grain boundaries rather than in  $\beta$ -Si<sub>3</sub>N<sub>4</sub> grains in the composite containing Lu additive. On the other hand, intragranularly located SiC particles were observed more frequently in the La-doped composite. We can presume that lower viscosity liquid phase (larger ion of RE<sup>3+</sup>) tends to form intragranular SiC particles whereas higher viscosity (smaller ion of RE<sup>3+</sup>) promotes formation of intergranular particles of SiC. To confirm this preliminary result a statistical analysis of the location of SiC nanoparticles in the composite microstructure is needed.

The XRD analyses revealed  $\beta$ -Si<sub>3</sub>N<sub>4</sub> as a major phase and RE<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> (where RE = Y, Yb or Lu) as a secondary phase in both the monolithic and the composite materi-



Figure 1. Microstructures of Si<sub>3</sub>N<sub>4</sub> sintered with different rare-earth oxide additives: a) La, b) Y and c) Lu

als. This crystalline phase was not detected in the Lacontaining materials. The apatite phase  $(Sm_{10}(SiO_4)_6N_2)$ was detected in the monolith and composite sintered with  $Sm_2O_3$ . The all  $Si_3N_4$  materials contain also  $SiO_2$  as a minor phase, whereas the  $Si_3N_4$ -SiC additionally contained SiC phase and also  $SiO_2$ ,  $Si_2N_2O$ .



Figure 2. Microstructures of Si<sub>3</sub>N<sub>4</sub>-SiC sintered with different rare-earth oxide additives: a) La, b) Y and c) Lu



Figure 3. Hardness values of investigated  $Si_3N_4$  and  $Si_3N_4$ -SiC materials



Figure 4. Fracture toughness values measured by IS method



Figure 5. Mean four-point bending strength of monoliths and composites

#### 3.2 Hardness

The hardness values of the composites were higher than those of the monolithic  $Si_3N_4$  (Fig. 3). This can be attributed to the finer composite microstructures as well as to the presence of harder SiC particles in the  $Si_3N_4$ matrix. Hardness values increased with decreasing ionic radius of RE element in both the monolithic and composite materials. The similar influence of RE<sup>3+</sup> on the hardness was observed by Lofaj et al. [10] in the case of RE-Si-Mg-O-N glasses where the hardness increased with increasing cationic field strength (CFS), i.e. with decreasing ionic radius of RE<sup>3+</sup>.

### 3.3 Fracture toughness

The fracture toughness measured by IS method was lower in the composites because of their finer microstructures (Fig. 4). It is known that in such microstructures there are fewer possibilities for toughening mechanisms.

Similarly to the aspect ratio values, the fracture toughness also increased with decreasing ionic radius of RE<sup>3+</sup> (Fig. 4). The materials doped with Lu exhibited the highest aspect ratio of  $\beta$ -Si<sub>3</sub>N<sub>4</sub> grains and also the highest fracture toughness in both monolith and composite materials. On the other hand, the materials with lower aspect ratio exhibited lower fracture toughness except the monolith and composite doped with Sm. This fact agrees with observations of the crack propagation in the materials. The fewest fracture toughness mechanisms were observed in the materials containing Sm<sub>2</sub>O<sub>2</sub> additive. Probably, different chemical composition of the intergranular phase (apatite phase  $Sm_{10}(SiO_4)_6N_2$  was detected by X-ray analyses) compared to other materials (RE<sub>2</sub>O<sub>3</sub> or amorphous phases) can be responsible for the lowest fracture toughness of Sm-containing materials.

Microstructure observations revealed that Lu-doped material contains many elongated grains with small diameter as well as some coarse elongated grains. It was reported by Šajgalík et al. [11] that the materials with microstructure with the finest and coarsest elongated  $\beta$ -grains exhibited the maximum value of fracture toughness, whereas materials with the microstructure with the mixture of elongated thin and thick  $\beta$ -grains had lower facture toughness. This can be attributed to the fact that pull-out and elastic bridging are dominant toughening mechanisms for the elongated grains with small diameter. On the other hand, the crack deflection is dominant mechanism for the coarser elongated grains.

#### 3.4 Strength

The mean four-point bending strength of studied monoliths and composites are illustrated in Fig. 5. The values of mean strength slightly increased with decreasing ionic radius of rare-earth elements except the  $Si_3N_4$  doped by  $Y_2O_3$  which exhibited the highest strength value. The SEM observations revealed pores (Fig. 6a) and

inclusions of Fe as the critical flaws in both monolithic and composite materials. In addition, agglomerate of SiC grains (Fig, 6b) and non-reacted carbon zones (Fig. 6c) were often observed in the case of  $Si_3N_4$ -SiC composites.

The Si<sub>3</sub>N<sub>4</sub> with La<sub>2</sub>O<sub>3</sub> and Sm<sub>2</sub>O<sub>3</sub> additive exhibited the lowest mean strength among all monoliths and similarly the Si<sub>3</sub>N<sub>4</sub>+SiC doped with La<sub>2</sub>O<sub>3</sub> and Sm<sub>2</sub>O<sub>3</sub> exhibited the lowest strength among all composites. This can be attributed to the fact that the technological flaws were the largest in these materials compared to the other systems as well as to the weaker interfacial strength. Weak interfaces could induce a growth of natural flaws to critical size at lower loads and thus yield, for a given flaw population, lower bulk strengths [1]. On the other hand, the material with the highest strength (Si<sub>3</sub>N<sub>4</sub>+Y<sub>2</sub>O<sub>3</sub>) exhibited no visible large fracture origins in the form of technological defects.

The refined microstructure of micro/nano-composites did not result in the higher strength compared to the strength of  $Si_3N_4$ . This is caused by the present processing flaws in the composites in the form of agglomerates of SiC grains and non-reacted carbon areas whose negative effect was more significant than the influence of the finer microstructure.

#### 3.5 Wear resistance

Wear resistance was evaluated by ball-on-disc method of tribology. Fig. 7a shows the average friction coefficient recorded during the test. It can be seen that the friction coefficient increased with increasing ionic radius of RE<sup>3+</sup>. Similarly, the wear volume also increased with increasing cation radius of rare-earth element (Fig. 7b). Wear resistance of composites was always higher because of beneficial effect of harder SiC particles. We can conclude that the materials (monolith as well as composite) sintered with the rare-earth element with the smallest cation size  $(Lu_2O_2)$ , i.e. the materials with the highest hardness and fracture toughness and with the strongest bond in glass network, exhibited the highest wear resistance among of all studied materials. This higher bonding strength restricts dropping of the individual silicon nitride grains during the wear experiments.

Wear mechanisms were estimated by the SEM observation of wear tracks. Examples of the worn surfaces of the tested plate specimens are given in Fig. 8. From the comparison between Fig. 8a  $(Si_3N_4+La_2O_3)$ , Fig. 8b  $(Si_3N_4+SiC+La_2O_3)$  and Fig. 8c  $(Si_3N_4+SiC+Lu_2O_3)$  it is seen that with increasing wear resistance the worn surface became rather smooth but adherent debris can be still observed. The coherent debris layer, which was





Figure. 6. Fracture origins: a) pore in the La-containing monolith, b) agglomerate of SiC grains in Lu-doped composite and c) non-reacted carbon zone in Yb-doped composite



Figure 7. Average friction coefficient (a) and wear volume (b) of the studied materials

observed in all studied wear tracks, constitutes a tribofilm that affords some protection to the ceramic surfaces decreasing the wear coefficient of materials. Higher amount of coherent debris was observed in the case of composites or materials doped with smaller ionic radius of  $RE^{3+}$  in both kinds of material. This fact is the explanation for lower friction coefficients in such materials.

It can be concluded that the wear mechanism in the present work was similar for all studied materials and that the transition zone consists of the combination of

100 µm



Figure 8. Comparison of worn tracks of the studied materials: a) La-doped monolith, b) La-doped composite and c) Lu-doped composite



Figure 9. Activation energy of creep at load of 100 MPa

features observed for mechanical wear (micro-fracture) and tribochemical reaction. The tribochemical reaction area is characterized by a relatively smooth surface and the micro-fracture area is characterized by a rough surface and accumulated wear debris.

## 3.6 Creep resistance

The monoliths as well as the composites containing the smallest ionic radius of RE<sup>3+</sup> (Lu), the largest radius of RE<sup>3+</sup> (La) and materials sintered with the middle-sized of radius of RE3+ were chosen for the creep resistance measurements. It was observed (Fig. 9) that the creep rate at 1300°C is almost 1 order of magnitude lower for Lu-doped composite in comparison with Ludoped monolith and almost 2 orders of magnitude lower than La-containing monolith or composite. Stress exponent was calculated from the slope of strain-stress dependencies for all studied material. Its value was close to 1 in all cases indicating diffusion (non-cavitation) as a main creep mechanism in these materials. It seems that the creep mechanisms in all studied materials are probably diffusion through the intergranular phase connected with the solution/precipitation and grain boundary sliding. These suggested mechanisms must be confirmed by TEM observation of crept samples in the future study.

No positive effect of SiC particles on the creep resistance was observed in the La-containing composite. This can be explained by the fact that SiC particles are located intragranularly rather than intergranularly in this material. On the other hand, more intergranularly located SiC particles in Lu-doped composite have more beneficial effect on the creep resistance. The SiC particles located between the  $Si_3N_4$  grains hinder the grain boundary sliding and hence improve the creep resistance. Another reason for the improved creep resistance is that SiC particles change the shape and chemistry of the grain boundaries and grain boundary phases.

It is known that the viscosity of secondary glassy phase has significant influence on the creep behaviour of silicon nitride and it was also reported that the viscosity decreases with increasing radius of  $RE^{3+}$  [3, 10]. Therefore, the highest creep resistance of composite sintered with  $Lu_2O_3$  is attributed to the positive effect of intergranularly located SiC particles as well as to the presence of intergranular phase with the lowest viscosity.

# **IV. Conclusions**

Influence of various rare-earth oxide additives on the microstructure and mechanical properties of the  $Si_3N_4$ /SiC micro/nano-composites has been investigated. The results were subsequently then compared to their influence on the microstructure and mechanical properties of monolithic  $Si_3N_4$  sintered with the same additives.

Sintering additives and the processing routes result in bimodal microstructures of silicon nitride as well as  $Si_3N_4/SiC$  composites with elongated  $\beta$ -Si<sub>3</sub>N<sub>4</sub> grains embedded in fine grained Si<sub>3</sub>N<sub>4</sub> matrix. The aspect ratio of  $\beta$ -Si<sub>3</sub>N<sub>4</sub> grains slightly increased with decreasing ionic radius of rare-earth element.

It was observed that the materials sintered with smaller ionic radius of rare-earth element exhibited higher hardness, fracture toughness, bending strength as well as wear and creep resistance.

As regards the influence of SiC particles on the mechanical properties of rare-earth doped silicon nitride the higher hardness as well as wear and creep resistance were observed in the case of composite materials. However, the composites exhibited lower fracture toughness in comparison with  $Si_3N_4$  monoliths due to their finer microstructure. Beneficial effect of finer composite microstructure on the strength values was not observed because of the technological flaws in their microstructure.

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