MECHANICAL PROPERTIES OF SI$_3$N$_4$ BASED CERAMICS WITH RARE-EARTH OXIDE SINTERING ADDITIVES

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Abstract

Room temperature hardness, microhardness and fracture toughness of hot-pressed Si$_3$N$_4$ and Si$_3$N$_4$+SiC nanocomposites prepared with different rare-earth oxides (La$_2$O$_3$, Y$_2$O$_3$, Yb$_2$O$_3$, Lu$_2$O$_3$) sintering additives have been investigated. Indentation strength and indentation fracture techniques were used to measure the fracture toughness. The higher hardness and microhardness of nanocomposites compared to monolithic Si$_3$N$_4$ is probably caused by the presence of the SiC particles and by the finer microstructure of the composites. The fracture toughness values were lower in the case of the composites due to finer microstructures and lack of the toughening mechanisms during crack propagation. In the samples with Lu or Yb additives crack deflection during crack propagation at grains with higher aspect ratio occurred more frequently compared to Si$_3$N$_4$ doped with La or Y, which was responsible for the higher fracture toughness.

Keywords: Si$_3$N$_4$, rare-earth oxides, hardness, fracture toughness

INTRODUCTION

Rare-earth oxides are often used as sintering aids in silicon nitride in order to improve mechanical properties at room and elevated temperatures. During the last years many researches have studied the influence of chemical composition of grain boundary phases (especially rare earth oxide additives) on the grain growth and mechanical behaviour of Si$_3$N$_4$ ceramics [1-6]. These oxides react with Si$_3$N$_4$ and SiO$_2$, which is originally present on the Si$_3$N$_4$ surface, to form an eutectic liquid phase which remains as a grain boundary phase in the form of thin films at grain boundaries and at triple grain pockets after cooling. More refractory rare-earth oxides result in better high temperature properties of these remaining phases and therefore the high temperature properties of Si$_3$N$_4$ ceramics improve. It was also found that the rare-earth oxide additives control α → β phase transformation rates of Si$_3$N$_4$, the grain growth anisotropy and the aspect ratio of the β-Si$_3$N$_4$ [1-3, 5-7]. Rare-earth elements with larger ionic radius RE^{3+} (i.e. with a smaller atomic number) produce slower phase transformation, higher aspect ratio [1-3] and weaker interfacial bonding, [3,6,7]. All these factors influence crack propagation and fracture toughness of ceramics.

Nanosized SiC-particle reinforced Si$_3$N$_4$ have been developed recently to improve hardness, strength, as well as resistance to creep, oxidation and corrosion of silicon ceramics. These composites were prepared by doping of the Si$_3$N$_4$ powder with amorphous SiNC precursor [8] or using carbothermic reaction (SiO$_2$+C) [9]. Park et al. [10] reported that nanocomposite Si$_3$N$_4$-SiC with Yb$_2$O$_3$ additive showed better oxidation resistance and

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higher strength retention than monolithic Si_3N_4 with Yb_2O_3. Significantly higher creep resistance of the Si_3N_4-SiC nanocomposite, in comparison with monolithic Si_3N_4, was also observed by Dusza et al. [11].

The main aim of the present work is to investigate the influence of the addition of SiC nanoparticles and different RE_2O_3 additives (La, Y, Yb and Lu) on the microhardness, hardness and fracture toughness of silicon nitride ceramics.

EXPERIMENTAL MATERIALS AND METHODS

The monolithic Si_3N_4 materials have been hot-pressed at 1750°C for 1 h in a N_2 atmosphere with the applied pressure of 30 MPa. The Si_3N_4+SiC nanocomposites were prepared by hot pressing under a specific heating regime and atmosphere at 1750°C for 1 h and the SiC particles were formed by the SiO_2 + C carbothermic reaction at 1500°C in vacuum. Rare-earth oxides (La_2O_3, Y_2O_3, Yb_2O_3, Lu_2O_3) were used as the sintering additives in both monolithic and composite materials. The chemical compositions of the studied Si_3N_4 are listed in Table 1.

Tab.1. Chemical composition of the investigated ceramics.

designations	Si_3N_4				Si_3N_4 + SiC			
	R3La	R3Y	R3Yb	R3Lu	C3La	C3Y	C3Yb	C3Lu
Si_3N_4 [wt.%]	91.36	94.05	90.67	90.62	81.12	83.51	80.51	80.46
Re_2O_3 [wt.%]	7.05	4.95	8.35	8.41	6.27	4.4	7.42	7.47
SiO_2 [wt.%]	1.59	1.00	0.98	0.97	8.41	7.89	7.87	7.87
C [wt.%]	-	-	-	-	4.2	4.2	4.2	4.2

X-Ray diffraction (XRD) was used for characterization of the crystalline phases of the materials. The microstructure analysis has been realized after plasma-etching of polished surfaces of the specimens using scanning electron microscopy (SEM). The hardness and microhardness have been measured on polished cross-sections of bars using standard Vickers indentation with loads of 98 N and 9.8 N, respectively.

Fracture toughness was measured by Indentation Strength (IS) and Indentation Fracture (IF) methods. Each of the IS bar specimens (3x4x45 mm³) was indented at the centre of the tensile surface using a Vickers indenter with an indentation load (P) of 98 N in air. The samples were then broken in 4-point-flexure mode and strength (σ_f) was determined using the maximum applied load. The fracture toughness (K_{IC}) was calculated using the following equation:

$$K_{IC} = 0,88.(\sigma_f.P_i^{1/3})^{3/4} \tag{1}$$

The indentation fracture toughness (IF) was determined by the measurement of crack lengths created by the Vicker's indentation load of 98 N. The calculation of the fracture toughness was done using the equation proposed by Anstis [12]:

$$K_{IC} = 0,016.\left(\frac{E}{H}\right)^{1/2}.\frac{P}{c^{3/2}} \tag{2}$$

where E is the Young's modulus and H is the hardness of the material, P is the indentation load and c is the indentation cracks length.

RESULTS AND DISCUSSION

Microstructural characterization

The microstructure observations of monolithic silicon nitrides and nanocomposites revealed their bimodal microstructure, consisting of elongated β-Si_3N_4 grains embedded in a matrix of much finer Si_3N_4 grains (Fig.1). The average Si_3N_4 grain size and aspect ratio of grains in the monolithic Si_3N_4 are significantly higher compared to those in composite materials, because the SiC particles formed at the grain boundaries of Si_3N_4 grains hinder the growth of β-Si_3N_4 grains during the evolution of the composite microstructure. The Si_3N_4-SiC nanocomposites contained globular nano and submicron sized SiC particles located intragranularly in the Si_3N_4 grains or intergranularly between the grains.
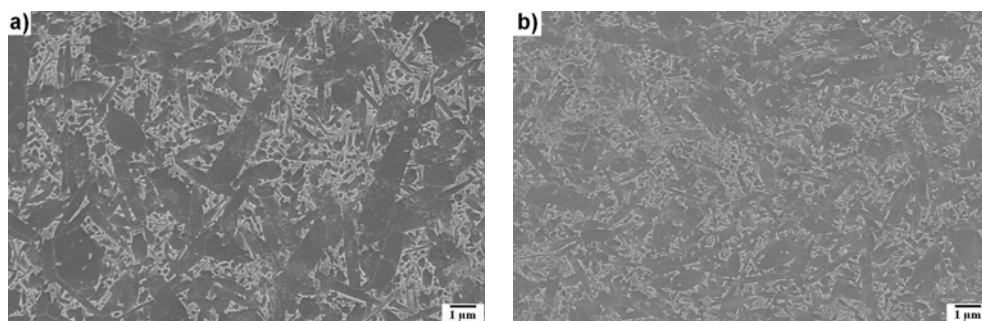

Fig.1. SEM microstructure of plasma etched samples, a) monolithic Si_3N_4; b) nanocomposite.

According to the results there is just a very slight influence of the rare-earth elements on the microstructure evolution both in the case of composites and in the monolithic ceramics. It means that aspect ratio decreases slightly when Lu is replaced by La. The influence is slightly more evident in the case of monolithic Si_3N_4, because of the SiC particles in the composite microstructures. These results show that the monolithic ceramics prepared with different rare-earth additives have similar bimodal microstructures and the same is valid for the composites, too. This fact is in a good agreement with the results presented by Hyuga et al. [13] and Hong et al. [14]. On the other hand, Satet and Hoffmann [1] showed that the presence of different rare-earth elements in the Si_3N_4 with RE_2O_3 and MgO yields differences in grain growth anisotropy as well as differences in aspect ratio and mean grain diameter.

The XRD results revealed β-Si_3N_4 as a major phase and $RE_2Si_2O_7$ as a secondary phase both in the monolithic and the composite materials. The monolithic Si_3N_4 contain also SiO_2 as a minor phase, whereas the Si_3N_4+SiC composites additionally contained SiC secondary phase and also SiO_2, Si_2N_2O as the minor phases.

Mechanical properties at room temperature

The values of the hardness, microhardness and fracture toughness are summarized in Table 2. The hardness and microhardness values of nanocomposites were higher than those of the monolithic Si_3N_4, in contrast the values of fracture toughness were slightly higher in the monolithic materials. This can be attributed to the finer microstructures and to the presence of harder SiC particles in the Si_3N_4 matrix. The composites with the finer microstructure exhibit lower fracture toughness because of the lack of toughening mechanisms (e.g. crack deflection at the boundaries of the elongated Si_3N_4 grains) in these materials.

Tab.2. Mechanical properties at room temperature.

Material	Microhardness [GPa]	Hardness [GPa]	Fracture Toughness (IS) [MPa·m$^{1/2}$]	Fracture Toughness (IF) [MPa·m$^{1/2}$]
R3La	17.16 ± 0.63	13.36 ± 0.40	5.26 ± 0.70	5.49 ± 0.48
R3Y	16.37 ± 0.88	14.08 ± 0.13	4.88 ± 0.63	6.49 ± 0.17
R3Yb	16.92 ± 0.51	14.11 ± 0.13	6.29 ± 0.50	6.94 ± 0.21
R3Lu	17.11 ± 0.75	14.28 ± 0.23	7.06 ± 0.39	7.04 ± 0.49
C3La	16.49 ± 0.61	13.87 ± 0.31	4.3 ± 0.40	5.25 ± 0.48
C3Y	17.75 ± 0.65	14.21 ± 0.39	4.95 ± 0.43	5.87 ± 0.24
C3Yb	18.97 ± 0.70	14.98 ± 0.23	5.21 ± 0.32	5.93 ± 0.19
C3Lu	18.40 ± 0.40	14.92 ± 0.22	5.37 ± 0.44	5.8 ± 0.42

Table 2 suggests that fracture toughness measured by indentation fracture method (IF) is slightly overestimated. This method is not reliable and can be used only in the case of material development. Nevertheless, the differences among the values achieved by these two methods are relatively low and the results show the same tendency in all materials.

A mixture of transgranular and intergranular fracture was observed both in monolithic and composite ceramics during crack propagation, however the monolithic materials exhibit higher fraction of intergranular fracture. Higher fraction of crack deflection at the elongated grains, which leads to further toughening, was also found. In contrast, transgranular rather than intergranular crack propagation was observed in the nanocomposites ceramics. Table 2 shows that the fracture toughness of specimens with Lu or Yb is higher in comparison with the materials containing La or Y, both in the monolithic and the nanocomposite Si_3N_4. It is also evident that the difference between K_{IC} of the monolithic materials with different sintering additives is higher than that in the corresponding Si_3N_4-SiC nanocomposites. This can be explained by the residual stresses introduced by the intra- or inter-granularly located SiC particles in the microstructure of the nanocomposites, but also by the changes chemical composition and interfacial energy of the grains/grain boundary phases. In the case of Si_3N_4 with Lu and Yb-based additives, crack deflection at boundaries and pull-out was observed more frequently than in Si_3N_4 doped with La or Y. This corresponds with the higher fracture toughness in Lu and Yb doped materials (Fig.2).
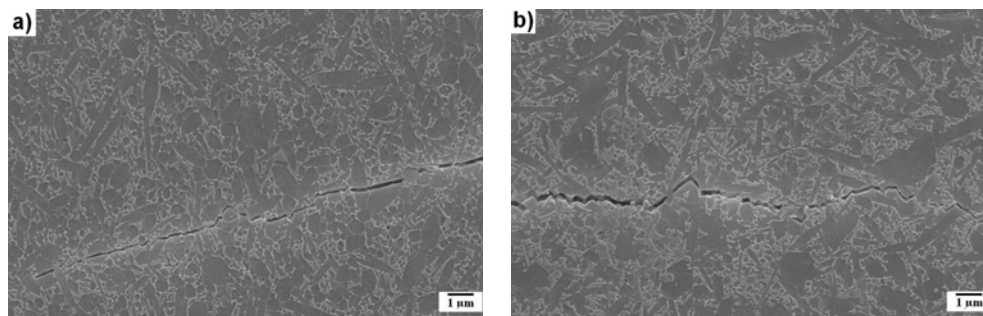

Fig.2. Crack propagation profile of the monolithic Si_3N_4 containing: a) La_2O_3; b) Lu_2O_3 additives.

Satet et al. [1] measured the fracture toughness using razor notched bending bars and the values of fracture toughness increased with the ionic radius of RE^{3+} from 5.5 MPa·m$^{1/2}$ (for the Lu-based ceramics) to 7.2 MPa·m$^{1/2}$ (for the Sm-based ceramics). They showed that debonding and pull-out events occurred more frequently when larger RE^{3+} cation was present in the grain boundary phase. Our results are contrary to those of Satet. However, they founded no crystalline secondary phase and their grain boundary phase was assumed to be fully amorphous. Their samples were processed to achieve comparable microstructures, thus the differences in processing (pressureless HIP sintering vs. hot pressing) as well as the differences in composition of secondary phases are responsible for the difference in fracture toughness of Si_3N_4 in our and Satet's investigations.

Becher et al. [4] observed no significant influences of various rare-earth oxides (La_2O_3, Gd_2O_3, Lu_2O_3) on the fracture toughness values of silicon nitrides with bimodal microstructures and with crystalline secondary phases at the triple-point pockets. The results of our study also showed no significant influence of the various rare-earth oxide additives in the Si_3N_4+SiC nanocomposites. The fracture toughness decreased slightly with increasing ionic radius (Lu → La) in the case of monolithic Si_3N_4. These facts agree with the microstructural observations both in nanocomposite and monolithic materials.

It seems that the intergranular crack propagation coupled with crack deflection at the boundaries of Si_3N_4 grains is necessary for fracture toughness increase. For the intergranular crack propagation, debonding at the interface between the grains and grain boundary phase should occur. According to the literature data, the interfacial debonding energy is directly influenced by the chemical bonding between the grain boundary phase and the grains [2, 4, 5-7, 14] as well as by the residual stress on the interface due to thermal expansion mismatch. Recent work [15, 16] has shown that thermal expansion mismatch between the grain boundary phase and Si_3N_4 grains generates residual tensile stresses which increase crack deflection and fracture toughness. Peterson et al. [15] also showed that creation of favourable tensile stresses along the interface is strongly affected by the chemistry of the secondary phase. In contrast, analytical modelling made by Sun et al. [17] indicated that the thermal expansion mismatch stress has no significant influence on the crack deflection.

CONCLUSIONS

Microhardness, hardness and fracture toughness measurements on different monolithic silicon nitride and Si_3N_4-SiC nanocomposites prepared by carbothermic reduction of SiO_2 with different rare-earth oxide additives revealed:

- Higher hardness and microhardness of nanocomposites compared to monolithic Si_3N_4 ceramics, which is probably caused by the presence of harder SiC particles and by finer microstructures of the composites.
- The fracture toughness values were lower in the case of the composites due to finer microstructures and due to lack of the toughening mechanisms during the crack propagation.
- In the case of materials with Lu and Yb additives, crack deflection at the elongated Si_3N_4 grains was observed more frequently compared to the ceramics doped with La or Y additives. This crack deflection generated further toughening mechanisms in the form of frictional and mechanical interlocking and pull-out, which were probably responsible for the higher fracture toughness of the ceramics with Lu and Yb additives.

Acknowledgement

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