MICROSTRUCTURE AND MECHANICAL PROPERTIES OF Si$_3$N$_4$-SiC NANOCOMPOSITES

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Abstract

Principal mechanical properties of Si$_3$N$_4$-SiC micro-nanocomposites with different weight fraction of SiC particles (1 and 5 wt%) have been studied. The Si$_3$N$_4$-SiC were formed by in-situ procedure utilizing carbothermal reduction of SiO$_2$ during hot pressed sintering. Hardness, fracture toughness, Young’s modulus and strength at room temperature were investigated. Creep behaviour and oxidation resistance were established at high temperatures. The presence of SiC particles refined the microstructure of Si$_3$N$_4$ grains in the Si$_3$N$_4$-SiC micro-nanocomposites and caused change of mechanical properties. Higher amount of SiC particles caused higher values of hardness, Young’s modulus and lower values of fracture toughness and flexural strength. The significant improvement of creep behaviour together with better oxidation resistance determines the main application of studied materials.

1. INTRODUCTION

Although structural ceramics has a number of excellent properties, which allow their applications as parts and tools for different combinations of load at temperatures, wider application is still limited by their brittleness, low flaw tolerance and low reliability.

Silicon nitride and silicon carbide are the promising materials for high temperature application because of their excellent high temperature strength, oxidation resistance and creep behaviour. Different approaches have been used to improve their reliability, lifetime and high temperature properties. One of the ways of further improvement of the mechanical properties is the incorporation of nanoparticles into ceramic matrix. However the attraction of silicon nitride ceramic matrix composites incorporated with SiC as a second phase is limited owing to their high cost. Several methods have been used for processing Si$_3$N$_4$-SiC composites based on: a) amorphous or crystalline composite powders [1]; b) mixture of Si$_3$N$_4$ and SiC powders [2]; c) polymer derived routes [3] and d) in situ synthesis of SiC during sintering [4]. Most of Si$_3$N$_4$-SiC nanocomposites are prepared by hot-pressing and hindered densification due to the presence of SiC particles is overcome using higher densification temperatures in comparison with that used for monolithic Si$_3$N$_4$. During the last decades an attempt has been made to substitute amorphous Si-C-N powder with carbon and SiO$_2$, which would be a cheaper alternative for the production of Si$_3$N$_4$-SiC nanocomposites with excellent mechanical properties. Other problem is connected with ambiguous influence of SiC nanoparticles on mechanical properties measured by different authors. Niihara and co-workers [5,6] showed that dispersions of fine SiC particles in the Si$_3$N$_4$ matrix lead to a remarkable improvement in the mechanical properties at room and elevated temperature. Other authors [7] demonstrated that Si$_3$N$_4$ composite with SiC nanosized particles exhibited only slight improvements or no improvement [8] to room temperature and high temperature mechanical properties compared to monolithic Si$_3$N$_4$. The aim of the present work is to investigate the influence of SiC particles on microstructure, phase composition and principal room temperature and high temperature mechanical properties of carbon derived Si$_3$N$_4$-SiC nanocomposites.
2. EXPERIMENTAL

2.1 Experimental materials

Two Si$_3$N$_4$ based materials were prepared from the starting mixture listed in Table I. Materials were prepared by densification of the starting mixture with weight fractions of SiO$_2$ and C 0.43/1.43 and 4.05/7.39 in order to produce composite with 1 and 5 wt% of SiC particles, respectively. The starting mixtures were homogenized in polyethylene bottle with Si$_3$N$_4$ spheres in isopropanol for 24 h. The dried mixture was sieved through 25 µm sieve in order to eliminate the large hard agglomerates. Green discs with the diameter of 48 mm and 5 mm thick were die pressed under the pressure of 30 MPa. Green discs were then embedded into a BN powder bed and positioned into the graphite uniaxial die. Samples were hot-pressed under a specific heating regime, atmosphere and mechanical pressure regime at 1750 °C and 30 MPa for 2 h. The details of fabrication were published elsewhere [4].

Table I Composition of the starting powders

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<th>Samples</th>
<th>Composition [wt.%]</th>
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<tr>
<td></td>
<td>Si$_3$N$_4$</td>
</tr>
<tr>
<td>Si$_3$N$_4$-1wt%SiC</td>
<td>93.23</td>
</tr>
<tr>
<td>Si$_3$N$_4$-5wt%SiC</td>
<td>84.13</td>
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2.2 Experimental methods

The microstructure of Si$_3$N$_4$-SiC composites were characterized on polished and plasma–etched sections of the bulk materials in scanning electron microscopy (SEM). Diameter of Si$_3$N$_4$ grain were estimated using the image analyzer DIPS (Digital Image Processing System 5.0). The phase compositions were identified by X-ray diffraction (XRD). Hardness was measured on polished cross-sections of bars using standard Vickers indentation at the load of 98 N. Young’s modulus was measured by spherical diamond indenter using depth sensing technique. Single edge V-notch beam (SEVNB) method was used for fracture toughness measurements. Sharp notch with tip radius less than 10 µm was introduced into specimen using a razor blade. Strength of specimens with dimensions 3 x 4 x 45 mm$^3$ was tested in four point flexure test. Specimens were ground to a 15 µm finish by diamond grinding wheel. Both edges on the tensile surface were chamfered to eliminate failure from the edges of the specimens. The specimens were broken with a cross-head speed of 0.5 mm/min in air. The creep test measurements were carried out in creep machine with a dead-weight loading system. Samples were loaded in four-point bending with inner and outer span lengths of 20 mm and 40 mm, respectively. Creep tests were performed in air, at temperatures from 1200°C to 1400°C, with outer fibre stresses in the range from 50 to 150 MPa. From the deflection data recorded continuously during the creep test, the outer fibre strain was calculated as a function of time, t, and taken as the creep strain, ε. The creep rate was calculated from the slope of the ε versus t curve. To characterize the creep behaviour, the parameters n and Q$_c$ were evaluated. Oxidation behaviour of materials were studied in air at 1350°C for 300 hours with the heating and cooling rate of 5°C/min. The phase composition and the thickness of the surface oxidized layer were determined by SEM with EDX analyzer. Formed oxidation products were identified and investigated by XRD.
3. RESULTS AND DISCUSSION

3.1 Microstructure

SEM microstructures of the studied materials are illustrated in Fig. 1. Microstructure of both micro-nanocomposites exhibits bimodal distribution of larger elongated $\beta$-$\text{Si}_3\text{N}_4$ grains and finer equiaxial $\beta$-$\text{Si}_3\text{N}_4$. Intergranular phases showing a brighter contrast surround Si$_3$N$_4$ grains. The average Si$_3$N$_4$ grain size (diameter) of Si$_3$N$_4$-1wt%SiC is 160 nm and of Si$_3$N$_4$-5wt%SiC is 140 nm. Slightly finer microstructure of composite with higher amounts of SiC nanoparticles is due to the presence of SiC particles which hinder growth of grains.

From X-ray diffraction pattern of both samples, Fig. 2, three crystalline phases: $\beta$-$\text{Si}_3\text{N}_4$ (hexagonal), $\delta$-$\text{Si}_3\text{N}_4$ (monoclinic), and orthorhombic yttrium disilicate (Y$_2$Si$_2$O$_7$) were identified. Silicon nitride was completely transformed to $\beta$-phase, no $\alpha$-$\text{Si}_3\text{N}_4$ peaks were observed in the diffraction patterns. Diffraction pattern of nanocomposite Si$_3$N$_4$-5wt%SiC revealed also $\beta$-SiC (cubic). Major secondary (intergranular) phase is orthorhombic yttrium disilicate (Y$_2$Si$_2$O$_7$) which belongs to the one of the most refractory silicates.
3.2 Room temperature mechanical properties

The measured values of room temperature mechanical properties are summarized in Table II. Higher hardness and Young’s modulus of material with higher amounts of SiC particles was expected due to the addition of harder and stiffer SiC inclusions into a softer Si₃N₄ matrix. The fracture toughness value of Si₃N₄-5wt%SiC nanocomposite is slightly lower than the fracture toughness of Si₃N₄-1wt%SiC. Determined value of fracture toughness is characteristic for fine grained Si₃N₄ with low aspect ratio. This can lead to the conclusion that probably nano-phase toughening [9] is not effective in this material.

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<tr>
<td>Si₃N₄-1wt%SiC</td>
<td>14.46 ± 0.15</td>
<td>299 ± 12</td>
<td>4.54 ± 0.07</td>
<td>786</td>
<td>8.7</td>
</tr>
<tr>
<td>Si₃N₄-5wt%SiC</td>
<td>16.34 ± 0.12</td>
<td>322 ± 10</td>
<td>3.75 ± 0.53</td>
<td>678</td>
<td>6.4</td>
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The two-parameter Weibull statistics of four point flexure strength values gives for nanocomposite Si₃N₄-5wt%SiC characteristic strength of \(\sigma_0 = 678\) MPa and Weibull modulus \(m = 6.4\). The Si₃N₄-1wt%SiC exhibits a higher characteristic strength and Weibull modulus than Si₃N₄-5wt%SiC nanocomposite; \(\sigma_0 = 786\) MPa and \(m = 8.7\). Lower flexural strength of Si₃N₄-5wt%SiC is caused by defects as revealed fractographic analysis. Technological flaws presented in Si₃N₄-5wt%SiC [10] are connected with the formation of SiC particles during sintering.

3.3 High temperature mechanical properties

The creep resistance of the Si₃N₄-5wt%SiC nanocomposite was found to be significantly higher when compared to the creep resistance of the Si₃N₄-1wt%SiC, Fig.3. Creep rate of the Si₃N₄-5wt%SiC nanocomposite is up to one order of magnitude lower than that of Si₃N₄-1wt%SiC. However, the apparent activation energy, \(Q_c\), calculated from the inverse temperature dependence are around 350 kJ/mol for both micro-nanocomposites. The minimum strain rates plotted as a function of stress for each temperature give
values of stress exponents \( n \) in the range of 0.79-1.18 and 0.8-1.28 for \( \text{Si}_3\text{N}_4\text{-1wt\%SiC} \) and \( \text{Si}_3\text{N}_4\text{-5wt\%SiC} \), respectively. The basic creep mechanism in both materials seems to be the same. Apparently, SiC nanoparticles effect only the processes controlling the deformation.

In the Fig. 4 surface and cross-section of oxidized layer of \( \text{Si}_3\text{N}_4\text{-5wt\%SiC} \) composite formed at 1350°C for 300 hours are shown. The oxidation products formed on the surface consist of mixture of \( \text{Y}_2\text{Si}_2\text{O}_7 \) and \( \text{SiO}_2 \). Needle like and fine globular crystalline of \( \text{Si}_3\text{N}_4\text{O}_7 \) are embedded into silica layer, Fig. 4a. Fig. 5a shows surface of oxidized layer of \( \text{Si}_3\text{N}_4\text{-1wt\%SiC} \) formed at the same experimental conditions. Oxidation products have similar composition compared to composite \( \text{Si}_3\text{N}_4\text{-5wt\%SiC} \), however, significantly different morphology of the formed oxides is observed. Globular particles are larger and the elongated crystals of \( \text{Y}_2\text{Si}_2\text{O}_7 \) have lower aspect ratio compared to these in \( \text{Si}_3\text{N}_4\text{-5wt\%SiC} \). Moreover, higher amount of oxidation products are observed at oxidized surface. Although the thickness of the oxidized layer of \( \text{Si}_3\text{N}_4\text{-5wt\%SiC} \) is slightly thinner (Fig. 4b) compared to \( \text{Si}_3\text{N}_4\text{-1wt\%SiC} \) (Fig. 5b), the main difference is in the distribution of yttrium in the oxidized layer (bright contrast in backscattered electron). Yttrium in oxidized layer of \( \text{Si}_3\text{N}_4\text{-1wt\%SiC} \) agglomerates on the surface and at the interface between oxide layer and bulk material. After 300 hours the surface of \( \text{Si}_3\text{N}_4\text{-1wt\%SiC} \) is extensively coved by layer of \( \text{Y}_2\text{Si}_2\text{O}_7 \). Higher concentration of
Y$_2$Si$_2$O$_7$ in oxide layer than that observed within the bulk material suggesting the diffusion of Y to the surface during oxidation. Many fine cracks caused by the difference of the thermal expansion between base material and oxidized layer during cooling down procedure are observed in silica layer. Presented preliminary results represent only the first step to the oxidation study. The understanding of oxidation mechanisms in silicon nitride-silicon carbide composites requires far more investigations.

4. CONCLUSIONS

The mechanical properties of carbon derived Si$_3$N$_4$ – SiC micro-nanocomposites with different amount of SiC particles have been investigated. It was found that the presence of SiC particles increases the hardness and Young’s modulus but on the other side decrease the fracture toughness. Lower strength characteristics of the nanocomposite with higher content of SiC particles are connected with inadequate technological process. Nanocomposite with higher content of SiC particles exhibits better creep resistance which is connected with the presence of SiC particles which change the chemistry of intergranular phases and act as mechanical obstacles to grain boundary sliding. The change of chemistry of grain boundary inhibits the migration of additives and improves the oxidation resistance of composite with higher amount of SiC particles.

ACKNOWLEDGMENTS

This work was realized within the frame of the project „Centre of Excellence of Advanced Materials with Nano- and Submicron- Structure”, which is supported by the Operational Program “Research and Development” financed through European Regional Development Fund, the Slovak Grant Agency project No. 2/7194/27, APVT-51-049702, APVV-0171-06, Centrum of Excellence NANOSMART and KMM NoE funded by the EU (NMP3-CT-2004-502243).

LITERATURE REFERENCES