Influence of Graphite Additives on Wear Properties of Hot Pressed Si₃N₄ Ceramics

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Two different groups of Si₃N₄ based composites were prepared within the present study. The first group consisting of materials containing SiC nano-inclusions in Si₃N₄ matrix, the second one with the same SiC/Si₃N₄ composition containing different size of graphite particles. Wet volume abrasive wear of these two groups of materials was studied. Wear mechanisms of the first group is mainly transgranular fracture. The dominant wear mechanism of second group is changed with the increased load from transgranular to the intergranular. Significant role plays the weak graphite/matrix interface. The pull-out of SiC/Si₃N₄ grain agglomerates from this area deteriorates a possible lubrication effect of graphite during the test. No significant benefit of the application of graphite particles in respect to the wear behavior was observed in the present study.

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1. Introduction

Silicon nitride ceramics have been expected to be a new kind of promising wear-resistance material for parts of machines. In order to improve tribological properties of the monolithic silicon nitride other phases are added into the Si₃N₄ matrix. Hyuga et al.¹,² achieved very good results which showed that the initial high friction coefficient of Si₃N₄/carbon fiber composite was reduced shortly after the beginning of the wear test and maintained a very low value throughout. This was attributed to the solid lubricating effect of carbon fibers in the composite, resulting in lower stress at the contact asperities and preventing the removal of the lubricating layer. The wear rate was around two orders of magnitude lower than the monolithic material. Respectable influence on the wear properties has different sintering additives. For example, samples sintered with Y₂O₃ as sintering additive showed evidence of fracture type wear although this was not observed in samples sintered with Y₂O₃ and Lu₂O₃. These smaller rare earths lead to higher grain boundary bonding strength and superior high-temperature properties and resulted in higher wear resistance during sliding contact without lubricant.³ There exist numerous parameters with unknown effect on friction and wear of ceramics materials. Hsu et al.⁴ have shown that the wear rate can differ by several orders of magnitude for the same material when tested under different experimental conditions (sliding velocity, contact, load, relative humidity). The tribological behavior of monolithic silicon nitride is well known for wide range of sliding speeds (0.001-5 m/s),⁵ temperature⁶ and different environment.⁷ Graphite is good material for solid lubrication because it has a layered lattice structure with weak van der Waals bonding between the layers resulting in a low friction coefficient. However, technical problems arise during the fabrication of the ceramic graphite composite, because graphite powder used is difficult to mix with the raw ceramics powder owing to the hydrophobic nature and adhesion to the milling balls and pot used for the ball milling.² The purpose of this study was to investigate the influence of some parameters (sliding distance, load and sliding velocity) on the wear behavior of Si₃N₄/graphite composite and the influence of different amount and size of graphite grains on wear resistance. The influence of graphite additive on mechanical properties at room temperature has been investigated.

2. Experimental

2.1 Preparation of the samples

Silicon nitride, SN-E10 grade, (UBE Industries, Ltd., Japan, oxygen content 1.3 wt%), and yttrium oxide (Y₂O₃, H. C. Starck, grade fine) were used for preparation of starting mixtures. Chemical composition of these mixtures is listed in Table 1. Each composition was prepared in two steps. In the first step silicon nitride and yttria powders were attrition milled for 3 h in isopropylalcohol and then dried by vacuum evaporation. Weight ratio of starting constituents Si₃N₄:Y₂O₃ was kept constant 19:1 for each sample. In the second step, the graphite powder shown in Fig. 1 was added to the mixture prepared in the first step. This mixture was homogenized in the plastic container for 48 h in isopropylalcohol with silicon nitride balls.

Dried mixtures were hot-pressed in graphite die with the

### Table 1. Chemical Composition of the Starting Mixture

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si₃N₄ [wt%]</th>
<th>Y₂O₃ [wt%]</th>
<th>Graphite [wt%]</th>
<th>Fraction size of graphite grains</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>93.1</td>
<td>4.9</td>
<td>2</td>
<td>&lt;25μm</td>
</tr>
<tr>
<td>G2</td>
<td>90.3</td>
<td>4.7</td>
<td>5</td>
<td>&lt;25μm</td>
</tr>
<tr>
<td>G3</td>
<td>85.5</td>
<td>4.5</td>
<td>10</td>
<td>&lt;25μm</td>
</tr>
<tr>
<td>G4</td>
<td>85.5</td>
<td>4.5</td>
<td>10</td>
<td>from 25 to 71μm</td>
</tr>
<tr>
<td>G5</td>
<td>85.5</td>
<td>4.5</td>
<td>10</td>
<td>from 71 to 125μm</td>
</tr>
<tr>
<td>G6</td>
<td>85.5</td>
<td>4.5</td>
<td>10</td>
<td>&gt;125μm</td>
</tr>
</tbody>
</table>

1061
inner part sprayed by BN at 1750°C, 0.2 bar over-pressure of nitrogen atmosphere and mechanical pressure of 30 MPa. Densities of hot-pressed samples were measured by the mercury immersion method. Surfaces of densified specimens were polished (3 μm finish) and plasma etched with a gas mixture of CF₄ and O₂ in the Polaron plasma barrel etcher PT 7150. The etched surfaces were examined by SEM (EVO, Zeiss). The phase composition of powdered samples was investigated by XRD analysis using STOE powder diffraction system with CoKα radiation. The hardness was measured on polished cross-sections using the standard Vickers indentation technique at the load of 9.81 N. The fracture toughness was estimated from the length of cracks introduced by Vickers indentation at the load of 98.1 N using the method described by Shetty.⁸

2.2 Test machine and specimens

Volume abrasive wear tests were carried out on the setup shown in Fig. 2. Samples cut from hot pressed specimens with size of (10 × 10 × 5) mm were fixed on the upper static head. The compressive force of the specimen to the bottom rotating disc was changed from 6.8 N to 15.8 N. The rotating disk was a standard diamond disk used for grinding with grains size of 120 μm. Rotating speed was constant (125 rpm). Each test was carried out with two samples. These were located in the different positions from the rotating axis, Fig. 2. Two different sliding speeds, 0.37 and 1.07 m/s, respectively were achieved by this way for each pair of samples. Samples were polished to 3 μm finish before wear test. Water was dropwise added into the contact zone. The weight of samples was measured after four different sliding distances of 640, 1280, 1920 and 3200 m. From the weight loss of the samples the volume grind off the sample was calculated. Surfaces of the samples were observed by scanning electron microscopy after wear tests.

2.3 Graphite powder characterization

The graphite powder was obtained by turning of graphite taper (G-437, SpecialGraphit-Svensk, Sweden). Batches with different particle size distribution were obtained by sieving the graphite saw-dust through sieves of different mesh, Fig. 1. The XRD pattern of used graphite is shown that no other phases besides graphite were observed.

3. Results

3.1 Characterization of Si₃N₄/graphite composites

Six different compositions were prepared within the present study. These can be divided into two groups. The first one is represented by the samples G₁, G₂ and G₃. In these materials the graphite almost completely reacted with the residual SiO₂ phase present in the silicon nitride starting powder. These groups are considered as materials with Si₃N₄ matrix rein-
forced with hard SiC inclusions. The microstructures shown in Fig. 3 prove the presence of SiC nanoparticles distributed within the major Si$_3$N$_4$ phase. The SiC phase is distributed within the Si$_3$N$_4$ grains and also along the grain boundaries. The materials are similar to those studied before.\(^{9,10}\) In spite of the fact that sample G2 is over etched there is a visible difference in the microstructures. Larger amount of SiC particles comparing to sample G1 are documented in sample G2, which has connection to the higher amount of graphite in the starting composition, while sample G3 contains remarkable amount of pores and less SiC nanoparticles. This corresponds to the results listed in Table 2, where density of sample G3 is much less than the calculated one. Large portion of graphite was removed by the reaction with SiO$_2$ at the formation of CO (g) at the simultaneous decrease amount of liquid phase\(^{11}\) necessary for densification. In these three samples the size of graphite starting powder was <25 \(\mu\)m. The TD was calculated by rule of mixture and because the formation of other phases after densification process the real value of densities are higher than 100\%, Table 2.

The second group of the samples consists of composites G4, G5 and G6. In these samples the remarkable amount of graphite survived the densification process, Fig. 4 and thus this group can be considered as group of materials with hard Si$_3$N$_4$/SiC matrix and soft graphite inclusions. The size of graphite particles increases from G4 to G6, while graphite amount remains almost constant, Table 1. The distribution of the graphite particles is more or less random with some imperfections, mainly graphite particles agglomerates, Fig. 4. The mean graphite particle distance of sample G5 and G6 is 206 \(\mu\)m and 332 \(\mu\)m, respectively and mean graphite area density of sample G5 and G6 is 8\% and 12\%, respectively. This difference in the graphite area density is probably a consequence of slower reaction kinetics in the sample G6 because of smaller surface area of the original graphite grains compared to the sample G5. As it is visible from Fig. 5, Si$_3$N$_4$ microstructures contain SiC nanoparticles shown by arrow, similarly to the samples G1 and G2. The graphite particles consist of graphite sheets with different orientation, pointed in Fig. 5 by circle. The interface between Si$_3$N$_4$ matrix and graphite particle seems to be weak and chemically modified. It can be concluded that both groups of samples have the same matrix containing SiC nanoinclusions and SiC microareas within the Si$_3$N$_4$ major phase with the chemically similar grain boundaries. The second group contains additionally the graphite particles with the size up to 150 \(\mu\)m.

### Table 2. Densities and Mass Loss of Hot Pressed Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Densities [g.cm$^{-3}$]</th>
<th>TD [%]</th>
<th>Mass loss [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>3.246</td>
<td>102.4</td>
<td>-</td>
</tr>
<tr>
<td>G2</td>
<td>3.239</td>
<td>104.6</td>
<td>7.22</td>
</tr>
<tr>
<td>G3</td>
<td>2.494</td>
<td>83.0</td>
<td>15.8</td>
</tr>
<tr>
<td>G4</td>
<td>2.822</td>
<td>94.6</td>
<td>14.35</td>
</tr>
<tr>
<td>G5</td>
<td>3.141</td>
<td>105.3</td>
<td>10.67</td>
</tr>
<tr>
<td>G6</td>
<td>3.090</td>
<td>103.6</td>
<td>7.83</td>
</tr>
</tbody>
</table>
As it is shown in Fig. 6, the area around the graphite particles is lighter compared to the rest of the matrix (back scattered image, Fig. 6), this light areas are most probably consisting of yttria rich phases because of the reduction of SiO$_2$ by graphite. The weakness of the interface caused by not dense areas of Si$_3$N$_4$/SiC matrix (lack of SiO$_2$ necessary for liquid phase formation at the sintering temperatures) is documented by removing the matter after polishing, indicated by the arrow. The microstructure contains also SiC and SiO$_2$ phases which presence is documented by the XRD pattern shown in Fig. 7.

3.2 Mechanical properties at RT

Vickers indentation hardness and fracture toughness of samples after hot-pressing are plotted in Figs. 8 and 9. It should be noted the imprints were located into the Si$_3$N$_4$/SiC matrix and graphite grains were omitted from indentation. The high mean value of the hardness of samples G1 and G2 is affected by the presence of SiC inclusions because of higher hardness of SiC compared to Si$_3$N$_4$. The hardness of sample G3 could not be determined because of high porosity, low hardness of sample G4 is also influenced by residual porosity, Table 2. Interestingly, fracture toughness decreases with the increased amount of graphite and is almost invariant to the size of the graphite particles, Fig. 9.

3.3 Wear resistance

The volume abrasive wear rate ($K_w$) has been determined from two-body wear test using commercial disc for grinding with diamond grains size of 120 µm according to the schematic picture plotted in Fig. 2. The volume abrasive wear rate was calculated according to the Eq. (1):\(^5\)

$$K_w = V/ F_{N,55}$$  

(1)
where $V_v$ is the volume of the worn material, $F_N$ is the normal load and $s$ is the distance, on which is wear realized.

**Figure 10** shows the dependences of volume abrasive wear rate as a function of sample composition and the distance at three different loads. As it is visible from this figure, sample G3 with the highest porosity (16%) has the highest abrasive volume wear rate. This sample will be omitted in the next discussion. Surprisingly, sample G4, with the closed porosity up to 5%, behaves similarly to the samples of full density. Here we can conclude that probably closed porosity is a necessary condition with respect to application of the wear resistant materials in the liquid environment. As the best materials with the lowest volume abrasive wear rate are samples G2, G5 and G6. While sample G2 is the sample without residual graphite in the microstructure, samples G5 and G6 are samples with the largest portion of survived graphite. The following discussion will be focused only on three samples G2, G5 and G6 with the lowest abrasive volume wear rate.

**4. Discussion**

The wear mechanism in the sample G2 is an abrasion of the $\text{Si}_3\text{N}_4/\text{SiC}$ matrix. Areas of several micrometers taken off the matrix are seldom observed, **Fig. 11-A, B**. Probably either $\text{Si}_3\text{N}_4$ grains or SiC/$\text{Si}_3\text{N}_4$ grain agglomerates are drawn up from the rest of the sample during the abrasion. SiC nanoparticles or microdomains increase the hardness and the fracture toughness of the composite, as it is shown in **Fig. 8**. Worn surface of sample G2 is without any visible macrodefects, **Fig. 11-C**. Occasionally appeared scratches indicate the sliding direction. Scratches are very probably a consequence of hard debris taken of the composite during the abrasion, as it is shown in **Fig. 11**. On the other hand surface of the sample G6 after the wear test at the same conditions is much more damaged, **Fig. 12**. In this case the break of the graphite–matrix interface is evident, and moreover a large portion of loosed graphite/matrix material is documented. In the detailed view one can recognize the graphite sheets located among the matrix ceramic grains. These are probably carried along with the hard matrix debris and caused the decrease of the wear rate with the increased distance of the sample G5 at the mild conditions (loads up to 11.3 N). The same is valid for
Influence of Graphite Additives on Wear Properties of Hot Pressed Si₃N₄ Ceramics

the sample G6 at the highest load of 15.8 N. The volume abrasive wear rate of sample G2 also moderately decreases with the sliding distance at all tested loads.

Figure 13 is re-plotted Fig. 10 on the smaller scale and only samples G2, G5 and G6 are taken into account. Sample G2 has the lowest wear rate compared to the other two at all loads. This is probably connected with the similar/same wear mechanisms at the all loads for this sample. The dominant mechanism is the transgranular fracture of Si₃N₄ grains, as can be documented in Fig. 14. The grain boundary phase is strong enough to keep the microstructure together, exceptionally intergranular cracks were observed. On the other hand, sample G6 has low volume abrasive wear rate at low and medium loads (6.8 and 11.3 N), but at the highest load of 15.8 N this rate increased. The reason can be the alternation of the wear mechanism, which is changed from mainly transgranular fracture (similar to the sample G2) to the mostly intergranular fracture.

The intergranular cracks between the Si₃N₄ particles were observed also in sample G5 at the highest load, shown by arrows in Fig. 12. This leads to the release of the SiC/Si₃N₄ matrix particle agglomerates, Fig. 14-B). This hard debris increased the wear rate, especially at highest load. The damage of SiC/Si₃N₄ matrix surface is more pronounced at this load for the sample G6 as for the sample G5. This is probably the reason for higher volume abrasive wear of this sample at the load of 15.8 N, Fig. 13-C). At the low and medium load the graphite sheets are easily loosed from large graphite grains of sample G6. They are able to align themselves to the grinding direction and can serve as a solid lubricant and thus, decrease the volume abrasion of sample G6.

The wear mechanism is also dependent on the grinding speed, Fig. 15. The all above presented results were obtained at the sliding speed of the grinding wheel of 1.07 m/s. These conditions were considered as more severe compared to the experiments performed at the sliding speed of 0.37 m/s. At this sliding speed all conclusions mentioned above can be drawn for the G2, G5 and G6 samples with the exception that sample G2 has slightly higher volume abrasive wear rate as the other both. In present case, the wear mechanisms of samples in not substantially changed. The sample G2 is worn by transgranular fracture while samples G5 and G6 are damaged by intergranular fracture and grain agglomerate pull out. The decrease of the volume abrasion of samples G5 and G6 is attributed to the lower damage of the graphite–matrix interface.

From the above results and the discussion one can conclude that there is no substantial differences in volume abrasive wear behavior between samples free of graphite grain and those containing graphite particles. The last mentioned are even better at the low sliding rate. On the other hand the discussion did not reflect the fact that defects of size about 100 μm (size of graphite particles) have crucial effect on the strength of such composite. When the critical matrix defect is 10 μm and the worn workpiece contains defect of 100 μm, the strength value decreases by factor 3.

The strength of materials prepared by the same way as sample G2 has strength close to 700 MPa, by this speculation the strength of sample G6 is 230 MPa. This strength value most probably disqualifies graphite containing materials for many applications.
5. Conclusions

SiC/Si$_3$N$_4$ composite without graphite particles:
The porosity has detrimental effect on the abrasive wear behavior.
Volume abrasive wear rate is the lowest at all presented conditions with the exception of low sliding speed.
A dominant wear mechanism is transgranular fracture.

SiC/Si$_3$N$_4$-graphite composite:
Weak SiC/Si$_3$N$_4$ matrix–graphite interface has detrimental effect on the wear behavior at high loads.

Volume abrasive wear rate for the best samples is slightly lower comparing to SiC/Si$_3$N$_4$ composite without graphite particles at higher sliding speed. This relationship is moderately changed at lower sliding speed.
No effect of the graphite grain size and/or distance of graphite grains on the wear behavior were observed.
Wear mechanism of these composites is changed from transgranular fracture to the intergranular fracture at increased load.
Influence of Graphite Additives on Wear Properties of Hot Pressed Si$_3$N$_4$ Ceramics

Fig. 15. Dependence of the volume abrasive wear rate of samples G2, G5 and G6 on the sliding speed (the grinding distance of all samples is the same 1280 m).

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