Wear resistance of hot-pressed Si₃N₄/SiC micro/nanocomposites sintered with rare-earth oxide additives

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Abstract

The wear resistance of hot-pressed silicon nitride/silicon carbide micro/nanocomposites as well as monolithic silicon nitrides sintered with the same rare-earth oxide sintering additives (La₂O₃, Nd₂O₃, Y₂O₃, Yb₂O₃ and Lu₂O₃) has been investigated under dry sliding conditions. The friction coefficient decreased with a decreasing ionic radius of rare-earth elements in both the monoliths and the composites. The friction coefficient of composites was always lower in comparison with that of Si₃N₄ monoliths. Similarly, the specific wear rate significantly decreased with a decreasing ionic radius of rare-earths either in monolithic or composite materials. The composites always exhibited lower specific wear rate compared to the monoliths. Mechanical wear (micro-fracture) and tribochemical reaction were found as the main wear mechanisms in all investigated materials. The higher bonding strength in the case of materials sintered with additives of a smaller ionic radius restricts dropping of the individual silicon nitride grains during wear experiments. This high bonding strength and the high fracture toughness are the reasons why the ceramics doped by Lu exhibited the best wear resistance. The Evans and Marshall lateral-crack chipping model based on the fracture toughness and hardness values well describes the wear rate of the investigated micro/nanocomposites.

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1. Introduction

Silicon nitride based ceramics exhibit very good mechanical properties at room and high temperatures, high thermal conductivity and outstanding tribological properties, which allow them to work at conditions required for wear resistant technological applications, such as valves, bearings, seal rings, cutting tools, etc. [1].

Their mechanical properties can be improved using suitable sintering additives and microstructure design resulting in acicular grains that grow in situ when sintering conditions and composition are appropriate [2]. In such a microstructure, the intergranular crack and crack deflection at the boundaries of elongated Si₃N₄ grains followed by bridging mechanisms in the form of frictional and mechanical interlocking were reported as the reason for the increasing fracture toughness. During recent years it has been reported that the chemical composition of the intergranular phases directly influences the interfacial strength and the ability of a crack to propagate intergranularly [3,4].

Rare-earth (RE) oxide sintering additives are considered as ideal additives for Si₃N₄ due to their high melting point and due to the fact that they control the α → β phase transformation rate, the grain growth anisotropy and the aspect ratio of the β-Si₃N₄ grains [3–6]. According to recent results the fracture toughness of silicon nitrides with rare-earth (RE)-MgO additives and amorphous intergranular phase increases, and the four-point bending strength decreases with an increasing ionic radius of RE³⁺ [3]. It was found that weaker grain-boundary interface connected with the addition of La³⁺ results in a higher toughness, but in lower strength of the bulk Si₃N₄ material. On the other hand, no significant influences of rare-earth oxides (La₂O₃, Gd₂O₃, Lu₂O₃) on the fracture toughness of Si₃N₄ with bimodal microstructures and crystalline secondary phases have been observed by Becher et al. [4,6]. They found similar behavior for seeded and un-seeded materials and the plateau value of the fracture resistance where unstable crack extension occurred was above 10 MPa m¹/² for each system. Silicon nitride ceramics sintered with the rare-earth oxide additives are also an important class of materials for high-temperature applications because they exhibit good high-temperature strength and thermal shock resistance along with good creep resistance and high resistance to oxidation [3,4,6]. It was found that the high-temperature strength of hot-pressed Si₃N₄ ceramic was significantly improved by the addition of Lu₂O₃ additive [7].

The mechanical properties of silicon nitride based ceramics have been improved by incorporation of second phase, micro- or nano-
sized, into their microstructure in the form of platelets, whiskers or particles. Introduction of SiC nanoparticles into the silicon nitride matrix improves hardness, strength, as well as the resistance to creep, oxidation and corrosion of Si3N4 ceramics [8]. Si3N4–SiC nanocomposites have been prepared recently by the doping of Si3N4 powder with amorphous SiNxC precursor [9] or using carbothermal reaction (SiO2 + C) [10] in order to improve hardness, growth, as well as resistance to creep, oxidation and corrosion of Si3N4 ceramics. Park et al. [11] reported that nanocomposite Si3N4–SiC with Yb2O3 additive showed better oxidation resistance and higher strength retention than the monolithic Si3N4 with Yb2O3. Significantly higher creep resistance of the Si3N4–SiC nanocomposite in comparison with monolithic Si3N4 was observed by Dusza et al. [12]. On the other hand, the lower fracture toughness and lower strength of Si3N4–SiC nanocomposite compared to the Si3N4 monolith were observed by Kašiarová et al. [13] and no additional toughening effect by the SiC addition was also observed by Herrmann et al. [8].

The majority of the previous investigations in the field of tribology of Si3N4 and Si3N4–SiC composites were focused on the study of the influence of different testing conditions and/or SiC addition on their friction coefficient and specific wear rate [14–18].

Recently, several authors investigated the influence of sintering additives and microstructures on wear resistance of Si3N4 based ceramics, however the reported relationships are often ambiguous [19–21]. Different authors reported that the wear resistance improved with a decreasing Si3N4 grain size despite the decreased fracture toughness [22,23]. It was reported that the “self-reinforced” microstructure with elongated grains suppressed the propagation of cracks, which not only improved the fracture toughness and strength but also enhanced the wear resistance [24]. Similarly, for Si3N4–SiC whisker composites, some authors reported that the pullout of SiC whiskers results in higher wear resistance in comparison with the monolithic silicon nitride while others observed only a little difference between their wear performances [9,18]. Miyazaki et al. [21] investigated the influence of microstructure on the friction and wear properties of Si3N4 ceramics in a sliding contact test without any lubricant and they found that tribological properties are significantly microstructure dependent. However, a clear relationship between the tribological characteristics and the grain size and mechanical properties was not found [19,20]. Hyuga et al. [19] showed that the materials sintered with smaller rare-earth elements, leading to stronger grain-boundary bonding strength, exhibited higher wear resistance. These results show that the wear properties of Si3N4 ceramics can be tailored by selecting the kinds of additives. The wear mechanism is also strongly influenced by the factors such as temperature, atmospheric humidity, sliding speed and contact load [2,14–17,25].

In the present work the influence of rare-earth oxide additives (La2O3, Nd2O3, Y2O3, Yb2O3 and Lu2O3) on the wear characteristics of Si3N4/SiC micro/nanocomposites and monolithic Si3N4 ceramics has been investigated.

2. Experimental procedure

The starting mixtures of the set of five Si3N4/SiC micro/nanocomposites consisted of the following powders: α-Si3N4 (grade SN-E10, UBE Industries, Japan), amorphous SiO2 (50 m2 g−1, Aerosil OX-50, Degussa, Germany), carbon black (1000 m2 g−1, Cabot) and different rare-earth oxides RE2O3 (RE = La, Nd, Y, Yb, or Lu): Y2O3 (Pacific Industrial Development Corporation), La2O3 (Merck, Germany), Nd2O3 (Johnson Matthey GmbH), Yb2O3 (Pacific Industrial Development Corporation), Lu2O3 (Treibacher Industrie AG). All compositions contained the same atomic amount of RE element. The amount of SiO2 and C was calculated to achieve 5 vol.% of SiC after in situ carbothermal reduction process [10]. Simultaneously, a set of five reference monolithic Si3N4 materials with the same composition of sintering additives were prepared in order to compare the microstructure and mechanical properties. The raw materials were homogenized and attrition milled in isopropanol for 4 h in polyethylene water cooled bin. The balls and blender were silicon nitride based. The slurries were subsequently dried and the powders sieved through a 25 μm sieve. The sieved starting powder was poured into a graphite rectangular die sprayed by a thin BN layer from inside. Bulk bodies of 65 mm × 65 mm × 5 mm were then hot-pressed at 1750 °C with a load of 30 MPa and 0.15 MPa pressure of nitrogen during 1 h. The heating regime was chosen in order to obtain RE2O3Si2O7 crystalline intergranular phases in all materials. Densities were measured by the mercury immersion method. The theoretical density was calculated by the rule of the mixtures. Relative densities of all samples were higher than 98% of theoretical density.

Analysis of microstructure has been realized after plasma-etching of the polished surface of the specimens (perpendicular to the hot-pressing direction) using scanning electron microscopy (SEM) (JEOL JSM-7000F, Japan). Grain diameter (width of the elongated silicon nitride grains) was distributed by measuring 2300 grains of each sample. The apparent aspect ratio (AR) of the Si3N4 grains was obtained by the measurements of grain width and length visualized on the micrographs taken at a magnification of 20,000.

X-ray diffraction (XRD) (Cu Kα radiation, STOE powder diffractometer, Germany) was used for the characterization of the crystalline phases of the materials.

The microstructure and the grain boundaries were characterized using TEM and HREM using a TECHNO G2 FEG SuperTWINN (200 kV) transmission-scanning electron microscope equipped with both side-entry wide angle SiO and on-axis bottom mounted Gatan 2K CCD cameras. The local chemical analysis was measured with an integrated X-ray energy dispersive attachment (EDS) with a EDAX UTW detector. The thin foils were prepared using the focused ion beam (FIB) Quanta 3D system equipped with an Omniprobe lift-out system.

The hardness values have been measured on polished cross-sections (perpendicular to the hot-pressing direction) of bars using the standard Vickers indentation method at a load of 9.8 N (LECO LM-700, USA).

Fracture toughness was measured by the Single Edge V-Notch Beam (SEVNB) method on the specimens with dimensions of 3 mm × 4 mm × 45 mm which were notched by sliding a 3 μm diamond paste in the root of a 600 μm thick and 600 μm long saw notch using a razor blade. Using this method, a notch root radius of 10 μm or less on a 1.2 mm long notch could be achieved. The radius of each notch was controlled with an optical microscope. The notched samples were then broken under 4-point-bending in a universal testing machine with cross-head speed of 0.5 mm/min. The peak load at failure was registered, and the mean notch length was calculated out of three measurements with an optical microscope along the thickness of the specimen. Five samples were tested for each composition. The toughness was then calculated using the following equation [26]:

$$K_{IC} = \frac{F}{B\sqrt{W}} \left(1 - \frac{S_1 - S_2}{2W(1 - \alpha)^{1.5}}\right)^{1/3} \sqrt{Y'}$$

(1)

$$Y' = 1.9887 - 1.326\alpha - (3.49 - 0.68\alpha + 1.35\alpha^2)\alpha(1 - \alpha)(1 + \alpha)^{-2}$$

(2)

where F is the fracture (maximum) load in four-point bending, B the specimen width, W the specimen height, S1 and S2 the outer and
inner roller span of the four-point bending fixture, respectively, \( a \) is the precrack depth and \( \alpha \) is the ratio \( a/W \).

The wear behavior of the materials was studied by unlubricated ball-on-disk experiments [27] (on the high-temperature tribometer DTHT 70010, CSM Instruments, Switzerland) against a polished commercial silicon nitride ball (with a diameter of 6 mm) at room temperature. The silicon nitride sintered bodies were machined into 15 mm × 15 mm × 4 mm as the plate specimens and the tested surface were grinded to final roughness of 3 \( \mu \)m. The specimens were tested on the plane normal to the hot-press direction. The tests were performed in air with a relative humidity of 55 ± 5%.

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 wear track and perpendicular to the sliding direction using the profilometer (Mitutoyo SJ-201, USA). The wear tracks were then examined by SEM to estimate the wear mechanisms. The specific wear rate \( r \) is defined as the worn volume per unit loading force, per unit sliding distance, i.e.

\[
    r = \frac{V}{FL} \quad \text{[mm}^3\text{Nm}^{-1}]
\]

where \( F \) is loading force \([\text{N}]\); \( L \) is total sliding distance \([\text{m}]\); and \( V \) is worn volume \([\text{mm}^3] \).

\[
    V = A2\pi r \quad \text{[mm}^3\text{]}
\]

where \( A \) is the average value of four different measurements of cross section area of the wear track estimated by profilometer \([\text{mm}^2]\); and \( r \) is the sliding radius \([\text{mm}]\).

Macro- and micro-fractography have been used for the study of the wear mechanisms in the investigated materials after the wear tests.

3. Results and discussions

All investigated materials exhibited a bimodal character of microstructures which consist of elongated \( \beta \)-Si3N4 grains embedded in the matrix of much finer Si3N4 grains. Fig. 1 shows the characteristic microstructures of monolithic Si3N4 and Si3N4–SiC composite sintered with the largest ionic radius of \( \text{RE}^{3+} \) (La3+) and with the smallest one (Lu3+). The composites additionally contain globular nano/submicron sized SiC particles, located intragranularly in the Si3N4 grains or intergranularly between the grains. These SiC particles can be clearly visible in the microstructure observed by TEM (Fig. 2). The microstructures of the composites were always finer than that of the monoliths because the SiC particles, formed at the grain boundaries of the Si3N4 grains, hinder the growth of the \( \beta \)-Si3N4 grains during the evolution of microstructure.

The XRD results revealed \( \beta \)-Si3N4 as a major phase and \( \text{RE}_2\text{Si}_2\text{O}_7 \) (where \( \text{RE} = \text{Y, Yb or Lu} \)) as a secondary phase in both monolithic and composite materials. This crystalline phase was not found in ceramics with La- and Nd additives. All Si3N4 materials also contain SiO2 as a minor phase, whereas the Si3N4–SiC additionally contained SiC phase and also SiO2, Si3N2O.

Table 1 illustrates the aspect ratio of \( \beta \)-Si3N4 grains in the microstructures as well as the room temperature mechanical properties of all the studied materials. It should be noted that the aspect ratio of \( \beta \)-grains slightly increased with a decreasing ionic radius of \( \text{RE}^{3+} \) in both the micro/nanocomposites as well as in the mono-

![Fig. 1](image1.png)

Fig. 1. Microstructures of the monoliths sintered with (a) La2O3; (b) Lu2O3 and composites sintered with (c) La2O3; (d) Lu2O3.

![Fig. 2](image2.png)

Fig. 2. TEM microstructures of the Si3N4–SiC composites doped by La2O3.
Table 1: Aspect ratio of β-Si3N4 grains and some of the room temperature mechanical properties of the investigated materials.

<table>
<thead>
<tr>
<th>Sintering additive</th>
<th>RE3+ (Å)</th>
<th>Si3N4 monoliths</th>
<th>Si3N4–SiC composites</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Aspect ratio</td>
<td>Hardness (GPa)</td>
</tr>
<tr>
<td>La2O3</td>
<td>1.06</td>
<td>5.8 ± 1.6</td>
<td>16.1 ± 0.6</td>
</tr>
<tr>
<td>Nd2O3</td>
<td>0.98</td>
<td>6.0 ± 1.8</td>
<td>16.2 ± 0.6</td>
</tr>
<tr>
<td>Y2O3</td>
<td>0.90</td>
<td>6.7 ± 2.3</td>
<td>16.4 ± 0.9</td>
</tr>
<tr>
<td>Yb2O3</td>
<td>0.87</td>
<td>6.6 ± 1.9</td>
<td>16.9 ± 0.5</td>
</tr>
<tr>
<td>Lu2O3</td>
<td>0.85</td>
<td>7.0 ± 2.3</td>
<td>17.1 ± 0.8</td>
</tr>
</tbody>
</table>

lithic ceramics. This observation is in good agreement with the fact that the larger RE ions delay phase transformation [4] and that the RE ions impact the temperature at which the phase transformation initiates [5].

The hardness values of the micro/nanocomposites were always higher than those of the monolithic Si3N4 (Table 1). This can be explained by the finer microstructures of the composites as well as by the presence of harder SiC particles in the Si3N4 matrix. According to the results, the hardness values slightly increased with the decreasing ionic radius of RE element in both the monolithic and the composite materials.

On the other hand, the fracture toughness of the Si3N4–SiC composites was always lower than that of the Si3N4 monoliths (Table 1) because of the finer composite microstructures. It is well known that in the case of finer microstructures there are only limited possibilities for the origination of toughening mechanisms during crack propagation (e.g. crack deflection at the boundaries of elongated Si3N4 grains). Similarly to hardness values, the fracture toughness also increased with a decreasing ionic radius of RE either in the monoliths or the composites (Table 1). The fracture toughness of silicon nitride is strongly influenced by the microstructure characteristics (such as grain diameter, aspect ratio of grains, amount of elongated grains, etc.) as well as by the chemical composition of secondary intergranular phases. From the comparison of the values of aspect ratio and fracture toughness, it is obvious that the fracture toughness values in various RE-doped materials correspond with the aspect ratio of Si3N4 grains in these materials. Both the monolithic Si3N4 and the composites doped with Lu exhibited the highest aspect ratio and also the highest fracture toughness values among all monoliths and composites, respectively. On the other hand, the materials with lower aspect ratio exhibited lower fracture toughness.

The friction curve had the same trend for all tests, i.e. starting at a relatively low level of friction coefficient value, increasing to a peak and then reducing to a reasonably constant level for the rest of the test. Examples of friction coefficient curves of the monolithic Si3N4 sintered with Nd2O3 and the Si3N4–SiC composite with Nd2O3, respectively are illustrated in Fig. 3. According to the results, the friction coefficients of Si3N4 monoliths with different additives were always higher compared to those measured for the Si3N4–SiC composites with the same type of additives, Fig. 4.

From the results illustrated in Fig. 4 it is also visible that the values of friction coefficient slightly decreased with a decreasing ionic radius of RE3+ from 0.74 to 0.70 in the case of monoliths and from 0.71 to 0.64 in the case of composites.

Fig. 5 shows the specific wear rate of the specimens as a function of the size of rare-earth cations for either the monolithic or the composite materials sintered with different oxide additives. The specific wear rate decreased with a decreasing ionic radius of RE3+ from the value of $3.22 \times 10^{-5}$ to $1.15 \times 10^{-5}$ [mm$^3$/Nm] for
the monolithic Si$_3$N$_4$ sintered with La$_2$O$_3$ and Lu$_2$O$_3$, respectively, and from $1.91 \times 10^{-5}$ to $0.89 \times 10^{-5}$ [mm$^3$/Nm] in the case of composites doped with the same additives. Another fact, which can be seen from Fig. 5, is that the specific wear rate of monoliths was always higher compared to the wear rate of composites with the same sintering additives.

Regarding the friction coefficient and wear rate, our results are in good agreement with the results of Gomes et al. [25] who investigated the influence of the microstructure on wear behavior of three different silicon nitrides tested at conditions similar (pin-on-disk, gated) the influence of the microstructure on wear behavior of three in good agreement with the results of Gomes et al. [25] who investigated the influence of the microstructure on wear behavior of three in good agreement with the results of Gomes et al. [25] who investigated the influence of the microstructure on wear behavior of three. They reported the values of friction coefficients from 0.58 to 0.78 and wear rates from $2 \times 10^{-5}$ to $7 \times 10^{-5}$ [mm$^3$/Nm]. Similar testing conditions have been also applied for characterization of tribological behavior of Si$_3$N$_4$–SiC composites with SiC platelets (10 μm) and SiC micro-nanoparticles (0.3 μm) and it was reported that the friction coefficient and wear rate for platelets and particles strengthened composites was 0.5/0.62 and 2 $\times$ 10$^{-4}$/5 $\times$ 10$^{-4}$ [mm$^3$/Nm], respectively [16]. These results show that both the friction coefficient and the wear rate were higher for composite strengthened by SiC particles in comparison with monolithic material, which is a different result compared to our work. Miyazaki et al. [21] investigated the wear behavior of silicon nitride with different microstructures, processed by a combination of different weight fraction of Al$_2$O$_3$ + Y$_2$O$_3$ sintered at 1950°C and by changing the sintering temperatures from 1750 to 1950°C for the materials with 5 wt.% of Al$_2$O$_3$ and 5 wt.% of Y$_2$O$_3$ additives. The materials prepared at the lowest sintering temperature (1750°C) and with the lowest volume fraction of sintering additive (1 + 1 wt.%), exhibited very high wear rate (approximately $4 \times 10^{-4}$ [mm$^3$/Nm]), whereas the other systems exhibited a similar wear rate to our results. Recently, Hyuga et al. [19] investigated the influence of rare-earth sintering additives (Lu, Yb and Y) on the wear behavior of silicon nitride ceramics and reported increasing wear rate with increasing ionic radius of RE, similar to our present work.

Examples of the worn surfaces of the tested plate specimens are given in Fig. 6. From the comparison between Fig. 6(a) (Si$_3$N$_4$ + La$_2$O$_3$), Fig. 6(b) (Si$_3$N$_4$ + SiC + La$_2$O$_3$) and Fig. 6(c) (Si$_3$N$_4$ + SiC + Lu$_2$O$_3$) it is seen that with increasing wear resistance the worn surface became rather smooth but adherent debris can be still observed. As can be seen, an addition of SiC into the Si$_3$N$_4$ with La$_2$O$_3$ results in a higher amount of coherent debris, whereas the highest amount of coherent debris was observed for the material with the highest wear resistance, i.e. for composite sintered with Lu$_2$O$_3$. The coherent debris layer, which was observed in all studied wear tracks, constitutes a tribofilm that affords some protection to the ceramic surfaces decreasing the wear coefficient of materials [16]. A 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. More fractured areas and a higher amount of silicon nitride debris have been observed in the wear tracks of the specimens having lower wear resistance. These fractured areas show a mixture of intergranular and transgranular failure modes in the worn surfaces. The wear tracks observed at higher magnification are given in Fig. 7(a) and (b).

During the room temperature tests the oxidation of the wear debris, related to roll formation, was observed in several investigations [14,15]. The formation of those rolls is attributed to the humidity and is associated with the reduction of friction and wear. Roll creation often occurs for silicon nitride based ceramics where tribochemical reaction with water results in the formation of hydrated silicon oxide or silicates [15,16]. In the present work, no significant amount of rolls was observed, on the other hand, the coherent layers formed on the wear surfaces contain large amounts of oxygen (observed by the EDX analyses), suggesting that the layers are composed mainly of the oxidation products of silicon nitride. The formation of oxide may be accelerated by the presence of small particles of silicon nitride formed by fracture under the high contact stresses at the wear interface. These particles have a high specific area, which would increase the amount of reaction product formed in comparison with a reaction with a solid piece of ceramics [14]. This would give some oxidization event at room temperature since the silicon nitride surface is likely to be rapidly covered with oxide layers. These oxides are products formed by tribochemical reaction at the wear interface [14] which can occur at loads less than 10 N and relatively low temperatures (<400°C) [15].

The main wear mechanism in the present work is similar for all studied materials in the form of mechanical wear (micro-fracture) and tribochemical reaction. The tribochemical reaction area is char...
acterized by a relatively smooth surface and the micro-fracture area is characterized by a rough surface and accumulated wear debris. The tribochemical reactions create a film on the tested samples and above a critical load the tribochemical film was partially removed, resulting in micro-fracture in discrete regions. Fig. 8 shows examples of details of such coherent layers (film) and their following fracture and removal from the surface of the worn surface.

The correlations between the fracture toughness and the wear rate of all investigated ceramics are illustrated in Fig. 9. As it can be seen the wear rate of Si$_3$N$_4$ as well as composite ceramics decreased with the increasing fracture toughness and these relationships are very evident.

Fig. 10 shows the relationship between specific wear rate and hardness for all investigated materials and it is evident that the materials with a smaller ionic radius of RE$^{3+}$ and having higher hardness exhibited a lower specific wear rate. It is interesting to note that the relationship between hardness and wear rate of silicon nitrides and composites is expressed by only one line, instead of two lines as in the case of relationships between fracture toughness and wear rate. This observation is contrary to the results reported by Miyazaki et al. [21] who observed a higher specific wear rate with increasing hardness values for Si$_3$N$_4$ ceramics hot-pressed with Al$_2$O$_3$ and Y$_2$O$_3$ as sintering aids.

It was reported [3,4,19,20] that the bonding strength between grains and grain-boundary phases of silicon nitrides increased with the decreasing ionic radius of RE$^{3+}$. This results in the highest bonding strength in Si$_3$N$_4$ containing Lu$_2$O$_3$ as a sintering additive and restricts dropping of the individual silicon nitride grains during the wear experiment. This fact together with its highest fracture toughness values are the reasons why Si$_3$N$_4$ doped by Lu exhibited the highest wear resistance among all studied monolithic materials.

Despite the lower fracture toughness the composites exhibited higher wear resistance compared to the monolithic silicon nitrides, probably due to their higher hardness whose positive effect was more significant than the influence of the lower fracture toughness.

It is evident that the material response to the wear is a reaction to a complex and complicated stress field, originating from contact geometry, load, speed, temperature, environment, and its description is very difficult [24]. In spite of this fact, however, design engineers sorely need a model which is able to predict the behavior of ceramics under a tribological environment. During the last decades different models have been developed which are similar and assume that subsurface lateral fracture is mainly responsible for the material removal during the abrasive wear [28]. The model developed by Evans and Marshall is described by the equation [28]:

$$ V = \alpha \frac{P^{9/8}}{K_{1c}^{1/2}H^{5/8}} \left( \frac{E}{H} \right)^{4/5} \ell $$

(5)

where $\alpha$ is the material-independent constant, $P$ the normal load, $K_{1c}$, $H$, and $E$ the fracture toughness, hardness and Young's modulus, respectively, of the abraded material and $\ell$ is the sliding distance. By gathering all of the material-specific constants into one parameter, $\beta$, the equation can be expressed as:

$$ V = \beta P^{9/8} \ell $$

(6)

where

$$ \beta = \frac{(E/H)^{4/5}}{K_{1c}^{1/2}H^{5/8}} $$

(7)
The relationship between the parameter $\beta$ and the wear rate is given in Fig. 11. According to the results the model well describes the wear behavior of the investigated ceramic composites under the applied tribological conditions. On the other hand, a deviation from linear dependence was observed in the case of monolithic materials as it is illustrated in Fig. 11. According to the literature, some deviations from this model were also observed in other studied cases. Miyazaki et al. [21] and Doğan and Hawk [24] used the same or slightly modified model for the prediction of wear behavior of silicon nitride ceramics with different sintering additives and different grain sizes and shapes. Miyazaki et al. [21] found a good relationship, especially when used indentation fracture toughness values instead of the values of the Single Edge Precracked Beam (SEPB) method. According to their results the difference is caused by the fact that the SEPB method with long crack length at the crack instability results in increased $K_{IC}$ values for ceramics with larger grains and describes incorrectly the wear behavior. Doğan and Hawk [24] found an inconsistent correlation between the parameter $\beta$ and volume wear for all investigated silicon nitrides. However they used a pin-on-drum abrasive wear test against 400- and 150-grit SiC. They concluded that fracture toughness or grain-boundary toughness can be assumed as the best indicator of the wear resistance of silicon nitride based ceramics. Our results show that the wear resistance of silicon nitride ceramics can be well described by the hardness and SEVN fracture toughness.

4. Conclusions

The wear resistance of hot-pressed silicon nitride/silicon carbide micro/nanocomposites sintered with various rare-earth oxide additives (La$_2$O$_3$, Nd$_2$O$_3$, Y$_2$O$_3$, Yb$_2$O$_3$ and Lu$_2$O$_3$) has been investigated. These results were subsequently compared to those obtained on the reference hot-pressed monolithic Si$_3$N$_4$ sintered with the same rare-earth oxide sintering additives. The following main results can be concluded:

- The friction coefficient slightly decreased with a decreasing ionic radius of the rare-earth element in both the monoliths and the composites and the SiC particles seem to be effective in reducing the friction coefficients of Si$_3$N$_4$ based materials as well.

- The specific wear rate significantly decreased with a decreasing ionic radius of rare-earths in both the monolithic and the composite material caused by the positive effect of the smaller ionic radius of RE on the bonding strength between grains and intergranular phase. This higher bonding strength restricts dropping of individual silicon nitride grains during wear, and together with the higher fracture toughness are the reasons why the materials doped by Lu exhibited the highest wear resistance. The higher wear resistance of composites can be explained by the positive influence of finer grain size and higher hardness which overcome the negative influence of the lower fracture toughness.

- Similar wear mechanisms have been observed for all studied materials which consist of the combination of mechanical wear (micro-fracture) and tribochemical reaction. A higher amount of coherent debris and fewer fractured areas (silicon nitride debris) were observed in the wear tracks on specimens having higher wear resistance.

- The Evans and Marshall lateral-crack chipping model based on fracture toughness and hardness values describes very well the wear rate of the investigated silicon nitride/silicon carbide composites. A slight deviation from this model was observed in the studied monolithic materials.

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