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A new slurry infiltration method to enhance the wear resistance of bulk graphite with development of reinforced graphitic composites including SiC or Si₃N₄ hard particles

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Abstract

Bulk graphite blocks are infiltrated by a Si slurry method to form composites of graphite containing SiC or Si₃N₄ reinforcements, in order to enhance the wear resistance of the graphitic structure. The microstructure of the SiC reinforcements includes nuclei grains and whiskers, while the microstructure of the Si₃N₄ reinforcements is a mixture of fine grains, grains of blade- and needle-like morphology. The wear rate of the SiC- and Si₃N₄-reinforced graphitic block is 77.7 and 42.8 μm³/Nmm, respectively, as measured using an unlubricated pin-on-disc test. These values are ~ 55% and 75% lower than the wear rate of the reference graphite (174 μm³/Nmm). The coefficient of friction of the composites is as low as the coefficient of friction of the reinforcement-free graphite, showing values of ~ 0.17.

Keywords

Infiltration; Composite graphite; SiC reinforcement; Si₃N₄ reinforcement; Wear

1. Introduction

Molded graphite stands out for its high thermal and electrical conductivity (159 W/mK and 7.6 μΩm at room temperature, respectively), refractory properties, thermal-shock resistance, chemical resistance, and good lubricious properties [1]. Graphite is used as a solid lubricant in many industrial applications, such as sealing rings, bearings, piston rings, as well as pump and valve parts [2]. However, graphite poses low hardness and as a result shows high wear under excessive tribological contacting [3], [4]. Thus the above tribological applications demand the improvement of the wear resistance of graphite without compromising its lubrication capabilities. This will lead to significant increase of the lifetime of the graphitic components used in tribological applications and reduced maintenance costs.

The increase of the wear resistance and hardness of bulk materials can be achieved by embedding harder particles (reinforcements) in the bulk than the material of the matrix [5], [6]. Hard SiC and Si₃N₄ reinforcement (~23 and 14 GPa, respectively [7], [8]) have already been used with success in carbon fibers, increasing their hardness and toughness [9], [10]. Similar effects are observed in other SiC and Si₃N₄ particle-reinforced composites with matrices of molde graphite, of bulk aluminum, copper and polymers [11], [12], [13], [14], [15], [16]. More specifically, reinforcing of molded polycrystalline graphite has been
reported using reactive melt Si infiltration with intention to improve the wear resistance of the graphitic matrix [11].

Reactive infiltration methods allow for fast and low-cost synthesis of ceramic materials, such as polymer infiltration and pyrolysis (PIP) [17], chemical vapor infiltration (CVI) [18], reactive melt infiltration (RMI) [19], reaction bonded (RB) [20], slurry infiltration [21], sol-gel infiltration [22], or combination of these [23]. The demands of metallurgical industry for mass production direct the fabrication of ceramic materials as refractories to more versatile and cost effective methods. Slurry infiltration is a simpler and more economical technique [24]. In comparison with the reactive melt Si infiltration, Si slurry infiltration requires lower temperature, is lower cost and the reinforcements formed do not contain unreactive Si [11]. In this method, powders of ceramics are dispersed in a solution, which is infiltrated into a porous block, which constitutes the matrix. Then, the infiltrated block is heated to generate the reaction between the ceramic powders and the matrix [25]. In the past, this technique has been used in order to introduce SiC and Si$_3$N$_4$ particles in carbon fibers [26].

The formation of SiC using graphite as source of C is favored by the high density of defects present in graphite [27]. Si, SiO and CO vapors are produced when Si and graphite powders are mixed and heated in coke bed at 1200 – 1400 °C, even at very low O concentrations in the gas flow of 0.001 % and form beta-SiC ($\beta$-SiC) nuclei and whiskers [28], [27]. Si$_3$N$_4$ can be formed by the direct reaction of Si with a N$_2$ gas at 1400 °C, in a process which is known as nitridation [28]. In this case, alpha-Si$_3$N$_4$ ($\alpha$-Si$_3$N$_4$) is formed by the reaction of molecular N$_2$ and gaseous Si and beta-Si$_3$N$_4$ ($\beta$-Si$_3$N$_4$) is produced by the reaction between atomic N and solid or liquid Si [28]. A dependency of the Si$_3$N$_4$ morphology with temperature, time of reaction, and gas flow rate is concluded [29].

Hard SiC and Si$_3$N$_4$ particles can be used to reinforce soft graphite (52.2 MPa [3]), forming reinforced ceramic composites. In this study, we propose for the first time, the fabrication of graphitic composites consisted of SiC or Si$_3$N$_4$ reinforcements by reactive infiltration. We describe the infiltration method as well as the kinetics and thermodynamics of the synthesis of reinforced graphitic matrices with SiC or Si$_3$N$_4$ particles. Moreover, we evaluate the wear resistance of reinforced graphite using an unlubricated pin-on-disk test, extracting as lower friction coefficient as in the graphite and wear rates which are ~ 55 % and 75 % lower than the wear rate of reinforcement-free graphite.

### 2. Materials and methods

Orthorhombic graphite specimens from a cathode block with dimensions of 12 mm x 12 mm x 3 mm (Bawtry Carbon International Ltd.) were grinded sequentially, using SiC papers with a grit size of 400, 800, 1200, and 2400 and polished using a diamond paste with a diameter of 1 μm. The polished samples were ultrasonically cleaned in ethanol for 10 minutes and dried at a temperature of 60 °C, using a hot plate in air. Figure 1 shows a flowchart of the procedure followed to synthesize composites of graphite containing SiC particles (g/SiC) and
composites of graphite containing Si$_3$N$_4$ particles (g/Si$_3$N$_4$). Si slurries were prepared using a mixture of Si powders (325 mesh, 99% trace metals basis, Sigma-Aldrich) in ethanol and a powder-to-ethanol ratio of 2:1. The mixture was stirred for 5 h. Then, 1.33 wt.% of dispersant (polyethyleneimine, Sigma-Aldrich) and 1.33 wt.% of binder (Butvar B-98, Sigma-Aldrich) were added in the Si slurry and was stirred for two days. After stirring, the graphite substrates were immersed in the slurry and placed in a vacuum chamber (Cast N’ Vac 1000, Buehler, USA), applying a low vacuum with a pressure of 85 kPa for 5 minutes. Then, the graphite substrates were removed from the slurry, placed again inside the vacuum chamber, and dried, applying a pressure of 85 kPa for 3 hours. The dry samples were heated at a temperature of 1400 °C for 2 hours in Ar atmosphere to form g/SiC and in N$_2$ atmosphere forming g/Si$_3$N$_4$, using a cyclic process with a heating-cooling rate of 400 °C/hour. After heating, the samples were grinded using SiC papers with a grit size of 400, 800, 1200, and 2400 and polished with diamond paste with a diameter of 1 μm in order to reveal their composite microstructure. The resulted specimens were cleaned ultrasonically in an ethanol bath for 10 minutes and dried at 60 °C in air, using a hot plate.

Figure 1: A flowchart showing the method followed for the synthesis of the graphitic composites. The graphite blocks were cut in a volume of 12 mm x 12 mm x 3 mm and subsequently were grinded and polished (1.1). A Si slurry was formed using Si powder, ethanol, a binder, and a dispersant (1.2.). The graphite blocks were infiltrated for 5 minutes (2) and dried for 3 hours in vacuum (3). Then, the infiltrated blocks were heated at 1400 °C for 2 hours in Ar or N$_2$ to form a graphitic composite containing SiC or Si$_3$N$_4$ reinforcements, respectively (4). After heating, the samples were grinded and polished in order to reveal their microstructure (5).

The open porosity and bulk density of the graphite as well as the composite samples were measured by immersion according to the ASTM C20 test procedure [30]. The phases of the materials were identified by x-ray diffraction (XRD) using a PANalytical X’Pert Pro comprising a Cu-K$_\alpha$ x-ray source at an energy of 40 keV and a current of 40 mA. The measurements were performed in a range of different tilting angles from 10 to 80°. A semi-quantitative analysis for the determination of the phases was carried out using the X’Pert HighScore software from PANalytical. The microstructure of the materials as well as the morphology of the wear tracks were observed using scanning electron microscopy (SEM, Q-250) in secondary electron (SE) mode and the composition of the composites was determined by energy dispersive x-ray spectroscopy (EDX), using an acceleration voltage of 20 kV, respectively. The images were studied using a qualitative digital analysis (QDIA), in ImageJ,
in order to estimate the total porosity of the reference graphite block and the composites formed after infiltration, the width of the worn surface, and the formed debris. The stability diagram of the Si-C-N-O system was constructed as a function of nitrogen and oxygen pressure following the steps described in the literature [31]. The Gibbs free energy, $\Delta G$, of the possible reactions were calculated using the software Thermo-calc (“Thermo-calc software”) at a temperature of 1400 °C and a pressure of 1 atm.

In order to measure the hardness (Hv) of the samples, we used a Vickers hardness tester-Armstrong Pedestal, utilizing a square-based pyramid diamond indenter with an included angle of 136°. A normal load of 10 kg was applied with an increasing rate of 3.4 kg/s and duration of 12 s at the surface of the samples. The values of the Vickers hardness, Hv, in MPa, were calculated, using the diagonal lengths of the indentation measured with an optical microscope [32].

The surface roughness, $S_a$, of the samples was measured on an area of 500 x 500 μm² using a laser scanning confocal microscope (Keyence VK-X200 series) and the data were treated using the software MultiFile Analyzer. For the calculation of the roughness of the composites, areas which included 50% graphite and 50% reinforcements on the surface were used.

A pin-on-disk rig (Pod-2, Teer Coatings Ltd) was used to measure the coefficient of friction (CoF) and the wear rate (Kd) of the materials. Different steel balls (graded 51200) with a diameter of 5 mm and a hardness of 7846 MPa (800 HV [33]) were used as pins for each wear test. The tangential force and the CoF were continuously recorded through a computer. The experiments were carried out using a normal load of 10 N, corresponding to a maximum contact pressure of 198.4 MPa, and a constant sliding speed of 4 cm/s, corresponding to a rotation speed of 400 rpm. The duration of the tests was 3600 s. The experiments were carried out at a temperature of 22 °C and a relative humidity of 50 %, without the use of liquid lubrication.

The width, a, of the worn surfaces was measured using an optical microscope. The depth of penetration, h, was calculated geometrically using eq. (1):

$$h = R - \sqrt{R^2 - (a/2)^2},$$ (1)

where R is the radius of the pin. The volume of the removed material, V, from the track was calculated geometrically using eq. (2):

$$V = 2\pi R_{Track} \cdot \left(1 - \frac{P}{100}\right) \cdot \left[R^2 \arccos \left(\frac{R-h}{R}\right) - (R-h)^2 \tan \left(\arccos \left(\frac{R-h}{R}\right)\right)\right]$$ (2)

where $R_{Track}$ is the radius of the wear track and P the porosity (%). Thus, an estimation of the wear rates (Kd) of the composites and the reference graphite sample were given by eq. (3),

$$K_d = \frac{V}{F \cdot s}$$ (3)

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where $F$ is the normal applied load and $s$ the sliding distance. After each test, the balls were ultrasonically cleaned with ethanol and weighed using an analytical balance.

3. Results

3.1 Structural and mechanical properties of the samples

The phase stability diagram of the system Si-C-O-N at 1400 °C as a function of O$_2$ and N$_2$ partial pressures ($P_{O_2}$ and $P_{N_2}$) is represented in Fig. 2. According to the stability phase diagram, under $P_{O_2}$ lower than $10^{-2.013}$ atm, the phase of SiC or Si$_3$N$_4$ is stable only for $P_{N_2} > 10^{0.017}$ atm or $P_{N_2} < 10^{0.017}$ atm.

Figure 2: Phase stability diagram of the system Si-C-O-N at 1400 °C as a function of the partial pressure of N$_2$ and O$_2$.

Figure 3(a) – 3(c) shows XRD patterns obtained from the reference graphite, the g/SiC, and the g/Si$_3$N$_4$ composite samples. The peaks assigned to graphite (black squares) appear in all samples, having the strongest intensity, suggesting that the graphite matrix is the major phase in these specimens. As indicated in Fig. 3(b), the composite containing SiC particles shows a beta phase ($\beta$-SiC) which corresponds to the SiC reinforcement (red circles). In the case of g/Si$_3$N$_4$ composite (Fig. 3(c)), the XRD pattern indicates the formation of a mixture of $\beta$-SiC, $\beta$-Si$_3$N$_4$ (blue triangles) and $\alpha$-Si$_3$N$_4$ (green diamonds) in the graphite matrix (black squares).
Figure 3: XRD patterns of the (a) graphite, (b) g/SiC, and (c) g/Si$_3$N$_4$ composite specimens. The peak positions of the graphite, the β-SiC, the α-Si$_3$N$_4$, and the β-Si$_3$N$_4$ phases are marked with black squares, red circles, blue triangles, and green diamonds, respectively. The inserts in Fig. 3(b) and 3(c) show a magnification of the 2θ angles between 30° and 80° for the better clarity of the peaks.

Table I shows the fraction of phases obtained from the XRD data in wt%.

Table I. The phase fractions of graphite and composites of graphite infiltrated by Si slurry and heated in Ar (g/SiC) and N$_2$ (g/Si$_3$N$_4$) extracted from XRD.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Graphite (wt.%)</th>
<th>β-SiC (wt.%)</th>
<th>α-Si$_3$N$_4$ (wt.%)</th>
<th>β-Si$_3$N$_4$ (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>g/SiC</td>
<td>89</td>
<td>11</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>g/Si$_3$N$_4$</td>
<td>79</td>
<td>2</td>
<td>11</td>
<td>8</td>
</tr>
</tbody>
</table>

The bulk density, open porosity, and average Vickers hardness of the original reference graphite block, the graphite infiltrated by SiC particles (g/SiC) and the graphite infiltrated by Si$_3$N$_4$ particles (g/Si$_3$N$_4$) are shown in Table II.

Table II. Bulk density, open porosity, and average Vickers hardness of graphite and composites infiltrated by Si slurry and heated in Ar (g/SiC) and N$_2$ atmosphere (g/Si$_3$N$_4$).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bulk Density (g/cm$^3$)</th>
<th>Open Porosity (%)</th>
<th>Average Vickers Hardness, H$_V$ (MPa)</th>
<th>Surface Roughness $S_a$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>1.60 ± 0.01</td>
<td>17.5 ± 0.4</td>
<td>58.6 ± 8.1</td>
<td>0.42 ± 0.02</td>
</tr>
<tr>
<td>g/SiC</td>
<td>1.69 ± 0.01</td>
<td>15.0 ± 0.6</td>
<td>144.1 ± 12.8</td>
<td>0.68 ± 0.03</td>
</tr>
<tr>
<td>g/Si$_3$N$_4$</td>
<td>1.70 ± 0.01</td>
<td>12.0 ± 0.7</td>
<td>171.6 ± 17.1</td>
<td>0.67 ± 0.04</td>
</tr>
</tbody>
</table>

The g/SiC and g/Si$_3$N$_4$ composites show similar bulk density of 1.69 g/cm$^3$ and 1.7 g/cm$^3$, respectively, which is slightly increased compared to the bulk density of graphite (1.60 g/cm$^3$), as measured using the Archimedes’ method [30]. The g/Si$_3$N$_4$ sample shows the
lowest open porosity of ~12% after infiltration, whereas the g/SiC composite has slightly increased open porosity of ~15%. The Hv of the reference graphite block is measured at a value of 59 MPa. The Hv values for the g/SiC and the g/Si₃N₄ composites are higher at 144 and 172 MPa, respectively. Although the composites are significantly harder than the reference graphite sample, the measured values of Hv across the surface of the composites show a wide spread, due to the presence of the random distribution of SiC or Si₃N₄ particles in the graphitic matrix, resulting in large values of standard deviation (Table II). The reference graphite block shows a roughness of 0.42 µm, while the composites show an increased roughness of 0.68 and 0.67 µm.

The surface morphology of the reference graphite, as well as, the g/SiC, and g/Si₃N₄ composites is shown in the SEM micrographs of Fig. 4(a)–4(c). The surface of the reference graphite is shown in Fig. 4(a) comprising grains and pores of different shapes and sizes. From Fig. 4(b) and 4(c), it is observed that the surfaces of the g/SiC and g/Si₃N₄ composites include dark and dispersed bright areas. The dark areas correspond to the graphite matrix, while regions with brighter contrast indicate the presence of SiC (Fig. 4(b)) or Si₃N₄ particles (Fig. 4(c)). The grains of the reinforcements in the g/SiC and g/Si₃N₄ composites have similar size and shape with the pores of the graphite reference sample. This means that most of the pores are filled with the reinforcements, while only pores with a length of less than 30 µm remain empty (insert of Fig. 4(b) and 4(c)). Also, a relatively homogeneous distribution of the reinforcements in the pores is observed throughout the volume of the pores (Fig. 4(b) and 4(c)). The composite containing Si₃N₄ reinforcement shows a higher concentration of particles and lower amount of pores than the g/SiC composite. Nevertheless, both composites show lower porosity than graphite, as indicated by Fig. 4. The morphology of pores varies from circular to acicular with sizes between ~5 µm and 1 mm for all samples. The total porosity of the samples is 26%, 17%, and 12% for the reference graphite, the g/SiC and the g/Si₃N₄ samples, respectively, as obtained from the SEM micrographs using QDIA calculations.

![SEM micrographs](image)

Figure 4: Plan-view SEM micrographs of the (a) reference graphite block, (b) g/SiC composite and (c) g/Si₃N₄ composite.

The morphology of the reinforcement of g/SiC and g/Si₃N₄ composite is assessed from Fig. 5(a) and 5(b), respectively. Figure 5 shows SEM plan views of the reinforcements.
in the g/SiC (Fig. 5(a)) and g/Si$_3$N$_4$ (Fig. 5(b)) composites, accompanied by EDX spectra acquired from different areas of the samples, corresponding to fine grains, blade-like and needle-like grains, as well as whiskers. In Fig. 5(a), spectra 1 and 2 correspond to whiskers and small grains of SiC, respectively, while in Fig. 5(b), spectra 1, 2, 3, 4, and 5 correspond to needle-like α-Si$_3$N$_4$, α-Si$_3$N$_4$ fine grains, blade-like β-Si$_3$N$_4$, β-SiC whiskers, and β-SiC grains, respectively. The plan view SEM micrograph of Fig. 5(a) suggests that the g/SiC composite is formed from stacked aggregates of SiC-nuclei (spectrum 2), including a small number of thin whiskers (spectrum 1), distributed around the aggregates. Figure 5(b) reveals that the g/Si$_3$N$_4$ reinforcement presents a mixture of blade-like (spectrum 3) and fine grains (spectrum 2), needle-like structures (spectrum 1) and whiskers (spectrum 4). This type of microstructure has been observed in the past for SiC and Si$_3$N$_4$ produced by mixture of graphite and Si powders and heating in the coke bed at 1200 – 1400 °C and by SiC and Si powders heated in a flame-isolation nitrition shuttle kiln at 1200 - 1450 °C in nitrogen [28], [27], [34], [35]. The grains with blade morphology appear to be the largest with a diameter of ~ 10 μm. The fine grains with a size of less than 0.5 μm are located around these blade-like grains (Fig. 5(b)). The needle-like grains and the whiskers appear to be surrounded by the blade-like and fine grains (Fig. 5(b)). In all EDX spectra of Fig. 5, the peak at an energy of ~ 0-0.1 keV corresponds to noise from the detector. The peak intensities differ possibly due to the fact that the spectra were obtained from areas of different porosity affecting it.
Figure 5: SEM micrographs, acquired in secondary electron mode, accompanied by EDX-spectra obtained from within the (a) g/SiC and (b) g/Si$_3$N$_4$ reinforcements of the composites. Fine grains, blade-like, needle-like features, and whiskers are observed.

3.2 Friction and wear

The CoF of the graphite, g/SiC, and g/Si$_3$N$_4$ samples, measured using a load of 10 N at a sliding speed of 0.04 m/s with an unlubricated pin-on-disk test, is shown as a function of time for a duration of 3600 s in Fig. 6(a). The CoF of the graphite and the composite samples ranges between ~ 0.15 and 0.20, with an average value of 0.17 as is shown in Fig. 6(b). The normalized wear rate ($K_D$) of all samples is calculated using eq. (3) and is shown in Fig. 6(b).
The g/SiC and g/Si$_3$N$_4$ composites exhibit wear rates that are 55% (77.7 μm$^3$/Nmm) and 75% (42.8 μm$^3$/Nmm) lower than the wear rate of the reference graphite sample (174.0 μm$^3$/Nmm).

Figure 6: (a) Coefficient of friction (CoF) as a function of time and (b) mean coefficient of friction and normalized wear rate ($K_D$) for the reference graphite block, the g/SiC, and the g/Si$_3$N$_4$ composite sample, after a pin-on-disk test using a normal load of 10 N and a sliding speed of 4 cm/s.

4. Discussion

4.1 Synthesis processes, structure, and mechanical properties of the composites.

The synthesis processes of graphite composites containing SiC or Si$_3$N$_4$ reinforcements in Ar or N$_2$ flow, respectively, include the penetration of the Si slurry in the pores of the graphitic block. Here, the formed Si-containing species infiltrate in the pores and are deposited on their surface. Eventually, they coalesce and create solid deposits, filling the voids, as can be seen in the SEM micrographs of Fig. 4. Two main factors assist the successful infiltration and the homogeneous distribution of the reinforcements in the pores of the graphitic blocks: (a) the use of dispersant in the Si slurry instead of the use of powder and (b) the application of a vacuum during the infiltration. The use of ceramic powders for filling the voids of porous materials is a well-known method of reinforcing composites, accompanied however by agglomeration of the powder [36]. Using a dispersant in the slurry instead, yields a homogeneous distribution of the Si powders in the solution. Hence, the agglomeration observed in the case of powders is avoided and it improves the penetration. The application of a vacuum during the infiltration removes the residual air from the pores of the graphite block and thus, the penetration of the slurry into the pores of graphite is facilitated. The successful infiltration is verified by the reduced total porosity of 17% and 12% for the g/SiC and g/Si$_3$N$_4$ composites, respectively, after processing, as indicated in Table II.

According to the phase diagram of Fig. 2, during the heat treatment at 1400 °C, gaseous phases of SiO and CO are formed due to oxidation of Si(s) and C(s), respectively, (eq.(4)-(5)) [27]:

4. Discussion
\[ 2\text{Si}(s) + O_2(g) \rightarrow 2\text{SiO}(g); \ \Delta G_1 (1400 \ ^\circ \text{C}) \sim -479 \text{kJ/mol} \quad (4), \]
\[ 2\text{C}(s) + O_2(g) \rightarrow 2\text{CO}(g); \ \Delta G_2 (1400 \ ^\circ \text{C}) \sim -517 \text{kJ/mol} \quad (5). \]

Moreover, CO(g) facilitates the formation of Si(g) and SiO(g) which are produced following the reactions of eq.(6) and eq.(7)) (Fig. 2) [37], [38]:

\[ \text{Si}(s) \rightarrow \text{Si}(g) \quad (6), \]
\[ \text{Si}(s) + \text{CO}(g) \rightarrow \text{SiO}(g) + \text{C}(s) \quad (7). \]

Here, the O\textsubscript{2} is consumed during the formation of CO and SiO gases. Also, it is established that the partial pressure of SiO is higher than of Si in the Si-O-C and Si-O-C-N thermodynamic systems (Fig. 2) [27]. The formation of SiC and Si\textsubscript{3}N\textsubscript{4} particles is better illustrated in Fig. 7(a) – 7(d) and Fig. 7(e) – 7(h) and occurs in an atmosphere which contains SiO-Si-CO (Fig. 7(a)) and SiO-Si-CO-N\textsubscript{2} (Fig. 7(e)), respectively.

According to our XRD and SEM results, the g/SiC composite contains only one phase, this of β-SiC (Fig. 3(b)), presenting two allotropic structures; nuclei and whiskers (Fig. 5). This suggests that two different reaction mechanisms are involved for the formation of β-SiC inclusion. Fig. 7(a) and 7(b) show the schematic illustration of the gaseous (Si(g), SiO(g), CO(g)) and solid phases (Si(s) and C(s)) of the substances partaking in the reactions during the formation process of the g/SiC composite. The schematic illustration of Fig. 7(a) – 7(d), describes the steps for the formations of the β-SiC nuclei and whiskers. It is safe to assume that Si(g) and SiO(g) are diffused in the graphite matrix at a temperature of 1400 °C and react with C dangling bonds of the matrix to form Si-C and Si-O-C bonds (Fig. 7(b)), according to the reaction of eq. (8) [39]:

\[ \text{Si}(s) + \text{SiO}(g) + 3\text{C}(s) \rightarrow 2\text{SiC}(s) + \text{CO}(g); \ \Delta G_2 (1400 \ ^\circ \text{C}) \sim -140 \text{kJ/mol} \quad (8). \]

The direct formation of SiC according to the reaction of eq. (9) [39]:

\[ \text{Si}(s) + \text{C}(s) \rightarrow \text{SiC}(s); \ \Delta G_3 (1400 \ ^\circ \text{C}) \sim -60 \text{kJ/mol} \quad (9), \]

cannot be entirely excluded, despite the fact that the \( \Delta G \) of the reaction of eq. (8) is \( \sim 45\% \) lower than the \( \Delta G \) of the reaction of (eq. 9). However, this implies that the reaction described by eq. (8) is the dominant mechanism for the formation of the β-SiC nuclei in our composite.
Figure 7: (a) Schematic illustration of the microstructures of Si(s) and C(s) in a gaseous atmosphere of Si(g), SiO(g) and CO(g) formed by Si vaporization and, Si and C oxidation. (b) Formation of β-SiC nuclei and (c) β-SiC whiskers during the reactions described by eq.(4) – eq.(9). (d) The β-SiC particles embedded in the g/SiC composite. (e) Schematic illustration of the microstructures of Si(s) and C(s) in a gaseous atmosphere of Si(g), SiO(g), CO(g) and N$_2$(g) formed by Si vaporization and, Si and C oxidation. (f) Formation of blade-like grains of β-Si$_3$N$_4$, fine grains of α-Si$_3$N$_4$, and aggregates of β-SiC in the g/Si$_3$N$_4$ composite. (g) Formation of α-Si$_3$N$_4$ needle-like grains and β-SiC whisker in the g/Si$_3$N$_4$ composite, and (h) the different α-Si$_3$N$_4$, β-Si$_3$N$_4$, β-SiC particles embedded in the g/Si$_3$N$_4$ composite.
The \( \beta \)-SiC whiskers are formed according to the following reactions, as described by Li et al. in ref. [27] (eq. (10) and eq. (11)) (Fig. 7(c)) [40], [41]:

\[
2Si(g) + 2CO(g) \rightarrow 2SiC(s) + O_2(g); \quad (10),
\]
\[
SiO(g) + 3CO(g) \rightarrow SiC(s) + 2CO_2(g); \quad (11).
\]

During the heat treatment at a temperature of 1400 °C, the carbon atoms of graphite are thermally oxidized forming broken C bonds, which favor the production of both SiC nuclei and whiskers (Fig. 7(c) and 7(d)) [27]. Thus, the reinforcement in the g/SiC is formed by \( \beta \)-SiC with the form of nuclei-like grains surrounded by whiskers structure (Fig. 7(d)).

In the case of g/Si\(_3\)N\(_4\) composite, the presence of three different phases, i.e., \( \alpha \)-Si\(_3\)N\(_4\), \( \beta \)-Si\(_3\)N\(_4\), and \( \beta \)-SiC, as well as, the variety of features that are observed in the morphology (Fig. 5(b) and Fig. 7(e) – 7(h)), suggest that several reactions occur during the infiltration process. Fig. 7(e) and 7(f) show the schematic illustration of the gaseous (Si(g), SiO(g), CO(g), and N\(_2\)(g)) and solid phases (Si(s) and C(s)) of the substances partaking in the reactions during the formation process of the g/Si\(_3\)N\(_4\) composite. The formation of g/Si\(_3\)N\(_4\) composite follows three steps. In the first step, N\(_2\)(g) reacts directly with Si(s) to form \( \beta \)-Si\(_3\)N\(_4\) with blade-like morphology according to the following reaction (eq. (12)) (Fig. 7(f-1)) [28]:

\[
3Si(s) + 2N_2(g) \rightarrow Si_3N_4(s); \quad \Delta G_4(1400 ^\circ C) \sim -195 \text{ kJ/mol} \quad (12),
\]

In the second step, following the reaction of eq. (12) the formation of \( \alpha \)-Si\(_3\)N\(_4\) with fine grain morphology originates from the reaction between Si(g) and N\(_2\)(g) [42] (insert 2 in Fig. 7 (f)). Here, nitride nuclei are formed, while Si(g) diffuses on the nuclei surface and condensates, leaving a zone occupied by a low N\(_2\)(g) content. Consequently, the pores around the \( \beta \)-Si\(_3\)N\(_4\) grains are filled with N\(_2\), which reacts with Si(g) or SiO(g), forming \( \alpha \)-Si\(_3\)N\(_4\) [42], [43], [29]. The formation of \( \beta \)-SiC aggregates (Fig. 7(f)), as observed in the g/SiC composite following the reaction described in eq. (8) cannot be excluded. However, the XRD results display very low intensity of the peaks corresponding to \( \beta \)-SiC, suggesting that the amount of SiC in the g/Si\(_3\)N\(_4\) composite is low (Fig. 3(c)), due to the fact that the \( \Delta G \) associated with the \( \beta \)-Si\(_3\)N\(_4\) (cf. eq. (12)) is \( \sim \) 55 kJ/mol lower than the \( \Delta G \) of \( \beta \)-SiC (cf. eq. (8)). Moreover, the simultaneous formation of \( \beta \)-SiC with a morphology of fine grains, similar to the morphology of fine grains of \( \alpha \)-Si\(_3\)N\(_4\), is not excluded either and thus, the \( \beta \)-SiC aggregates cannot be resolved with certainty.

The third step includes the formation of few whiskers containing \( \beta \)-SiC, following the reactions described in eq. (10) and eq. (11). The low concentration of SiC whiskers observed in the pores of the g/Si\(_3\)N\(_4\) (cf. Fig. 5(b)) suggests that these reactions are completed by consuming a relatively small amount of residual Si, SiO, and CO gases. The formation of \( \alpha \)-Si\(_3\)N\(_4\) with a needle-like morphology follows the reactions of eq. (13) and eq. (14) (Fig 7(g)) [43], [28],

\[
3SiO(g) + 2N_2(g) \rightarrow Si_3N_4(s) + \frac{3}{2} O_2(g); \quad (13),
\]
Thus, the blade-like grains of $\beta$-Si$_3$N$_4$ particles are surrounded by fine grains of $\alpha$-Si$_3$N$_4$ and aggregates of $\beta$-SiC; and these are surrounded by $\alpha$-Si$_3$N$_4$ needle-like grains and $\beta$-SiC whiskers (Fig. 7(h)) forming an onion-like structure (Fig. 7(h)).

The significant increase of the hardness of the composites compared to the reference graphite sample can be attributed to the increased density and decreased porosity of the composites after the infiltration (Table II) [44]. This is a result of the deposition of hard SiC and Si$_3$N$_4$ particles in the pores of the soft graphitic matrix, contributing to the measured hardness values, which is confirmed by the relatively high errors of the measurements. Here, the Si$_3$N$_4$ particles contribute to the increase of the toughness of graphite to a higher degree than the SiC particles due to the higher hardness of 10 GPa of the Si$_3$N$_4$ compared to the hardness of 7 GPa of the SiC [45], [46]. Moreover, it can be inferred that both increased density and decreased porosity contribute to the improvement of the mechanical properties of the graphite sample when the reinforcements are added in the pores. However, the density of g/SiC and g/Si$_3$N$_4$ composites is similar with values of 1.69 and 1.70 g/cm$^3$ (Table II) and the difference between these composites can be associated to the lower porosity of g/Si$_3$N$_4$ (12%) against the porosity of g/SiC composite (15%) (cf. Table II).

4.2 Wear and friction of composites.

The wear rate of the samples shows a dependency on the hardness of the samples (cf. Fig. 6(b) and Table I), which agrees with Archard’s law of wear [44], [47]. The harder g/Si$_3$N$_4$ composite is the more wear resilient among all tested samples and the reference graphite sample exhibits the highest wear rate and also the lowest hardness (cf. Fig. 6(b) and Table II). This dependency of the wear rate on the hardness of composite materials has been investigated also by Lim et al. and our composites follow a similar trend [34].

A notable observation is that the reference graphite sample and the two reinforced composite samples exhibit very similar coefficient of friction. This implies that the friction mechanism is governed by the main body of the composite, which is the soft graphitic matrix in all samples. This is an important observation since the reinforcements achieve much higher wear resistance by the introduction of harder particles in their structure, yet retaining the friction coefficient value at the same level as graphite, which is considered as solid lubricant (Fig. 6(a)). In all cases, the nature and origin of the wear debris do not seem to influence the friction mechanism. Here, the most possible scenario is that the higher volume of the wear debris was generated and pushed at the sides of the wear tracks during run-in, contributing least to the friction mechanisms. The amount of the remaining debris in the wear tracks though is not adequate to affect the values of friction coefficient. Thus, we assume that the values of the coefficient of friction are controlled by the graphitic nature of the surface and by possible passivation of the surface with H. Here, C dangling bonds are created after the first pass of the pin from the surface, which bond to H before the next cycles (~ 50% humidity during tests) [48]. This hydrogenated graphitic surface contributes greatly to the modulation of the values of friction [49]. This is supported by the very similar friction values of all tested samples (Fig. 6(a)).
The pronounced fluctuations in the values of friction coefficient (Fig. 6(a)) can be related to the continuous production and loss of wear debris at the contact. During the production of wear debris, the CoF increases and during the debris loss, the CoF decreases again. This operation is verified by the cyclic trend observed in CoF, where the fluctuations in the values occur every 250-300 s (Fig. 6(a)). This trend is due to the soft and lubricious nature of the graphite matrix, which allows for effortless creation of the soft debris [50].

5. Conclusion
SiC or Si₃N₄ particles were incorporated in porous graphite blocks using a Si slurry infiltration method and carbonization or nitration at 1400 °C for 2h, respectively. SiC and Si₃N₄ reinforcing graphite composites show wear rate of 55% and 75 %, respectively, significantly lower than the wear rate of graphite. Here, the hardness increase of 146% in the SiC-reinforced graphite composite and 193% in the Si₃N₄-reinforced graphite composite, contributes significantly to the enhancement of the wear performance. The decreased porosity (14-31% lower porosity than graphite) and increased density (6% higher density than graphite) also contribute to wear reduction, but to a lesser extent. Furthermore, the Si₃N₄ reinforcements show the best performance, offering the highest wear resistance in the study (wear rate of 42.8 μm³/Nmm), without impairing the lubricious properties of graphite.

As a result, the enhanced tribological operation of the composites is due to two different factors:

(a) The wear resistance of the composites is governed by the hard SiC and Si₃N₄ particles in the morphology of bulk graphite and in this case no contributions from the soft matrix are involved.

(b) The graphite matrix of the composites contributes mostly to the lubrication of the contacts during testing and to the friction evolution with debris creation and circulation in the contact, resulting in the highly desirable low values of the coefficient of friction (0.17).

Hence, our method of infiltration, which incorporates SiC and Si₃N₄ particles in the porosity of bulk graphite is proven very effective for increasing its wear resistance through alterations in its morphology, leading to longer lifetimes. These properties are very useful for applications, such as sealing rings, bearings, and piston rings which can use protected graphitic-based films and coatings, or components, such as electrodes, extrusion guides, crucibles, and molds.

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