Tribological performance under dry sliding conditions of graphene/silicon carbide composites

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Institutions: Spanish National Research Council

Published on: 01 Feb 2016 - Journal of The European Ceramic Society (Elsevier)

Topics: Graphene oxide paper, Graphene, Silicon carbide, Silicon nitride and Tribology

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Tribological performance under dry sliding conditions of graphene/silicon carbide composites

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Abstract

The role played by graphene in the friction and wear behaviour of graphene/silicon carbide (SiC) composites, tested under dry sliding conditions and using silicon nitride balls as counterbodies, is investigated as a function of the graphene nanoplatelets (GNPs) content and the graphene source. GNPs composites show an enhanced wear resistance as compared to monolithic SiC, with maximum improvements of ~ 70% for the material containing up to 20 vol.% of GNPs; whereas the friction performance depends on the sliding distance and GNPs content. The analysis of the wear debris by micro-Raman spectroscopy evidences that the tribological behaviour of the GNPs/SiC materials is linked to the formation of an adhered lubricating and protecting tribofilm. Multilayered graphene fillers participate more actively in the protecting tribofilm than other graphene sources such as reduced graphene oxide or in-situ grown graphene flakes.

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Keywords: graphene; wear; friction; ceramic matrix composites; silicon carbide.

1. Introduction

Silicon carbide (SiC) ceramics are non-oxide structural materials with remarkable tribological, thermal and mechanical properties, as well as good oxidation resistance [1-2]. Based on those properties, SiC is used in many technological applications under demanding working conditions, such as bearings, valves or cutting tools, where friction and wear processes predominate. At present, considerable efforts have been done to improve the tribological performance of SiC ceramics, especially through the microstructural design of the material. In this way, Guiberteau’s group have carried out numerous studies on this topic, reporting clear improvements on the SiC wear resistance by means of either the development of in situ toughened ceramics by the growth of elongated α-SiC grains [3,4] or by reducing the amount of the intergranular phase [4,5] or the hardening of this phase [6].

On the other hand, C/C-SiC composites obtained by silicon infiltration of a carbon fibre preform appear as promising candidates for advanced friction systems [7]. Carbon short fibre and nanofibers reinforcements also have proved to enhance the tribological behaviour of SiC. In this way, Tang et al. [8] found that the friction coefficient and the wear rate decreased with increasing short carbon fibres contents up to 42 vol.% due to the solid lubrication effect and the fracture toughness enhancement of the composite both promoted by the fibres. Similar results were reported by Borrell et
al. [9] adding up to 50 vol.% of carbon nanofibers, despite the lack of the densification in the composites.

Recently, graphene, the 2-dimensional carbon allotrope with outstanding electronic and physicochemical properties [10], has attracted great interest as self-lubricating solid or as additive for lubricating oils [11,12]. There are numerous works on tribology of graphene/polymer and graphene/metal composites (see ref. 13 and 14 for a review), but considerably less work can be found on graphene/ceramic materials. At the time of writing, silicon nitride [15-17], alumina [18,19], silica [20] and zirconia [21] ceramics containing graphene have been tribologically characterized. Some of the present authors [15] observed that the addition of 3 wt.% of graphene nanoplatelets (GNPs) to a silicon nitride (Si$_3$N$_4$) matrix reduced the friction and improved the wear resistance up to 56% under isooctane lubricated conditions due to the exfoliation of the nanoplatelets and the creation of an adherent protective tribofilm. Hvizdos et al. [16] reported a 60% improvement in the wear performance under dry sliding conditions for 3 wt.% GNPs/Si$_3$N$_4$ composites, although GNPs did not decrease the friction coefficient. Graphene/alumina (Al$_2$O$_3$) composites [18-19] also showed remarkable improvements (up to one order of magnitude) on the wear resistance when compared to the monolithic alumina, jointly with slight decreases on friction. This tribological performance was related to the development of a hard and lubricating graphene layer on the Al$_2$O$_3$ grains that shielded the specimen surface from wear environments and prevented the cracking of these ceramics. Porwal et al. [20] found that the addition of 5 vol.% of GNPs to a silica (SiO$_2$) matrix improved the wear resistance up to 8.5 times. Finally, plasma
sprayed 1 wt.% GNPs/zirconia (ZrO$_2$) coatings developed by Li et al. [21] reduced the wear rate (50%) and the friction (29%) of the monolithic ceramics.

To the best of our knowledge, the tribological properties of graphene/SiC composites have not been reported hitherto. Therefore, the aim of this work was to study the friction and wear behaviour of graphene/SiC composites under dry sliding conditions. For that purpose, we investigated the role of graphene content as well as the type of the graphene source on the tribological properties. GNPs, graphene oxide (GO) that was further reduced to graphene (rGO) during the spark plasma sintering (SPS) of the composite and, finally, graphene grown in-situ within the SiC ceramics using SPS were selected as graphene sources.

2. Experimental procedure

2.1. Material fabrication. Commercial GNPs (type N006, Angstron Materials Inc., USA with nominal thickness and x-y dimensions of 10-20 nm and 14 µm, respectively) and GO platelets prepared in-house from graphite flakes by the modified Hummers method [22] (< 5 nm thickness, < 5 µm x-y dimensions) were selected as graphene fillers. The different composites were processed as detailed below. The fillers were first dispersed in alcohol, ethanol for GOs and isopropyl alcohol for GNPs, and sonicated for 1 h in an ultrasonic bath. Meanwhile, the ceramic powder composition, formed by 93 wt.% of β-SiC powders (BF-17A, H.C. Starck, Germany) plus 5 wt.% of Y$_2$O$_3$ (Grade C, H.C. Starck, Germany) and 2 wt.% of Al$_2$O$_3$ (SM8, Baikowski Chimie, France), both used as sintering additives, was attrition milled in alcohol (ethanol or isopropyl alcohol
depending on the further filler addition) using alumina grinding media for 2 h. The ceramic slurry and the graphene-based dispersion were blended together for 1 h using a paddle blade mixer in conjunction with a sonication bath. Solvent was evaporated in a rotary-evaporator at 93 °C, and the powder mixture was dried at 120 °C and sieved through a 63 μm mesh. GNPs/SiC compositions containing 0 (monolithic), 5, 10 and 20 vol.% of GNPs were prepared, as well as 5 vol.% of GOs/SiC composition. Disc specimens of 20 mm × 3 mm were SPSed (SPS, Dr. Sinter, SPS-510CE, Japan) at 1800 °C for 5 min, applying a uniaxial pressure of 50 MPa during the heating cycle, and using a vacuum atmosphere of ~6 Pa.

2.2. Mechanical properties. The elastic modulus (E) and hardness (H) at room-temperature were measured by depth sensing indentation (Zwick/Roell, Zhu 2.5, Germany) using a Vickers diamond indentation force of 9.8 N. The load and the penetration depth were continuously and simultaneously recorded during each test. E was obtained from the unloading branch of the curve and corrected from the frame compliance of the instrumented indenter. H was calculated from the peak load and the indentation area measured on the optical microscope. At least five well-defined indentations were considered on each ceramic. Flexural strength (σf) was determined by three point bending tests using small bars of 15.0 mm x 2.0 mm x 2.5 mm, an outer span of 8 mm, and a displacement rate of 0.5 mm·min⁻¹. Fracture toughness (KIC) was measured by the surface crack in flexure (SCF) method Knoop indenting at 100 N the centre of the bars (similar dimensions as for σf) in their tensile surfaces and, then, performing three point bending tests with the same outer span and displacement rate as for σf. At least four bars were tested per material and mechanical parameter.
2.3. Tribological properties. Dry sliding tests were performed with a UMT-3 tribometer (Bruker Nano Inc, formerly CETR, USA) using a linear reciprocating ball-on-plate configuration. Commercial Si₃N₄ balls (10.3 mm diameter, SN101C, Saint Gobain, France) were used as counterbodies. The composite plates were polished to a surface roughness (Ra) below 0.02 µm, and both counterbodies were ultrasonically cleaned (2 min in acetone plus 2 min in ethanol) and dried with air. The tests were carried out at 25 ± 3 °C and < 20% of relative humidity with the following parameters: stroke length of 2.5 mm, frequency of 20 Hz (0.1 m·s⁻¹), sliding distance of 360 m, and a normal applied load of 5 N that corresponded to Hertzian pressures of 0.7-1.1 GPa at the very beginning of the tests. It is important to remark that the tested surface was always that perpendicular to the SPS pressing axis. At least three tests were carried out for each material, and data represent their average. Friction coefficient, µ, was continuously registered during the tests, estimating the steady-state (µ_{ss}) value within the 200-360 m interval. The wear volume of the plates (Wᵥ) was calculated as follows:

\[ Wᵥ = Δx · A + \frac{d^2}{8} W_l \]  

considering the sum of two terms: the first one represents the main Wᵥ according to the ASTM G133 standard [23], which recommends measuring three 2D profiles for each track to determine the cross section area beneath the 2D curves (A), and then multiply that values by the nominal stroke (Δx). The second term is a correction factor that takes into account the two edges of the wear tracks [24]. This term is assessed considering the width (d) and depth (W_l) of each wear track. The 2D track profiles were recorded with a stylus profiler (Dektak XT, Bruker, Germany). The wear rate of the plates (W_R) was then calculated according to the following equation:
\[ W_r = \frac{W_v}{sF} \]  

where \( F \) is the normal force and \( s \) the sliding distance. The wear volume for the balls was not calculated considering that the ASTM G133 standard recommends to provide this parameter only if 3D measurement methods are employed. Worn surfaces of the plates were characterized by field emission scanning electron microscopy (FESEM, S-4700, Hitachi, Japan) and micro-Raman spectroscopy (Alpha300 WITec GmbH, Germany) using the 532 nm laser wavelength excitation. Raman maps of 25 x 25 pixels, recording one spectrum per pixel and using 1 s of acquisition time, were acquired on 50 x 50 \( \mu \text{m}^2 \) scanned areas.

3. Results and discussion

All materials exhibited nearly full densification, in particular, 3.24 g·cm\(^{-3}\) for SiC (99.9% of the theoretical value, \( \rho_{\text{th}} \)), 3.19 and 3.13 g·cm\(^{-3}\) for SiC composites containing 5 and 10 vol.% of graphene fillers (\( \rho_{\text{th}} = 99.9\% \)), respectively, and 3.03 g·cm\(^{-3}\) for 20 GNPs composite (\( \rho_{\text{th}} = 99.0\% \)). Besides, they contained \( \beta \)-SiC (3C polytype) as main crystalline phase, with a low intense X-ray diffraction signal associated to \( \alpha \)-SiC phase (6H polytype) and \( \text{YAlO}_3 \) (YAP) or \( \text{Y}_3\text{Al}_5\text{O}_{12} \) (YAG), the latter compounds formed by the reaction between the sintering additives [25,26]. Moreover, micro-Raman spectroscopy evidenced that GNPs remained undamaged after the SPS process, while GOs were effective reduced to graphene (rGOs) during the SPS process [27]. Both graphene flakes (rGOs and GNPs) were homogenously distributed within the matrix, as Figure 1 shows through the analysis of the fracture surfaces of the
different materials. These flakes appeared preferentially orientated with their ab plane perpendicular to the SPS pressing axis. On the other hand, the monolithic SiC contains ~3 vol.% of graphene multilayers, which were grown in-situ at the SiC grain boundaries during the SPS process, as it was reported by some of the authors in a previous work [28]. These multilayers are formed by bilayers, trilayers, and up to tenths of layers, being the latter observable by FESEM (as pointed by arrows in Fig. 1a and the inset shows). In addition, matrix grain size and aspect ratio are very similar (0.6-0.7 µm and 1.4, respectively) for the different materials [26].

Figure 1. FESEM micrographs corresponding to the different tested materials: a) monolithic SiC, and composites containing (in vol.%): b) 5 rGOs, c) 5 GNPs, d) 10 GNPs, and e) 20 GNPs. The arrows in a) point the location of graphene multilayers in-situ formed and the inset corresponds to a high magnification image of one of those multilayers.
Table 1 collects the mechanical properties of the different materials. The monolithic SiC exhibited higher E and H values than the composites, a trend previously observed in other graphene-based ceramic composites [29-31] that is related to the sliding of the graphene layers within the flakes under shear stresses, helped by the waviness of the platelets following the boundaries of the matrix grains (Fig. 1). The more pronounced reduction in E and H for rGOs composites was expected considering the lower E value of rGO sheets as well as its higher waviness when compared to GNPs [32]. Interestingly, $K_{IC}$ considerably increased for any graphene-based composite, independently of the GNPs content or type of graphene source, when compared to SiC [26]. In this way, GNPs composites exhibited a maximum increment in $K_{IC}$ of 86% (10 GNPs composite) with respect to the monolithics; whereas rGOs induced an outstanding toughness enhancement (162%) with a $K_{IC}$ value of $8.3 \pm 0.7 \text{ MPa} \cdot \text{m}^{1/2}$ ($3.2 \pm 0.4 \text{ MPa} \cdot \text{m}^{1/2}$ for SiC). This behaviour can be explained by the development of crack shielding mechanisms associated to the graphene flakes [29]. Finally, the flexure strength increased up to 70% as compared to the monolithic SiC, which is linked to the toughness enhancement in the composites.

Table 1. Mechanical properties of the different materials: Elastic modulus (E), hardness (H), fracture toughness ($K_{IC}$) and flexure strength ($\sigma_f$) [26].

<table>
<thead>
<tr>
<th>Material</th>
<th>E (GPa)</th>
<th>H (GPa)</th>
<th>$K_{IC}$ (MPa$\cdot$m$^{1/2}$)</th>
<th>$\sigma_f$ (MPa)</th>
</tr>
</thead>
</table>

Figure 2 collects the friction response of the different materials. At the first instants of the tests, during the running-in period (Fig. 2b), $\mu$ decreased with the graphene content up to 66% for 20 vol.% of GNPs. While the friction evolution with the sliding distance was quite constant for all composites (Figs. 2a,b), friction rapidly diminished in the case of the monolithic SiC during the first 60 m until reaching the steady-state regime with a $\mu_{ss}$ value of 0.78 (Fig. 2c). Within the steady-state region, the reduction in friction due to the increasing amount of GNPs fillers considerably diminished -just 6-10% for contents up to 10 vol.%- and even increased (23%) for the 20 vol.% GNPs composite (Fig. 2c), as it also happens for rGOs composite.

It is well known that the surface roughness affects friction at the first instants of the tests. In this way, as a general rule, initial rougher surfaces would lead to lower $\mu$ values (as the real contact area is smaller) and reach the steady-state regime at larger sliding distances [33-34]. In the present work, despite the surface polishing process was equal for all materials, slightly different $R_a$ values were obtained: 5 nm (SiC), 20 nm (5 rGOs), 10 nm (5 GNPs), 9 nm (10 GNPs), and 13 nm (20 GNPs). It is interesting to
remark that the observed differences in the friction response cannot be explained by the roughness as, for example, the roughest (rGOs) and the smoothest (SiC) materials did not lead to the lowest and highest friction, respectively, as predicted. In addition, the steady-state regime was reached at a longest distance for the smooth SiC plates. Moreover, matrix grain size and aspect ratio are very similar (0.6-0.7 µm and 1.4, respectively) for the different materials [26]. Therefore, it can be inferred that the friction response is directly linked to the graphene additions with respect to the reference material during the running-in period, GNPs leading to an enhanced friction performance as compared to rGOs. When the whole test is considered, graphene led just to a slight steady-state friction reduction of 6-10% for 10 GNPs and 5 GNPs composites; whereas ρss increased for 5 rGOs and 20 GNPs materials. This process is controlled by the formation of a third body between mated surfaces.
Figure 2. Friction coefficient evolution ($\mu$) for the different materials showing: a) the whole reciprocating sliding tests and b) the running-in period. The average steady-state friction coefficient ($\mu_{ss}$) values are plotted in (c).

In contrast, the wear resistance of the plates significantly enhanced with the graphene content, as shown by the 2D profiles of representative wear tracks for each tested composition (Fig. 3a) and $W_V$ values (Fig. 3b). Actually, $W_V$ decreased from 0.11 mm$^3$ for SiC to 0.03 mm$^3$ for the 20 GNPs composite, which corresponds to a 70% better wear performance for the latter material. A similar trend was observed for $W_R$ behaviour (Fig. 3c), diminishing from $1.5 \times 10^{-3}$ (monolithic SiC) to $0.5 \times 10^{-3}$ mm$^3$·N$^{-1}$·m$^{-1}$ (20 GNPs composite). Slight differences in the wear response of composites as a function of the graphene source for the same filler content (5 vol.%) were observed, in particular, rGOs composites led to a 9% lower $W_V$ as compared to the equivalent GNPs composites.
Figure 3. a) 2D profiles of representative wear tracks, b) wear volume ($W_V$), and c) wear rate ($W_R$) of the different materials.

FESEM observations of the wear scars of the plates (Fig. 4) enable to establish that severe wear process occurred in all the materials with different wear processes. For the monolithic SiC (Fig. 4a), a smooth surface with some abrasion grooves and a revealed grain microstructure (inset in Fig. 4a) can be observed. For the composites (Figs. 4b-e), in addition to the abrasive grooves, some cavities both empty and filled by debris are observed, probably produced by material spalling due to the nucleation and subsequent growth of microcracks because of the cyclic surface and internal stresses developed during the wear tests. Moreover, a tribofilm is formed as the GNPs content
increased, but not for the monolithic SiC. These observations are in good agreement with the $W_R$ values attained, all of them in the order of $10^{-3}\text{ mm}^3\cdot\text{N}^{-1}\cdot\text{m}^{-1}$ (Fig. 3c).

Figure 4. FESEM micrographs of the tested surfaces for all materials. The inset in (a) corresponds to a high magnification image.

The differences in the friction and wear response among the materials can be explained by the distribution and nature of the graphene fillers. During the sliding motion, wear debris from both counterbodies would be produced by abrasion and fracture processes and, therefore, would contain SiC and graphene-based particles from the plates as well as some Si$_3$N$_4$ particles from the balls. As the added graphene fillers are oriented within the composites with the ab plane parallel to the tested surface, they are pulled-out more easily than the random in-situ grown graphene multilayers of the monolithic SiC, which are smaller, thinner and better anchored to the matrix, and, hence, GNPs and rGOs have a more pronounced lubricant effect during the running-in period and lead to lower $\mu$ values (Fig. 1b). Besides, GNPs produced a better lubrication
along the whole tribotests through the development of a more stable lubricating
tribofilm (Fig. 4c) than rGOs (Fig. 4b), being then more effective in reducing the
friction. In the case of monolithic SiC, a protecting tribofilm was not observed
indicating that most debris particles were thrown out of the wear scar, and the high
mechanical pressures attained during the tests promoted the surface polishing, revealing
the grain microstructure as seen in the inset in Fig. 4a. In this material, the absence of
the protecting tribofilm led to a larger wear volume compared to the composites with
added graphene fillers (Fig. 3b).

To go in depth into the role played by graphene in the friction and wear
behaviour as well as in the mechanism of debris formation, an extensive study of the
wear debris was carried out by micro-Raman spectroscopy. Following a similar
procedure as described in a previous work [15], and taking into account the Raman
spectra of the different materials (see an example of average spectrum in Fig. 5a), 2D
false coloured Raman images (Fig. 6) were created by merging the intensity maps of
two well established intense bands, in particular, the SiC band at 796 cm$^{-1}$ of the
transverse-optical mode (TO), and the G-band of the graphene-based species at ~ 1591
cm$^{-1}$. Features in the Raman images (Fig. 6) with a high intensity of the SiC band are
coloured in blue; whereas those in red correspond to graphene sheets. In addition, the
increments in percentage of the I$_D$/I$_G$ ratio after testing the different materials ($\Delta$D/G),
determined from their respective average Raman spectra on the untested and worn
surfaces, are collected in Fig. 5b, which could give an idea of the damage suffered by
the graphene species during the sliding process. From the $\Delta$D/G evolution and the
analysis of the Raman images on the untested and tribologically tested surfaces, few
conclusions can be drawn. In this way, the area covered by graphene-based structures progressively augments in the worn surfaces of the composites (Figs. 6g-j) with rising graphene content as compared to the corresponding untested surfaces (Figs. 6b-e), proving an increasing graphene pulling-out with the filler content. Besides, $\Delta_{D/G}$ increased with the GNPs content, ranging from ~25% (monolithic SiC) to ~400% (20 GNPs composite). That lowest $\Delta_{D/G}$ value attained for monolithic SiC, jointly with the absence of changes on the area covered by graphene-based structures after testing, are in agreement with the higher pulling-out resistance of the in-situ graphene multilayers as they are strongly anchored to the SiC matrix and they are not oriented as in the rest of composites. Therefore, in-situ graphene multilayers played almost an irrelevant role during the wear process and the tribological behaviour of SiC is dominated by abrasion and the absence of any protecting tribofilm.

Figure 5. a) Raman spectrum corresponding to a 10 GNPs composite showing the bands associated to SiC (transverse-optical, TO, and longitudinal-optical, LO, modes) and GNPs (D, G, and 2D), and b) increments in percentage of the $I_D/I_G$ ratio after testing the different materials ($\Delta_{D/G}$).
Considering the decrease in $W_V$ of the composites (Fig. 3b), especially for the 20 GNP
material, the observed augment in the area covered by the nanoplatelets with the GNP
content would imply a more pronounced nanoplatelet exfoliation degree. Interestingly, $\Delta_{D/G}$ progressively increased with the GNP's content (Fig. 5b), which would be associated to a more extensive crushing and exfoliation of the pulled-out graphene stacks (Fig. 6) and, hence, to a more wear protecting carbon-based tribofilms (Figs. 3b,c). However, a larger GNP's exfoliation did not entail lower friction (Fig. 2c). This fact could be explained because the tribofilm of the 20 GNP's composite, created by the plastic deformation of the compacted fine wear debris (Fig. 4e), could lead to a possible adhesion mechanism that would enhance the friction. Furthermore, this increase in friction is also promoted by the cracking of the tribofilm once the mechanical stability is lost (Fig. 4e), roughening the film, as it is clearly demonstrated in the 2D profile of this specimen (Fig. 3a).

Finally, when compared the same amount of graphene fillers (5 vol.%), a more severe damage for 5 GNP's composites ($\Delta_{D/G} = 275\%$) was observed in respect to 5 rGOs ($\Delta_{D/G} = 138\%$), together with a slightly larger area covered by the graphene-based species (Figs. 6g,h). This would indicate that GNP's are more easily removed, exfoliated, and crushed than rGOs, forming a smooth compacted tribofilm (Fig. 4c) that reduced the friction (Fig. 2c), although the wear resistances for both composites were very similar (Fig. 3b).
Figure 6. False coloured Raman images of the debris created by merging the intensity maps of the SiC band (796 cm\(^{-1}\)) and G-band of graphene-based structures (1594 cm\(^{-1}\)) for the untested and tested surfaces of the different materials. Blue and red colour features are related to SiC and graphene sheets, respectively. (For interpretation of the
Conclusions

The tribological behaviour of SiC composites containing different kinds and amounts of graphene-based sources demonstrates the important role played by graphene as wear resistant filler. Wear resistance of SiC ceramics significantly enhances with the addition of GNPs. This response is linked to the ability of the graphene fillers to be pulled-out and exfoliated, creating a wear protecting graphene-based tribofilm. GNPs arise as the best graphene filler as compared to rGOs or in-situ grown graphene flakes because they are more easily removed, exfoliated, and crushed to create a protecting tribofilm. The choice of the most suitable material for tribological and mechanical applications will depend on their specific working requirements, 20 GNPs composites clearly showing the best wear resistant performance (72% increment as compared to the monolithics), whereas 5 rGOs composites exhibit an outstanding fracture toughness (162% increment).

Acknowledgements

This work was supported by the Spanish Government under project MAT2012-32944.

References


Figure 5

(a) Raman spectra of SiC-GNs composite. The peaks at 2900, 650, and 520 cm$^{-1}$ correspond to SiC (TO), SiC (LO), and D (G) respectively. The 2D peak is observed at around 2700 cm$^{-1}$. The intensity of the G peak decreases with the addition of rGOs, indicating a decrease in the GNPs content. (b) Variation of the intensity ratio $I_{D}/I_{G}$ with respect to the GNPs content (vol.%). The ratio increases with the addition of rGOs, indicating a decrease in the GNPs content.
Figure 1. FESEM micrographs corresponding to the different tested materials: a) monolithic SiC, and composites containing (in vol.%) b) 5 rGOs, c) 5 GNPs, d) 10 GNPs, and e) 20 GNPs. The arrows in a) point the location of graphene multilayers in-situ formed and the inset corresponds to a high magnification image of one of those multilayers.

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Figure 3. a) 2D profiles of representative wear tracks, b) wear volume ($W_V$), and c) wear rate ($W_R$) of the different materials.

Figure 4. FESEM micrographs of the tested surfaces for all materials. The inset in (a) corresponds to a high magnification image.

Figure 5. a) Raman spectrum corresponding to a 10GNPs composite showing the bands associated to SiC (transverse-optical, TO, and longitudinal-optical, LO, modes) and GNPs (D, G, and 2D), and b) increments in percentage of the $I_D/I_G$ ratio after testing the different materials ($\Delta_{D/G}$).

Figure 6. False coloured Raman images of the debris created by merging the intensity maps of the SiC band (796 cm$^{-1}$) and G-band of graphene-based structures (1594 cm$^{-1}$) for the untested and tested surfaces of the different materials. Blue and red colour features are related to SiC and graphene sheets, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
Manuscript Number:

Title: Toughened and strengthened silicon carbide ceramics by adding graphene-based fillers

Article Type: Regular Article

Keywords: graphene; ceramic matrix composites (CMC); mechanical properties; toughness; fracture

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Abstract: Graphene nanoplatelets (GNPs) and reduced graphene oxide (rGO) were selected as fillers to develop reinforced silicon carbide (SiC)/graphene composites. The mechanical properties of the materials were investigated as a function of the graphene source and content. Composites containing just 5 vol.\% of rGOS exhibited an outstanding mechanical performance, increasing both the fracture toughness in about 162\%, with a maximum value of 8.3 MPa·m\(^{1/2}\), and the strength in ~ 60\% (600 MPa) when compared to SiC monolithics. The preferential alignment of the graphene fillers, their dimensions, and the graphene-SiC mechanical interlock are key factors to promote crack shielding mechanisms.

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Outstandingly toughened and strengthened SiC materials are developed incorporating graphene fillers to the ceramic matrix. We report that the addition of just 5 vol.% of reduced graphene oxide (rGO) leads to toughness and strength increments of 162% and 60%, respectively, when compared to SiC monolithics, reaching maximum values of 8.3 MPa·m$^{1/2}$ and 600 MPa. The role of the graphene source (rGO and graphene nanoplatelets) and content (up to 20 vol.%) in the mechanical properties of the composites is analysed. Our findings indicate that the preferential alignment of the graphene fillers, their dimensions, and the graphene-SiC mechanical interlock are key factors to promote crack shielding mechanisms.

Sincerely,

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Toughened and strengthened silicon carbide ceramics by adding graphene-based fillers


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Abstract

Graphene nanoplatelets (GNPs) and reduced graphene oxide (rGO) were selected as fillers to develop reinforced silicon carbide (SiC)/graphene composites. The mechanical properties of the materials were investigated as a function of the graphene source and content. Composites containing just 5 vol.% of rGOs exhibited an outstanding mechanical performance, increasing both the fracture toughness in about 162%, with a maximum value of 8.3 MPa·m$^{1/2}$, and the strength in ~ 60% (600 MPa) when compared to SiC monolithics. The preferential alignment of the graphene fillers, their dimensions, and the graphene-SiC mechanical interlock are key factors to promote crack shielding mechanisms.

Keywords: graphene; ceramic matrix composites (CMC); mechanical properties; toughness; fracture

Introduction

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Silicon carbide (SiC) is one of the most demanded engineering ceramics due to their excellent corrosion and wear resistances, jointly with a high thermal conductivity and good mechanical performance at high temperature [1]. However, the Achille’s heel of these ceramics is their relatively low toughness. To overcome this problem, different approaches have been employed in the past for enhancing the fracture toughness ($K_{IC}$), among others, by inducing the in-situ growth of elongated SiC grains through thermal treatments (the so-called in-situ toughened SiC [2]) or by developing carbon fibre- or SiC fibre-reinforced SiC composites [3,4]. In both approaches, the fibres or the elongated grains deflect and/or bridge the cracks, arresting them or at least limiting their growth.

Recently, graphene-based nanostructures have attracted a great interest as efficient reinforcement fillers for toughening some oxide and non-oxide ceramics due to their capability for promoting toughening mechanisms [5-14]. Alumina ($\text{Al}_2\text{O}_3$)/graphene and silicon nitride ($\text{Si}_3\text{N}_4$)/graphene composites are the most investigated systems, and for which the most remarkable $K_{IC}$ results have been obtained until now. Focussing on the $\text{Al}_2\text{O}_3$-based composites, Lee et al. [5] reported $K_{IC}$ values up to 10.5 MPa·m$^{1/2}$ when 2 vol.% of reduced graphene oxide (rGO) was added, which corresponded to an increment of ~150% on this mechanical parameter as compared to the monolithic ceramics. Besides, the strength of the composite was also increased in 21%; whereas Centeno et al. [6] found improvements in $\sigma$ up to 80% for 0.22 wt.% rGOs composites, suggesting that the restriction of the $\text{Al}_2\text{O}_3$ grain growth during the sintering process due to the presence of graphene is the cause for that increment. In the case of $\text{Si}_3\text{N}_4$/graphene composites, a toughness increase of 135% was reported by Walker at al. [7] and Ramirez et al. [8]. The latter authors reached a maximum $K_{IC}$ value of 10.4 MPa·m$^{1/2}$ when 4.3 vol.% rGOs was added to the $\text{Si}_3\text{N}_4$ matrix, jointly
with an augment on $\sigma$ of 10% (maximum value of 1050 MPa) [8]. Other ceramics have been explored in this sense (for graphene reinforcement) with dissimilar results. For example, Shin et al. [9] increased the fracture toughness of yttria-stabilized zirconia (YSZ) ceramics in ~ 34% by adding 4 vol.% of rGOs; while Nieto et al. [10] reached $K_{IC}$ improvements of ~ 100% for tantalum carbide (TaC) ceramics with 5 vol.% of graphene nanoplatelets (GNPs), attaining top $K_{IC}$ values of 11.7 MPa·m$^{1/2}$. Yun et al. [11] recently reported the mechanical performance of aluminium nitride (AlN)/1.5 vol.% GNPs composites, showing increases on $K_{IC}$ and $\sigma$ of about 30% and 17%, respectively. In the case of SiC ceramics, some of the present authors were pioneering on the manufacturing of SiC/graphene composites by the in-situ growth of graphene sheets (~ 3–4 vol.%) into bulk SiC ceramics during the spark plasma sintering (SPS) process [12], which improved both the fracture toughness in about 55% [12] and the resistance to cone/ring cracking under Hertzian contact stresses [13]. Lately, Rahman et al. [14] reported a 40% $K_{IC}$ improvement when adding 2 wt.% of GNPs to a polymer SiC precursor, despite the remaining porosity in the composites.

The aim of this work is to investigate the fracture toughness and strength performances of dense SiC ceramics as a function of the GNPs content and the graphene source, in particular, comparing the mechanical properties attained with different graphene fillers, such as GNPs, rGOs—from GOs and reduced along sintering—, and finally, graphene epitaxially grown in-situ within the SiC ceramics.

**Experimental**

GO nanoplatelets (< 5 nm thickness, < 5 µm x-y dimensions), prepared in in-house from graphite flakes using the modified Hummers method [15], and commercial
GNPs (Angstron Materials Inc., USA, nominal thickness and x-y dimensions of 10-20 nm and 14 µm, respectively) were selected as fillers. SiC/graphene composites were prepared as detailed next. First, graphene fillers were sonicated in alcohol-ethanol for GOs and isopropyl alcohol for GNPs- for 1 h and, meanwhile, an alcohol-based ceramic slurry containing 93 wt.% of β-SiC powders (BF-17A, H.C. Starck, Germany) plus 5 wt.% of Y₂O₃ (Grade C, H.C. Starck, Germany) and 2 wt.% of Al₂O₃ (SM8, Baikowski Chimie, France), both used as sintering additives, was attrition milled for 2 h. Both suspensions were blade mixed and sonicated for 1 h, dried at 120 °C, and sieved through a 63 µm mesh. The following compositions were prepared: monolithic; 5 vol.% of GOs, and 5, 10 and 20 vol.% of GNPs. Finally, disc shaped specimens of 20 mm × 3 mm were SPSed (SPS, Dr. Sinter, SPS-510CE, Japan) at 1800 ºC for 5 min, applying a uniaxial pressure of 50 MPa during the heating cycle, and using a vacuum atmosphere of ~6 Pa.

Apparent density was measured by the water immersion method. The different materials were characterized by field emission scanning electron microscopy (FESEM, S-4700, Hitachi, Japan) and micro-Raman spectroscopy (Alpha300 WITec GmbH, Germany) using the 532 nm laser wavelength excitation. Median grain diameter (d₅₀) and aspect ratio (AR₅₀) of the SiC matrix were quantified by imaging analysis methods on FESEM micrographs took on polished and plasma etched surfaces, and considering at least 500 features. For the mechanical tests small bars of 15.0 mm x 2.0 mm x 2.5 mm were prepared. Flexural strength (σ) was determined by three point bending tests using an outer span of 8 mm and a displacement rate of 0.5 mm·min⁻¹. Fracture toughness (KIC) was measured by the surface crack in flexure (SCF) method Koop indenting at 100 N the centre of the bars in their tensile surfaces and, then, performing three point bending tests with the same outer span and displacement rate than for σ. At
least four bars were tested per material and mechanical parameter. Besides, to observe in detail the crack paths, Vickers indentations at loads ranging from 20 to 100 N were performed at the cross section of the bars that corresponded to the plane parallel to the SPS pressing axis.

**Results and discussion**

Highly homogenous and fully dense $\beta$-SiC materials were obtained, where the graphene fillers appeared preferential oriented with their ab plane perpendicular to the SPS pressing axis (Fig. 1). The reference monolithic material also contained ~ 3-4 vol.% of graphene multilayers (Fig. 1a), which were grown in-situ at the SiC grain boundaries during the SPS process [12]. GNPs remained undamaged after the SPS process, as the intensity ratio between D and G Raman bands ($I_D/I_G$) slightly increased, i.e., the GNPs become more defective, changing from 0.21 for the pristine GNPs to 0.23-0.28 after the sintering step. Conversely, $I_D/I_G$ for GOs considerably decreased from 1.20 (as-produced) to 0.29 (after SPS), which constitutes a proof of the effective reduction of GO (rGO) to graphene by the SPS method [16]. Regarding the microstructure, it should be noticed that all the materials presented the same matrix grain size and shape ($d_{s0} = 0.6-0.7 \mu m$ and $AR_{s0} = 1.4$).

The strength and fracture toughness data as a function of the graphene source are plotted in Figures 2a,b. At the first glance, the graphene composites exhibited better mechanical performance than the reference material. In this way, the strength of SiC ceramics increased in about 60-70% when 5 vol.% of fillers either GNPs or rGOs were added to the matrix (Fig. 2a), reaching a maximum $\sigma$ value of 622 MPa for the GNPs composite. Furthermore, almost no differences ($< 4\%$) in the strength were observed when varying the graphene source. The strengthening of the graphene composites is
quite remarkable considering that the matrix grain size remains unchanged and much smaller, about one order of magnitude, than the maximum lateral filler size (< 5 and 14 µm for GOs and GNP s, respectively), which, therefore, controls the critical defect size. Accordingly, the observed strengthening should be linked to an expected toughness increase in the composites, as presently occurs in all composites and it can be seen in Fig. 2b. In fact, rGOs led to an outstanding increase on $K_{IC}$ (8.3 MPa·m$^{1/2}$) in respect of the monolithic SiC (3.2 MPa·m$^{1/2}$) that corresponded to a toughness increment of 161%. Interestingly, this $K_{IC}$ value is one of the highest toughness data reported for SiC materials, with the exception of some three dimensional textile C/SiC and SiC/SiC composites with $K_{IC}$ over 20 MPa·m$^{1/2}$ [1], being also remarkable the low reinforcing phase content (5 vol.% rGOs) required to achieve these results. Comparing to other ceramic/graphene composites, this exceptional $K_{IC}$ improvement is even higher than that for Al$_2$O$_3$/rGOs [5] and Si$_3$N$_4$/rGOs composites [7,8]. The benefits of adding GNP s are less pronounced, as a lower $K_{IC}$ value was assessed (4.8 MPa·m$^{1/2}$), although these nanoplatelets still promoted a significant toughness enhancement of 50% as compared to the monolithics. Finally, the monolithic material exhibited a $K_{IC}$ value (3.2 MPa·m$^{1/2}$) just slightly higher than that reported by Borrero-Lopez et al. [17] for hot pressed SiC ceramics ($K_{IC} = 2.9$ MPa·m$^{1/2}$) with a similar amount of sintering additives and grain size than in the present case but without graphene fillers. Despite the current monolithic material already contained ~3-4 vol.% of graphene multilayers in-situ grown, their random distribution within the matrix contributed less to the development of toughening mechanisms.

FESEM observations of Vickers indentation imprints performed in the plane parallel to the SPS pressing axis (Fig. 3), i.e., perpendicular to the plane containing the oriented graphene sheets, clearly illustrate that well defined vertical and horizontal
cracks were developed in the reference material (Fig. 3a). However, for SiC/graphene composites, especially that containing rGOs (Fig. 3b), vertical cracks are mostly horizontally deflected and propagated freely. A FESEM image at higher magnification of one of the short vertical cracks reveals the reason for their arresting (Figs. 3c,d). As it can be seen, extrinsic crack-tip-shielding mechanisms associated to GNPs (Fig. 3c) and rGOs sheets (Fig. 3d) effectively bridged the crack, thus reducing the local stresses and strains at the crack tip and, hence, inhibiting the crack growth and enhancing the toughness of the composite [18]. Crack deflection is also evidenced in the indentation cracks, as shown by the brisk change in crack direction when impinging the graphene planes, which produces mix-mode crack propagation that also results in a reinforcing effect. These toughening mechanisms are particularly favoured in the vertical direction because the ab planes of the graphene fillers are mostly oriented perpendicular to that direction. Conversely, those mechanisms were not as effective when the horizontal cracks run parallel to the ab planes of the fillers. The superior toughness achieved on the rGOs composite (Fig. 2b) could be explained attending to several reasons. First, rGOs are smaller and thinner than GNPs and, hence, for the same volume fraction, the number of potential graphene-based ligaments to bridge the cracks would be higher in the case of rGOs. In addition, these graphene fillers may exhibit a certain mechanical interlock with the matrix, as they appear wavy following boundaries of the SiC grains (pointed by arrows in Fig. 1b), which would result in larger energy consumption when rGO are debonded by the cracks [19].

The role of the graphene filler content on the mechanical parameters has been evaluated in the composites containing GNPs (Figs. 2c,d). These nanoplatelets were chosen, instead rGOs, because their higher availability and also considering that they produced reasonable toughening and strengthening effects. Regarding the flexure
strength (Fig. 2c), the response was better for any composite as compared to the monolithic SiC, even for materials containing up to 20 vol.% of GNPs (8% increase on σ). Despite the maximum σ value was attained for SiC/5 vol.% GNPs composite (622 MPa, 67% improvement), the strength just slightly decreased (602 MPa) when the amount of GNPs was doubled (10 vol.%). For larger nanoplatelets contents, a percolated graphene network is formed that leads to an increased critical flaw size, decreasing the strength of the material. Interestingly, the fracture toughness increased for materials containing up to 10 vol.% of GNPs (Fig. 2d) to a value of 5.9 MPa·m$^{1/2}$ that represents an improvement of 86% as compared to the monolithic material. Figures 4a-c are clear examples of the multiple bridging, branching and deflection events occurring in indentation cracks propagating in the vertical direction, which led to their arresting. However, when cracks propagate along the parallel direction respect to the ab plane of the GNP, the nanoplatelets are mostly delaminated and exfoliated (Fig. 4d). Similarly to the strength plot, toughness values dropped for GNPs contents of 20 vol.% because the formed graphene network weakens the material, controls its failure and stabilizes the contribution of bridging mechanisms [19].

Conclusions

Toughened and strengthened SiC ceramics are developed incorporating graphene fillers to the ceramic matrix. Reduced GOs arise as the best graphene filler considering the outstanding toughness increment (162%) and strengths up to ~ 600 MPa (61%) attained by adding just 5 vol.% of rGOs to the ceramic matrix. The lower dimensions and the better mechanical interlock to the matrix of rGOs, when compared to GNPs, support the excellent mechanical performance of SiC/rGOs composites. In the case of GNPs composites, filler contents up to 10 vol.% are required to potentially
promote a larger occurrence of crack shielding mechanisms and a maximum toughness increase of 86%, while keeping a constant strength value around 600 MPa.

Acknowledgements

This work was supported by the Spanish Government and CSIC under projects MAT2012-32944 and PIE201360E063, respectively.

References


Figure captions

Figure 1. FESEM micrographs of the fracture surface corresponding to the different materials: a) monolithic SiC materials containing graphene multilayers in-situ grown, and composites containing: b) 5 vol.% rGOs, c), 5 vol.% GNPs, d) 10 vol.% GNPs, and e) 20 vol.% GNPs (e). Arrows in (a) and (b) point graphene multilayers in-situ formed in SiC and rGOs showing waviness, respectively.

Figure 2. a) and c) Flexure strength, σ, and b) and d) fracture toughness, $K_{IC}$, for SiC/graphene composites: a) and b) containing a fixed amount (5 vol.%) of different graphene sources, and c) and d) varying the GNPs content.

Figure 3. FESEM micrographs of the cracks developed by Vickers indentation at 100 N on the plane parallel to the SPS pressing axis of the materials: a) and b) imprints performed in monolithics and 5 vol.% rGOs composite, respectively. Toughening mechanisms events are observed in composites containing 5 vol.% of: c) GNPs and d) rGOS.

Figure 4. FESEM micrographs of the cracks developed by Vickers indentation at 100 N for SiC composites containing: a,b) 10 vol.% GNPs and c,d) 20 vol.% GNPs. In a-c) the cracks run in the plane parallel to the SPS pressing axis; whereas in d) they run in the perpendicular plane.
Figure 1
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Figure 2
Figure 3