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Abstract: The short-crack domain and contact damage resistances of silicon carbide (SiC) ceramics containing graphene fillers (graphene nanoplatelets -GNPs- or reduced graphene oxide sheets -rGOs) are investigated by performing Hertzian contact tests. A progressive deviation from the linear Hertzian elastic response with increasing graphene content takes place, the nanocomposite containing 20 vol.% GNPs being the most deformable material. When adding GNPs, the damage beneath the contact zone turns from the well-defined cone crack of the monolithic SiC to a widespread subsurface damage where microcracks are generated due to the matrix/graphene interface debonding by a shear faulting process. This mechanism enhances the contact damage resistance of the nanocomposites, redistributing the stresses at the contact and limiting the long-crack formation. The nanocomposite containing 5 vol.% rGOs fully precludes the cone cracks development and enlarges the quasi-plastic damage zone, extraordinarily enhancing the contact damage resistance that approaches to that of a ductile material.

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Contact damage resistant SiC/graphene nanocomposites

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Abstract

The short-crack domain and contact damage resistances of silicon carbide (SiC) ceramics containing graphene fillers (graphene nanoplatelets -GNPs- or reduced graphene oxide sheets -rGOs) are investigated by performing Hertzian contact tests. A progressive deviation from the linear Hertzian elastic response with increasing graphene content takes place, the nanocomposite containing 20 vol.% GNPs being the most deformable material. When adding GNPs, the damage beneath the contact zone turns from the well-defined cone crack of the monolithic SiC to a widespread subsurface damage where microcracks are generated due to the matrix/graphene interface debonding by a shear faulting process. This mechanism enhances the contact damage resistance of the nanocomposites, redistributing the stresses at the contact and limiting the long-crack formation. The nanocomposite containing 5 vol.% rGOs fully precludes the cone cracks development and enlarges the quasi-plastic damage zone, extraordinarily enhancing the contact damage resistance that approaches to that of a ductile material.

Keywords: contact damage; graphene; silicon carbide; machining; composites

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1. Introduction

The inherent brittleness of silicon carbide (SiC) ceramics jointly with their high hardness hinder their machinability and limit the widespread use of SiC components in a broader range of structural applications, among others, in transportation, energy or microelectronics industries [1]. It is well known that ceramics can fail in service under intense loads due to the structural damage induced by the stresses developed beneath the contact [2]. The nature of this damage is determined by both the microstructure and the resistance of the material in the short-crack region, which also define the machinability of the materials. B. R. Lawn and co-workers have extensively investigated the short-crack domain and the contact damage resistance of numerous ceramic materials, including SiC, by performing Hertzian tests with spherical indenters [3]. These authors found an elastic-brittle behaviour with well-defined cone cracks beneath the contact for homogeneous SiC ceramics with a microstructure of fine and equiaxed grains [4,5]. By contrast, for heterogeneous tough SiC materials -with typical microstructures of large, elongated grains and weak interphase boundaries- the development of a single cone crack was suppressed while exhibited a yield response characteristic of ductile solids [5]. In these materials, a subsurface damage zone of distributed intergranular microcracks along the weak matrix-boundary phase interfaces was formed, which reduced the strength degradation from contact damage. After cyclic loadings, this subsurface damage zone expanded and produced the material removal, hence, improving the machinability of these hard materials without compromising their strength and toughness [6]. Alternative reported strategies for enhancing the damage resistance and machinability of SiC consisted in the addition of fillers that introduce weak interfaces. In this way, Kusunose et al. [7] observed quasi-plastic deformation and significant interfacial microcracking at the SiC grain boundaries when adding 30 vol.%

of boron nitride (BN) nanoparticles, whereas the monolithic material or the composite containing BN microparticles exhibited classical Hertzian cone fracture and many large cracks. For similar SiC/BN nanocomposites, Wang et al. [8] reported also outstanding machinability in drilling tests.

Along this research line of creating ceramic materials having weak interfaces, carbon nanostructures (CNs) arise as quite opportune fillers. Actually, there are several examples showing that the addition of carbon nanotubes (CNTs) to both alumina [9] and silicon nitride [10] ceramics enhanced their contact-damage resistances, as these composites became highly shear-deformable under Hertzian indentation. Recently, graphene, the two dimensional CN, has emerged as a very promising filler because of the outstanding multifunctional properties that imparted to ceramics and its comparatively easier processing/dispersion [11]. At present, to the best of our knowledge, there are just few works devoted to the contact damage and machinability of ceramic/graphene composites [12,13]. In particular, some of the present authors [12] found for in-situ grown graphene/SiC composites that the presence of the multilayered graphene at grain boundaries, in a low amount (~4 vol.%), augmented both the resistance to cone/ring cracking and the toughness. However, the damage mechanisms beneath the contact and the effect of increasing contents of graphene flakes were not investigated in that work. On the other hand, Porwal et al. [13] were able to drill holes into Al_2O_3 just by adding large graphene nanosheets, which was explained by the grain boundary sliding at the weak Al_2O_3 -graphene interfaces.

Therefore, the aim of the current work is to deeply analyse the short-crack endurance of SiC/graphene nanocomposites as a function of the graphene filler content (0-20 vol.%) and source -graphene nanoplatelets (GNPs) or graphene oxide sheets (GOs)- by performing Hertzian contact tests and to investigate the damage mechanisms.

Those graphene fillers led, as present authors previously reported [14], to an outstanding improvement of the long-crack fracture resistance of SiC ceramics (up to 160% toughness increase) by the occurrence of crack-shielding phenomena. Various toughening mechanisms were demonstrated to jointly act, such as deflection, crack-bridging, debonding and pull-out. In the present work, low-speed grinding tests were also carried out to explore the effect of the graphene filler on the machinability of these materials.

2. Experimental procedure

SiC/graphene nanocomposites containing commercial GNPs (10-20 nm nominal thickness and 14 μm x-y dimension, Angstrom Materials Inc.) or in-house prepared GOs (< 5 nm thickness, < 5 μm x-y dimension) were manufactured as described elsewhere [15]. Briefly, two separate suspensions using alcohol (ethanol or isopropyl alcohol) as liquid media were first prepared to disperse and homogenize their components, in particular, one attrition milled ceramic slurry with a powder composition formed by 93 wt.% of β -SiC powders (BF-17A, H.C. Starck GmbH) plus 5 wt.% of Y_2O_3 (Grade C, H.C. Starck) and 2 wt.% of Al_2O_3 (SM8, Baikowski Chimie), and another one containing the selected graphene fillers (GNPs or GOs) that was sonicated. Afterwards, both suspensions were blade mixed and sonicated, and the dried and sieved powders were spark plasma sintered (SPS, SPS-510CE, Fuji Electronic Industrial Co., Ltd.) at 1800 $^\circ\text{C}$ for 5 min, applying 50 MPa of uniaxial pressure and using a vacuum atmosphere of 6 Pa. Disc shaped specimens of ~ 20 mm diameter and ~ 3 mm height were obtained. The different materials selected for this study were the reference monolithic SiC ("SiC") and SiC nanocomposites containing 5, 10 and 20 vol.% of GNPs ("5GNPs", "10GNPs", "20GNPs"), and a nanocomposite with 5 vol.% of

reduced GOs (“5rGOs”), the latter recalculated after the reduction of GOs to graphene during the SPS process.

Hertzian contact tests were performed in air by indenting (Zhu 2.5, Zwick/Roell GmbH & Co.) 1 µm diamond polished and gold coated specimen surfaces (Figure 1a) with tungsten carbide (WC-6% Co) spheres of 1.25 and 2.50 mm of radius (r). The specimens were placed so that the basal plane of the graphene fillers was parallel oriented to the tested surface, i.e., perpendicular to the SPS pressing axis. Several indentations were done at increasing loads (P) from 25 to 1300 N. The contact radius (a) of the imprints left on the gold coating was measured by optical microscopy with Nomarski interference contrast and, then, indentation stress ($p_0 = P/\pi a^2$) and indentation strain (a/r) values were assessed. In addition, the damage beneath the contact zone was analysed using the bonded-interface configuration [3]. In essence, for each material, two rectangular half-blocks were polished in the cross-section plane, parallel to the SPS pressing axis, and, afterwards, bonded face-to-face with an adhesive layer. The top surfaces -perpendicular to the SPS axis- were then ground and polished, and indentations with WC spheres of $r = 2.5$ mm at increasing loads were done centred over the bonded interface. Finally, the adhesive layer was dissolved and the damage patterns (Fig. 1b) were examined by both optical microscopy with Nomarski interference contrast and field emission scanning electron microscopy (FESEM, S-4700, Hitachi).

The machinability of the different materials, i.e. the ease to remove material during a grinding process, was evaluated conducting low-speed grinding tests on an automatic lapping machine (Phoenix 4000, Buehler). The specimens were ground under water lubrication on a 20 µm diamond grinding foil (ATM GmbH) clockwise rotating respect to the sample holder at 150 rpm. The height of the specimens (h) was measured at 0.5-2 min intervals until a total grinding of 15 min.

Figure 1. Scheme of the Hertzian contact test showing: (a) the graphene sheets orientation with respect to the direction of loading and (b) the bonded-interface configuration where observations of the top and subsurface damages beneath the contact are enlarged in optical micrographs.

3. Results and discussion

Both the reference SiC material and the graphene-based nanocomposites reached densities $\geq 99\%$ of their respective theoretical values [16], with an excellent homogenous distribution of the graphene fillers within the matrix, as Figure 2 shows. Besides, a clear preferential orientation with their basal plane perpendicular to the SPS pressing axis was observed. The monolithic SiC also contained $\sim 3\text{-}4\text{ vol.}\%$ of graphene multilayers in-situ grown at the SiC grain boundaries as a consequence of the SPS conditions, as previously stated [17]. Moreover, micro-Raman spectroscopy analysis allowed identifying the location of graphene flakes within the composite, and confirmed that the sintering conditions did not damage GNPs and led to the effective reduction of GOs to graphene [14].

Figure 2. FESEM micrographs of the fracture surfaces of: a) SiC, b) 5GNPs, c) 10GNPs, d) 20GNPs, and e) 5rGOs materials showing the preferential orientation of graphene fillers with their basal plane perpendicular to the SPS pressing axis. The inset in a) corresponds to a high magnification image of graphene multilayers in-situ grown within the matrix (pointed by arrows in the low magnification image).

The indentation stress-strain curves for the different materials (Figure 3) reveal a progressive deviation from the linear Hertzian elastic response with increasing GNPs content, 20GNPs resulting the most deformable nanocomposite under the same testing conditions. That deviation from the characteristic elastic-brittle behaviour is distinctive of ductile materials, hence defined as quasi-plastic deformation regime. No significant differences were detected as a function of the graphene source, although 5rGOs nanocomposites were slightly more ductile than 5GNPs ones. The Hertzian contact response of the SiC/graphene nanocomposites studied in this work is typical of heterogeneous ceramics containing shear-weak second phases [3,4,7]. Although an elastic-brittle behaviour should be expected for the present reference SiC material considering its microstructure based on an homogenous distribution of SiC grains of

0.5-0.6 μm in diameter [12], the stress-strain curve slightly deviated from the linear response at $p_0 \sim 5.3$. This behaviour can be explained by the presence of the graphene sheets grown during the SPS process that soften to some extent the monolithic material [12].

Figure 3. Indentation stress-strain curve of the different materials. Dashed lines represent empirical fits through the data.

The subsurface Hertzian contact damage on bonded-interface cross-sections (Figure 4) revealed that in the case of the monolithic SiC, cone cracks were formed (Fig. 4a), which were visible at indentation loads of 400 N and followed almost straight paths (Figure 5a). For this material, no signs of quasi-plastic damage beneath the contact were detected within the whole range of applied loads up to the catastrophic fracture of the specimen. In the case of SiC/graphene nanocomposites, larger indentation loads (700-900 N) were required to unveil their damage modes. For 5GNPs nanocomposite, the formation of the cone fracture was still evidenced (Fig. 4b),

1 although cracks were significantly shorter than those of the reference SiC. This may be
2 in part due to the occurrence of crack shielding mechanisms such as crack branching or
3 bridging, as displayed in Fig. 5b. At the same time, a subsurface quasi-plastic damage in
4 the strong shear-compression zone below the contact was identified using Nomarski
5 illumination (confined area defined by dashed lines in Fig. 4b). In that zone, the shear
6 faulting process promoted the matrix/graphene interface debonding (Fig. 5c), nucleating
7 mode II microcracks. This mechanism enhances the contact damage resistance of the
8 material, redistributing the stresses at the contact and limiting the long-crack
9 propagation [4,9,10]. At present, this is the first evidence of the shear faulting process in
10 ceramic/graphene nanocomposites.
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25 As the GNPs content increased, a progressive transition from well-defined cone
26 crack to a more intense subsurface damage takes place (Figs. 4c,d). This intensification
27 in the subsurface damage is due to the degraded short-crack toughness linked to the
28 weakened grain or interface boundaries characteristic of soft heterogeneous materials
29 with increased long-crack toughness [18]. In fact, as it has been previously reported by
30 the present authors [14,16], the addition of GNPs to SiC led to a remarkable increment
31 in the fracture toughness (from 3.2 to 5.9 MPa·m^{1/2}) jointly with a substantial decrease
32 in the hardness (from 27.8 to 9.8 GPa). In addition, for larger fillers contents,
33 neighbouring microcracks nucleated at the matrix/graphene interfaces coalesced (Fig.
34 5d) allowing ultimately an extensive material removal, as it happened for 20GNPs
35 nanocomposite (Fig. 4d). This type of damage response is expected to benefit the
36 material machinability.
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Figure 4. Nomarski optical micrographs corresponding to the cross-section views of Hertzian contact damage in the following bonded-interface specimens: a) SiC, b) 5GNPs, c) 10GNPs, d) 20GNPs, and e) 5rGOs materials. Tests were performed with a WC sphere of $r = 2.5$ mm using loads of 400 N (a), 700 N (c, d) and 900 N (b, e). Arrows point the cone cracks, whereas the dashed lines confine the quasi-plastic damage zones.

Figure 5. FESEM micrographs of the cone cracks for monolithic SiC (a) and 5GNPs nanocomposite (b), and debonding through the matrix/graphene interface by a shear faulting process for 5GNPs (c) and 10GNPs (d) nanocomposites. Arrows in (b) point examples of crack deflection-bridging. Note that the darker features correspond to the GNPs location.

The graphene filler source clearly affected the subsurface Hertzian contact damage behaviour of the nanocomposites (Figs. 4b,e), although it did not translate into substantial differences in the stress-strain curves (Fig. 3). Interestingly, rGOs fully precluded the cone cracks formation in the whole range of indentation loads selected; whereas the quasi-plastic damage zone was considerably enlarged (Fig. 4e) as compared to that of 5GNPs nanocomposite (Fig. 4b), observing arrays of microcracks parallel aligned to the tested surface (Figure 6). This can be explained considering that GOs are smaller and thinner than GNPs and, then, 5rGOs nanocomposite will present a larger

number of matrix/graphene interfaces, mostly oriented perpendicular to the SPS pressing axis, than 5GNPs one. Therefore, the stresses created at the Hertzian contact will be easily redistributed through those interfaces leading to an enlarger quasi-plastic damage zone, and considerably enhancing the contact damage resistance of the 5rGOs nanocomposite, approaching its response to that of a ductile material. Besides, the microcracks hardly coalesced probably due to that largest stress distribution.

Figure 6. FESEM micrographs of the subsurface damage (a) and debonding through the matrix/graphene interface (b) for 5rGOs nanocomposite. Note that the dark features correspond to the rGOs location.

Assuming that the contact damage response of the different materials can affect their machinability, the worn height of the specimens during a low-speed grinding process was progressively examined as a function of time (Figure 7). All plots exhibited a parabolic fitting to experimental data, typical trend of the tool flank wear in machining processes where high wear initially occurs prior to reach a steady-state region [19]. The results evidenced that the machinability of SiC ceramics was clearly enhanced by introducing GNPs fillers, in particular, an augment of ~45% in the matter removal after 11 min of grinding time was assessed for 5GNPs and 10GNPs, increasing up to ~110% for 20GNPs. The weak SiC-graphene interfaces promoted that enhanced machinability,

in the same way as occurred for Al_2O_3 /graphene nanosheets nanocomposites [13]. Considering that the contact damage performance of SiC/GNPs nanocomposites changed with the fillers content, certain machining differences among the nanocomposites can be expected, but this is not the case for 5GNPs and 10GNPs (Fig. 7). Bearing in mind the bonded-interface observations described above, this could be explained by the opposite effect of two different competing processes: i) the occurrence of shear fault microcracks coalescence beneath the contact (enlarged for 10GNPs as compared to 5GNPs) that would favour the material removal and ii) the enhanced long-crack toughening associated to the GNPs that is also higher (23%) for 10GNPs than for 5 GNPs, which would limit material removal [14]. In the case of 5rGOs nanocomposites, the elastic-plastic behaviour did not allow a higher machinability and its machining performance is quite similar to that of SiC (Fig. 7). Besides, the coalescence of microcracks beneath the machined surface in the 5rGOs nanocomposite was highly restricted (Fig. 4e), limiting the material removal by detachment of individual grains, and, simultaneously, the high long-crack toughness of this material ($8.3 \text{ MPa}\cdot\text{m}^{1/2}$) [14] would also hinder the material removal by chipping.

Figure 7. Worn height (Δh) of the different specimens as a function of the grinding time.

Conclusions

The contact damage response of the graphene/SiC nanocomposites is affected by the amount of fillers and the graphene source. The addition of increasing amount of graphene fillers progressively changes the elastic-brittle response of SiC towards a quasi-plastic deformation regime distinctive of heterogeneous ceramics containing shear-weak second phases, 20GNPs nanocomposite being the most deformable material. By increasing the GNPs content, the subsurface damage beneath the contact zone enlarges, which is due to microcracking associated to the matrix/graphene interface debonding. This process allows redistributing the stresses and, hence, the contact damage resistance of the materials is enhanced. This is the first time that this type of shear faulting process is reported in ceramic/graphene nanocomposites. Smaller and thinner GOs, as compared to GNPs, lead to nanocomposites with a larger number of matrix/graphene interfaces that easily redistribute the Hertzian contact stresses, increasing the contact damage resistance and closely behaving as a ductile material. The machinability of SiC ceramics is considerably enhanced by introducing GNPs fillers, augmenting up to ~110% for 20GNPs due to the weak SiC-graphene interfaces and the coalescence of neighbouring microcracks. The balance between that microcracks coalescence and the long-crack toughening controls the machinability. Finally, graphene fillers emerge as excellent candidates to increase the contact damage resistance of certain ceramics, limiting the long-crack formation as well, which certainly favours the structural applications of these nanocomposites as they are less prone to failure under concentrated loads.

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