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Author Contribution Statement

M.B. manufactured the materials and J. L. performed the tribological tests. Both authors carried out the characterization of the tested materials, discussed the results and wrote the manuscript.

Rolled and twisted graphene flakes as self-lubricant and wear protecting fillers into ceramic composites

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Abstract

Dry reciprocating sliding tests have been performed on cubic yttria-stabilized zirconia ceramic composites containing graphene nanoplatelets. The composites exhibit an excellent friction response and, especially, an outstanding improvement of the wear resistance of more than two orders of magnitude, as compared to unfilled ceramics. The enhanced tribological response of these composites is much greater than that commonly reported for ceramic/graphene materials. The deep analysis of worn surfaces by combining confocal Raman, scanning electron and atomic force microscopies reveals the presence of abundant twisted graphene-based rolls on top of a thick carbonaceous tribofilm that played a decisive protagonist to extraordinarily improve the tribological performance of the composites through a roller-bearing like effect.

1. Introduction

The lubricating properties of graphene at nano- and micro-scale as additive for oils and/or as self-solid lubricant in coatings and composites have extensively been demonstrated [1,2]. The improvement of the tribological properties of bulk graphene-based composites [1,3] is explained, to a large extent, because of the development of a

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carbon-rich protective tribofilm on polymeric [4], metallic [5] or ceramic [6] composites. However, very little is still known about how the graphene fillers promote the formation of this tribofilm and enhance the tribological response.

The friction and wear performance of graphene-based composites seems to depend on the testing parameters, mainly the use of dry or lubricated conditions and the range of applied loads, and composite characteristics (graphene filler type, content and dispersion degree, and mechanical properties). Focusing on ceramic/graphene composites [7-9], graphene fillers are able to achieve maximum friction coefficient reductions up to ~ 50%, as compared to the unfilled material, and wear resistance improvements up to 100% [7]. The most accepted mechanism for explaining this enhanced tribological performance is the formation and stabilization of a carbon protecting tribofilm coming from the exfoliation and crushing of the pulled-out graphene stacks [6,10]. However, in some works this carbon tribofilm was not observed [11] or not justified the results [12] and, that, jointly with the large diversity of tribological results associated to distinct composite characteristics and testing conditions makes necessary to get more conclusive experimental evidences of the role played by graphene fillers.

Here we investigate for the first time the friction and wear resistance of 8 mol% yttria-stabilized zirconia ceramics (8YSZ) containing graphene nanoplatelets (GNPs) with filler amounts up to 20.7 vol.%. These composites are a good alternative to perovskite-based materials in electrochemical applications [13]; while 8YSZ ceramics are employed as electrolyte in solid oxide fuel cells and in new micro-energy conversion devices [14,15], where the internal friction and contact resistance between their components can reduce the efficiency. Therefore, the aim of the present work is to shed

light on the active contribution of graphene fillers in the tribological response of 8YSZ ceramics.

2. Experimental

2.1 Materials fabrication

The processing of 8YSZ/GNPs composites is described elsewhere [13]. In brief, the ceramic powders (8YSZ, TZ-8YS grade, Tosoh Co.) and the fillers (GNPs, N006 grade, Angstrom Materials Inc., 10-20 nm of thickness and 14 μm of lateral size) were first individually dispersed in isopropyl alcohol using attrition milling and sonicating procedures, respectively. Then, the ceramic and GNPs alcohol suspensions were mixed, with the appropriate mass ratio to achieve the different composites (0, 7.0, 10.5, 13.5 and 20.7 vol.% of GNPs that have been labelled as 8YSZ, 7GNPs, 11GNPs, 14GNPs and 21GNPs), and mechanically stirred and sonicated for 1 h. The dried powder mixtures were spark plasma sintered (SPS, SPS-510CE, Fuji Electronic Industrial Co., Ltd.) under vacuum atmosphere (6 Pa), applying 50 MPa of uniaxial pressure during the heating ramp at temperatures of 1310-1350 $^{\circ}\text{C}$ for 7 min, looking for developing materials with the same density ($> 99\%$ of the theoretical value) and matrix grain size ($\sim 1.0 \mu\text{m}$). Fully dense discs (20 mm diameter and 2.2 mm height) were obtained for all compositions. An excellent dispersion of the GNPs into the 8YSZ matrix has been confirmed for the different composites (Figure 1), including that with the largest filler content (20.7 vol.%), avoiding the formation of GNPs agglomerates.

Figure 1. FESEM micrographs of the fracture surfaces of 7GNP (a) and 21GNP (b) composites showing a homogenous dispersion of the GNPs into the ceramic matrix. Notice that GNPs appear preferentially oriented with their ab planes perpendicular to the SPS pressing axis.

2.2 Tribological tests

The specimens were ground and polished to achieve mean roughness values below 0.02 μm and, afterwards, they were acetone/ethanol cleaned and dried. The tribological properties of the materials were studied using a linear reciprocating ball-on-plate configuration (UMT3, Bruker), where the plates and balls corresponded to the developed materials and commercial ZrO_2 (Hightech Ceram GmbH, 10.318 mm of diameter), respectively. The sliding tests were performed in air (25 $^{\circ}\text{C}$ and 20% of relative humidity) applying a load of 5 N on the specimen surface perpendicular to the SPS pressing axis. A stroke length of 2.5 mm, frequency of 20 Hz ($0.1 \text{ m}\cdot\text{s}^{-1}$) and total sliding distance of 360 m were selected as main tribological conditions. The friction coefficient (μ) was on-line recorded during the tests and the steady-state value (μ_{ss}) was

estimated considering the 200-360 m interval. The wear rate (W_R) of the plates was assessed from the following equation: $W_R = W_V/F_N \cdot s$, where W_V is the wear volume calculated from the 2D profiles of the wear track [16], F_N is the normal load, and s is the total sliding distance. At least three valid tests were done for each material and data shown in the present work correspond to their average values. Wear tracks of the plates were investigated by field emission scanning electron microscopy (FESEM, S-4700, Hitachi) and atomic force microscopy (AFM) coupled to confocal Raman microscopy (Alpha 3000, WITec GmbH) that employed a laser wavelength of 532 nm and 2 mW of power. Dimensions of the scanned areas, pixels and acquisition time (t_i) varied with the features analyzed in order to record the maximum intensity of the Raman signal avoiding, at the same time, the damage of the carbon nanostructure. In this way, at least two scanned areas of $50 \times 50 \mu\text{m}^2$ were selected for each untested and tested surfaces of all materials. Raman maps of 25×25 pixels were acquired, recording one spectrum per pixel and using t_i of 1.0 s. In the case of the cross-section of the tribofilm, three scanned areas of 20 (width) $\times$ 10 (height) μm^2 , maps of 20×20 pixels and t_i of 1.0 s were chosen. The analysis of the rods in the X-Y plane was performed scanning up to ten fields of $3 \times 3 \mu\text{m}^2$, 40×40 pixels and t_i of 0.6 s. Finally, the $6 \mu\text{m}$ depth-scan in the Z-direction across the rod was done in two scanned areas of 4 (width) $\times$ 6 (height) μm^2 , maps of 40×60 pixels and t_i of 0.5 s.

3. Results and discussion

Figure 2a shows a scheme illustrating the dry linear reciprocating ball-on-plate tests performed on the specimen surface parallel to the alignment of the nanoplatelets, occurred during the densification process of GNPs composites by spark plasma

sintering (SPS) [7-9]. The friction coefficient (μ) evolution with the sliding distance (Figure 2b) evidences that, at very beginning of the test, any addition of GNPs leads to a substantial reduction of this tribological parameter as compared to the reference material (8YSZ). As the test progressed, a clear dependence with the graphene content was observed. Actually, the steady state friction coefficient (μ_{ss}) exhibited an almost linear relationship of μ_{ss} with the amount of fillers (Figure 2c), decreasing from 0.90 for 8YSZ ceramics to 0.29 for 21GNPs composite, which corresponds to a ~68% of reduction. This improvement in the friction performance when using just 5 N of load is much higher than those reported for other ceramic/graphene tribosystems [7]. As expected, μ_{ss} value for the reference material is in the order of that estimated for ceramic-ceramic contacts under dry sliding friction [17]; whereas in the case of 21GNPs composite, the friction would be within the range attained for oil lubricated ceramic-ceramic pairs [18], although in the present case the test were conducted under dry testing conditions. Therefore, it seems that GNPs are acting as self-lubricant material.

Figure 2. a) Schematic of the linear reciprocating ball-on-plate testing configuration also showing the cross-section view of the microstructure of 21GNPs composite and the preferential alignment of GNPs within the matrix with the nanoplatelet basal plane perpendicular to the SPS pressing axis, b) friction coefficient (μ) evolution for the different materials, c) steady-state friction coefficient (μ_{ss}) versus the GNPs content, including the linear fitting to the experimental data, and d) wear rate (W_R) for the different tested materials. Dashed line in this case is only for eye guide.

Another key tribological parameter is the wear rate (W_R). Figure 2d shows that all GNPs composites are above two orders of magnitude more wear resistant ($W_R \sim 7.3 \times 10^{-7} \text{ mm}^3 \cdot \text{N}^{-1} \cdot \text{m}^{-1}$) than the unfilled ceramics ($W_R \sim 1.5 \times 10^{-4} \text{ mm}^3 \cdot \text{N}^{-1} \cdot \text{m}^{-1}$). Besides, no significant differences between the composites were found. These results evidence that the tribosystem evolved from severe (reference material) to mild (composites) wear

by introducing just 7.0 vol.% of graphene fillers into 8YSZ ceramic matrices. The wear resistance improvement is one of the highest reported until now, jointly with a recent work reported by Gutierrez-Mora et al. [12] where the authors found similar increments for tetragonal 3YSZ/GNPs composites containing 2.5 vol.% of fillers when tested at 10 N. In that work, the wear resistance decreased with the filler content due to the presence of GNPs agglomerates.

The wear tracks of the tested materials, analysed by FESEM, are shown in Figure 3a-e. While a rough surface and severe abrasive wear are observed in the reference material (Figure 3a), confirmed by its high W_R exponent (10^{-4}), worn surfaces in composites (Figure 3b-e) are smoother and present a tribofilm that becomes more compacted as GNPs content increased. For 14GNPs (Figure 3d) and 21GNPs (Figure 3e) composites, the mechanical stresses during the sliding motion promote the cracking of the tribofilms, which seem to be much thicker than for 7GNPs and 11GNPs composites.

As it was previously mentioned, the development of a carbon- rich protecting lubricant tribofilm on the wear track of graphene composites is commonly pointed as the main responsible for improving their tribological response [3-5]. As expected, this tribofilm is also formed in the present case, confirmed by optical (Figure 3f) and confocal Raman (Figure 3g) microscopy observations on the cross section of 21GNPs composite that was taken as example. Taking into account that the average Raman spectrum of the untested composite surface contains four main bands (Figure 3h) associated to YSZ ($\sim 629 \text{ cm}^{-1}$) and GNPs (D-, G- and 2D bands), a false coloured Raman image of the cross-section of the wear track was created (Figure 3g) by merging the YSZ band at $\sim 629 \text{ cm}^{-1}$ (in blue colour) and the most intense one for GNPs (G band at $\sim 1594 \text{ cm}^{-1}$, in red colour). As a result, a $\sim 1 \text{ }\mu\text{m}$ thick film was clearly observed (enclosed between the dashed lines in Figure 3g), which is mostly formed by defective carbonaceous material

with a low YSZ contribution, as the single Raman spectrum in position 1 confirmed (Figure 3h). Beneath the tribofilm, the YSZ matrix and pristine GNP fillers (positions 2 and 3 in Figure 3h) were distinguished.

Figure 3. (a-e) FESEM micrographs of the worn surfaces for: a) 8YSZ ceramics and b) 7GNPs, c) 11GNPs, d) 14GNPs and e) 21GNPs composites. Optical (f) and false coloured Raman (g) images of the cross-section for 21GNPs composite wear track with the tribofilm enclosed between the dashed lines. The Raman image is built by merging the intensity maps of the YSZ (blue) and G (red) bands. h) Average Raman spectrum of the untested 21GNPs composite showing the main YSZ and GNPs (D, G, 2D) bands; and single Raman spectra taken in positions 1, 2, and 3 of the Raman image in g). For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.

Interestingly, a closer observation at high magnification of all tested composite surfaces revealed the existence of hundreds of rolls on top of the tribofilms (see an example of a magnified field in Figure 4a). The rolls, with lengths ranging from 0.5 to 1.5 μm and diameters of ~ 100 nm (see inset in Figure 4a), were not found on the reference material and, hence, they must be associated in some way to the graphene fillers. The analysis of these rolls was done by observations on the same area using different microscopies. In this way, two close rolls on a smooth tribofilm were chosen by FESEM (Figure 4b,c) and, afterwards, analysed by AFM coupled to confocal Raman microscopy (Figure 4d-g). The Raman spectrum of a scanned area of $3 \times 3 \mu\text{m}^2$ where the rolls were located, according to the AFM image (Figure 4d), did not show differences in composition, D and G being the unique Raman bands identified in the whole map (see Supplementary information Figure S1). To distinguish the rolls in a Raman image, the Raman fluorescence background given by the topography was then analysed, considering that particles on a flat substrate lead to increased fluorescence intensity as compared to smooth surfaces. Based on this, a Raman image was created where the rolls on the tribofilm are perfectly distinguished (Figure 4e), with notable differences in the fluorescence of positions 1 and 2 (Figure 4g) associated to the tribofilm and rolls, respectively. To complete this study, a $6 \mu\text{m}$ depth-scan in the Z direction across one roll was performed. The differences in the reflectance by collecting the Rayleigh scattered light intensity allowed to build a new Raman image (Figure 4f). Here, the section of the tribolayer and one roll on the tribofilm is plainly visible, and position 3 in Figure 4g illustrates the characteristic Raman spectrum of this carbonaceous materials. The pristine composite beneath the tribofilm that also includes the YSZ band and 2D one linked to GNPs is shown at position 4 in Figure 4g.

The rolls found on the worn composite surfaces could be the key for the important reduction of the friction and, especially, for the extraordinary wear resistance improvement through a roller bearing-like effect. Actually, a similar effect is well-known in some ceramics (Al_2O_3 , SiC and Si_3N_4) tested under water lubrication or water vapour containing environments [19-21], where aluminium hydroxide or silica rolls are formed as a consequence of the tribochemical reaction between the ceramics and water molecules. Nevertheless, dry conditions are used in the present work. On the other hand, the formation of graphitic scrolls in sliding tests was described time ago. Actually, J. Spreadborough observed for the first time in 1962 the development of rolled-up graphitic foils when a copper stylus passed on a graphite layer mounted on polished copper substrates [22]. Recently, Berman et al. [23] reported the formation of nanoscrolls based on nanodiamonds wrapped by graphene patches that were created during the sliding motion of a graphene coated surface containing diamond nanoparticles against a diamond-like carbon coated counterface. Those nanoscrolls decreased the contact area, leading to macroscopic superlubricity and a reduction in the friction coefficient. Lately, other authors have described the formation of graphene nanoscrolls from graphene coatings [24] or amorphous carbon films [25] when tested against ceramic balls. However, to the best of our knowledge, this is the first time that the presence of this kind of scrolls in bulk graphene composites has been reported.

Figure 4. a) FESEM micrograph showing numerous rolls on top of the 11GNPs composite tribofilm and a detail of two rolls at the bottom-left side. b) and c) FESEM and d) topographic AFM images of rolls selected for the Raman analysis. e) and f) False coloured Raman images in the X-Y plane, taken from the AFM illustration, and depth-scan in the Z direction along the dashed line in d), respectively. The yellow colour intensity in e) augments with the fluorescence degree; whereas it increases in f) with the Rayleigh scattering. g) Single Raman spectra taken in positions 1-4 of Figures e) and f).

Figure 5 shows a schematic of the possible roll formation mechanisms and some real exemplary experimental observations to illustrate the process. In the pristine composite, GNPs are embedded into the YSZ matrix with their basal plane parallel to the sliding direction (Figure 5a). When GNPs are exposed to the counterpart during the tribological test, some layers of the nanoplatelets slide over others due to the shear forces, being pulled-out from the composite (Figure 5b). The sliding motion tends to crush many graphene flakes, producing numerous carbonaceous debris that form the tribofilm (Figure 5c). Some pulled-out GNPs, as well as some flakes detached from the

tribofilm, rolled up, probably from their edges as it is energy favoured, to produce scrolls (Figure 5a,d). This rolling process continues due to the prevalence of van der Waals forces [26]. Additionally, two or more of these scrolls can merge, forming compacted twisted rolls on the tribofilm (Figure 5e) that would enhance the bearing capability. The rolls are mostly located on the tribofilm, but they occasionally appear trapped on cavities (Figure 5f). We have observed the formation of similar GNPs-based rolls, although in less concentration, in dry tested SiC/GNPs composites (see Supplementary Information Figure S2).

Figure 5. a) Schematic of the roll formation. (a-f) FESEM micrographs of GNPs within the matrix (a), an exfoliated GNPs flake (b), a tribofilm (c), a long GNPs-based roll (d), a twisted roll formed by the combination of different rolls (e), and accumulation of rolls trapped into a cavity (f).

4. Conclusions

We have demonstrated that the addition of graphene-based fillers to a 8YSZ matrix extraordinarily increases its tribological response under dry testing conditions. High friction coefficient reductions and outstanding wear resistance improvements, well

above than those attained in other ceramic/graphene tribosystems, are achieved. The wear also suffers a strong evolution from a severe regime in the unfilled material to a mild one in composites containing just 7.0 vol.% of graphene fillers. This response is clearly associated to first, the development of a well adhered and continuous thick carbonaceous tribofilm on the worn surface of composites that acts as self-lubricant and wear protecting layer and, more importantly, to the formation in the composites of hundreds of graphene-based twisted rolls on top of the tribofilms that produce a bearing-like effect, considerably contributing to lower friction and wear. This study definitively clarifies the role played by graphene fillers in the tribological behaviour of ceramic composites.

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: