ARTICLE IN PRESS

Feature article

Friction and wear behavior of alumina-based graphene and CNFs composites

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ABSTRACT

Alumina – carbon nanofibers (CNF) and alumina – graphene oxide (GO) composites were prepared by spark plasma sintering using freeze-dried powders prepared from optimized suspensions of the mixtures. The tribological behavior was studied using the ball-on-disk technique in dry sliding at ambient conditions and compared to a monolithic alumina used as a reference. At low loads there was little difference between friction and wear behavior, whereas at moderate loads the composites showed a noticeable reduction in wear rate over monolithic alumina, five and 2.5 times for the GO and the CNF composite respectively; the friction coefficient slightly decreased for the alumina – GO material. This behavior is related to the presence of a carbon-rich protecting tribofilm. The film present in the alumina – GO showed better tribological performance due to the absence of coalescence of cracks that led to delamination events in the case of the alumina – CNF composite.

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1. Introduction

Carbon-based composites (carbon nanofibers – CNF, carbon nanotubes – CNT and graphene) have created great expectations due to their excellent mechanical, electrical and thermal properties [1–5], regarding their possible benefits in many potential technological and industrial applications, especially in those where tribological aspects are involved, such as power generation, transportation or manufacturing [6].

Materials in general and ceramics in particular, reinforced by carbon phases have shown improved wear resistance and reduced friction coefficients. Two different effects can affect the friction and wear behavior of these composites: the improvement in mechanical properties due to the inclusion of the carbon structures in the ceramic matrices and also the wear-induced formation of a carbon-rich tribofilm that acts lubricating and protecting the contact surfaces. Superior mechanical properties (fracture toughness) have been reported for 2.5 vol% CNF-reinforced alumina [7], CNF reinforced-zirconia [8] and a composite of CNF and hydroxyapatite [9]. Although there is some controversy about the reinforcing effect of the CNT, many authors have found a noticeable improvement on the mechanical properties on ZrO_2/multiwalled carbon nanotubes (MWCNTs) composites [5,10,11], on alumina reinforced with 0.1 wt% CNTs [12] or in the system CNT/Si_3N_4 [13]. Toughening mechanisms such as CNT bridging, crack deflection and crack pinning are reported as the origin of wear resistance improvement in alumina reinforced with 10 wt% CNTs [14]. Similar toughening mechanisms have been proposed for graphene-reinforced ceramics: graphene pull-outs, crack bridging, crack deflection and crack branching. Alumina reinforced with graphene platelets (GPs) showed from 30% to 50% increase in fracture toughness with respect to monolithic alumina [15,16] whereas the addition of graphene nanoplatelets to Si_3N_4 increased the fracture toughness up to 235% [17].

Moreover, all these carbon-based composites are good candidates for solid lubricants due to the excellent lubricating properties of graphite [18]. The presence of a tribolayer that protects the contact surface while reducing friction force has been reported for different tribosystems. Hvizdos et al. [19] found a graphite layer in CNF/ZrO_2 composite as a result of friction tests as a result of grounded CNFs, both present in the worn surface and from pull-outs. Similar observations were reported by Borrell et al. [20] in CNF-reinforced alumina. Likewise, CNTs/ceramic composites are

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reported to display a lubricating film under dry friction testing due to the exfoliation of CNTs and the incorporation of the debris into this film over the contact area [21–25]. González-Julián et al. [23] studied this film using microRaman and found out that it was formed by debris consisting on Si_3N_4 particles from the ceramic matrix and graphitized and crushed CNTs pulled out from the composite. Different authors have also reported the presence of a tribolayer after friction experiments in graphene composites [26–29]. This layer, which is believed to be formed due to the exfoliation of graphene layers from GNPs, enhanced the wear resistance and decreased the friction coefficient of these tribosystems. Raman studies have shown a substantial presence of GNPs in this layer [26,28].

Although apparently the nature of these tribolayers is different depending on the reinforcement used in the ceramic composite, graphitic in the case of CNFs and CNTs and graphene enriched for graphene composites, their effect in the tribological behavior is similar. Thus the aim of this work is to compare the tribological behavior of two carbon-based reinforced aluminas (with CNFs and GO) fabricated by spark plasma sintering and to study the influence of the different phases on the formation and nature of these protecting tribolayers.

2. Experimental

2.1. Materials

A starting commercial α-alumina (Celarox, Conclea HPA05, USA) with an average particle size of 0.35 μm and a surface area of 9.5 m^2/g, was used in this study. As nanodispersoid, two different carbon sources were used as a reinforcement in the ceramic matrix: graphene oxide (GO, Nanoinnova Technologies, Spain), with a length of 1–4 μm, a thickness of 0.7–1.2 nm, and a surface area of 103 m^2/g, and carbon nanofibers (CNFs, GANF – Grupo Antolin, Burgos, Spain), with an outer diameter of 20–80 nm, a length of more than 30 μm and a surface area of 150–200 m^2/g.

Suspensions were dispersed using as deflocculant a polyacrylic acid-based polyelectrolyte, PAA (Duramax D-3005; Rohm & Haas, Dow Chemical, Midland, MI) with an active matter content of 35% and a molecular weight of 2400.

Concentrated suspensions of alumina with and without carbon dispersoids were prepared by colloidal processing. An alumina suspension (A) was previously dispersed and studied as a reference, as it has been proven that an accurate dispersion optimization leads to a more homogeneous material in terms of particle size than the commercial materials [30]. Once its rheological behaviour was optimized, the dispersion parameters of the suspensions with the carbon nanodispersoids, i.e. alumina-carbon nanofibers (ACNF) and alumina-graphene oxide (AGO) were studied. The carbon nanodispersoids were always added in a concentration of 2 vol.% referred to dry ceramic powders and, due to its strong influence on the rheology, the mixtures were prepared to lower solids loadings (i.e., 45 vol.% for ACNF and 40 vol.% for AGO suspensions).

The alumina (A) suspension was prepared to a solid loading of 53 vol.%, adding firstly the deflocculant to a concentration of 0.8 wt% referred to the ceramic dry powder. The rheological behaviour was optimized applying ultrasonication for consecutive periods of 1 min using an ultrasounds probe (UP400S, Dr. Hielscher GmbH, Germany) in a pulsed mode (0.5 cycles).

To prepare the ACNF suspension, the carbon nanofibers were dispersed by the addition of 1 wt% (with regard to the dry weight of CNFs) of Hypermer KD7 as a deflocculant and 4 min of sonication in pulsed mode (0.5 cycles), and the mixture was maintained under mechanical stirring for 15 min to allow the deflocculant to be adsorbed to the particle surfaces. Afterwards, the relative amount of PAA needed to disperse the ceramic powders was added (0.8 wt% PAA with regard to alumina), and subsequently the ceramic powders were added and the mixture was maintained under mechanical stirring for 30 min before the rheological characterization.

The AGO suspension was prepared in a similar way, that is, the graphene oxide was dispersed before the addition of the ceramic powder because, being the minority phase it distributes more homogeneously within the volume of the suspension. To achieve this, the required amount of GO was added to the water and dispersed applying sonication for 2 min. Once it was dispersed the mixture pH was quite acidic (pH ∼ 4), so that a strong base (tetramethylammonium hydroxide, TMAH, Aldrich-Chemie, Germany), supplied as a 25 wt% aqueous solution, was added to the suspension in order to obtain the desired value of pH (9.0 ± 0.1) since this value helps to the dispersion of the ceramic matrix powder and both the powder and the GO have negatively charged surfaces. The ceramic powder and the deflocculant were added after the dispersion of GO in the same way as in the previous suspension.

The rheological behaviour of all suspensions was determined using a rheometer (Haake RS50; Thermo, Karlsruhe, Germany) operating at controlled shear rate by loading the shear rate from 0 to 1000 s^{-1} in 5 min, maintaining at 1000 s^{-1} for 1 min and unloading from 1000 to 0 in 5 min. The measurements were performed at 25 °C using a double cone and plate system.

The so prepared suspensions were frozen in a rotatory chamber using as refrigerant liquid nitrogen (−196 °C). The frozen suspension was introduced in a freeze-dryer (CRYODOS-50, Telstar, Spain) for 24 h. The condensator temperature was −50 °C, and the conditions of the storage camera were 20 °C and 0.050 mbar.

Bulk composite samples were sintered using a SPS process (Dr. Sinter Lab Inc., Model 515S, Kanagawa, Japan (pulsed high DC current 20 V, 0–1500 A)). The powder mixtures were poured into a cylindrical graphite die of 15 mm in diameter. A sheet of graphitic paper was placed between the punch and the powder and between the die and the powder for easy removal of the sintered sample and in order to ensure their electrical, mechanical and thermal contact. The sintering process was conducted under a vacuum of 4–6 Pa. A uniaxial pressure of 75 MPa was applied throughout the sintering cycle. The sintering temperature was increased to 1300 °C at a rate of 100 °C/min and a cooling rate of 50 °C/min. The holding time was 5 min. The temperature was measured and controlled using an optical pyrometer focused on the surface of the graphite die and automatically regulated from 600 °C to the final sintering temperature.

The temperature of 600 °C was reached via a preset heating program. The setup is provided with a dilatometer for recording the shrinkage and shrinkage rate, and the data were stored on a computer. The following parameters were also recorded: temperature, pressure, current, and voltage.

2.2. Microstructural and mechanical properties

The bulk density of the sintered samples (15 mm diameter × 3 mm thickness disks approximately) was measured by the Archimedes method with distilled water as the immersion medium using 3.98, 2.1 and 2.1 g/cm^3 as densities of alumina, graphene oxide and carbon nanofibers respectively. The microstructural characterization was performed using field emission scanning microscopy (FESEM, S5200, Hitachi, Japan) to characterize grain size distributions on polished surfaces, and conventional scanning electron microscopy (SEM, 6460LV, JEOL, Japan) and high resolution scanning electron microscopy (HRSEM, Teneo, FEI, USA), to perform fractography analysis on worn tracks. Grain size was determined by analysing FESEM images using the Image-J software, main planar grain diameter was obtained measuring at least 200 grains