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Wear resistant coatings: Silica sol–gel reinforced with carbon nanotubes

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ABSTRACT

Pin-on-disc wear experiments have been carried out on sol–gel silica coatings reinforced with 0.1 wt.% carbon nanotubes (CNTs) deposited on WE54 magnesium alloy substrates by the dip-coating technique. Sol–gel solutions were fabricated using two different procedures: mechanical mixing (MM) and ultrasonic probe mixing. Dry sliding wear tests have been carried out at load of 1 N, speed of 0.1 m/s and sliding distance of 60 m. Friction coefficients were obtained from the tests and the specific wear rates (k) were calculated. The fabrication procedure of the coating influences its morphology and wear resistance. Friction coefficient was found to vary slightly with the addition of the CNTs. The wear volume of the magnesium substrate coated decreased by 40% and 80%, in terms of k, by using unreinforced and CNT-reinforced MM coatings, respectively. In MM layers reinforced with CNT uniform dispersion of the nanotubes was reached and toughening of the ceramic coating by pull-out and crack bridging mechanisms was observed.

1. Introduction

Since the discovery of carbon nanotubes (CNTs) [1], and due to their outstanding mechanical properties [2], they have attracted much attention as potential nanoscale reinforcement for composite materials. Addition of CNTs into ceramic matrices is expected to lead them to higher fracture toughness values [3] and to higher wear resistance [4]. Uniform dispersion of the nanoreinforcement and good CNT/matrix interfacial adhesion are the main requirements that must be fulfilled to improve these mechanical properties regarding to those of the unreinforced material. The promotion of molecular mixing by previous functionalization of the CNTs with hydroxyl groups has shown benefits, in terms of mechanical development of the final composite, when the matrix of the composite was fabricated through the sol–gel organic route [4,5]. Ultrasonic mixing of the sol–gel precursor and the CNTs has been studied as an alternative process to traditional mechanical mixing for the fabrication of ceramic monoliths reinforced, in order to achieve better distribution of the CNTs in the matrix [6].

Some papers have been focused on the toughening effect of the addition of carbon nanotubes to bulk ceramic matrices. Different fracture mechanisms take place because of this CNT incorporation, such as crack deflection at the CNT/matrix interface, crack bridging by CNTs and CNT pullout on the fracture surface [7], being crack bridging the most reported mechanism participating in the toughening of this kind of reinforced materials [5–10]. Authors have recently proved that in sol–gel silica coatings reinforced with CNTs the toughening effect (24%) was also caused because the CNT bridging mechanism [11].

Recently, attention has focused on the wear properties of carbon nanotubes reinforced monolithic ceramic nanocomposites. Ahmad et al. [12] reported the improvement on the tribological performance of the carbon nanotubes reinforced alumina composite consolidated via hot press process. The nanoreinforcement indirectly influenced the microstructure of the ceramic (reducing the grain size by restricting the grain growth) and mechanical properties (improving hardness, fracture toughness and flexural strength) and directly acting as lubricant medium reducing the coefficient of friction.

However, little attention has been given, up to now, to the wear characterization of ceramic coatings reinforced with carbon nanotubes. Agarwal et al. [13] reported the improvement (27% drop in the volume loss) of the wear resistance of plasma sprayed alumina coatings reinforced with CNTs, mainly because of the graphitization of the nanotubes due to pressure applied with the counterbody (50 N).

Wear and corrosion protection of light metallic alloys with structural applications have increased the interest of the scientific community. For instance, magnesium alloys are among the most promising materials to minimize weight in the transportation industry and in the portable electronics market. However, several drawbacks restrict the application of bare magnesium alloys, especially their low wear and corrosion resistance. Sol–gel silica coating is one of the few techniques that allow obtaining wear and corrosion protective ceramic layers at temperatures below the melting temperature of these alloys. Therefore, the more the mechanical performance of the silica coating the more the protection offered to the metallic substrate.

This paper reports the wear performance of sol–gel silica coatings reinforced with CNTs deposited on WE54 magnesium alloy substrate. The influence on the wear development of the sol–gel fabrication

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procedure, mechanical mixing or ultrasonic mixing, and addition of CNTs were studied. Pin-on-disc tests in dry sliding conditions were performed. The coefficient of friction was obtained and specific wear rates were calculated. The main wear mechanism for each specimen was established after observation of the worn tracks and of the wear debris by scanning electron microscopy (SEM).

2. Experimental details

2.1. Substrate material

The substrate samples were obtained from an extruded bar of 60 mm diameter of the WE54 magnesium alloy supplied by Magnesium Elektron. The composition of the alloy was (in wt.%): 5.5 Y; 2.0 heavy rare earths (Yb + Er + Dy + Gd); 2.0 Nd; 0.4 Zr and balance Mg. The bar was cut down perpendicularly to the extrusion direction and the samples size was $22 \times 22 \times 2$ mm^3. The substrates were in the T5 state and showed a Vickers Hardness of 81 ± 3 at 2 kg load.

To improve the adhesion and the thickness of the sol–gel coatings, the surface of the substrates were ground to P800 with SiC grit papers, degreased with propanol and dried in warm air.

2.2. Coatings synthesis

Tetraethyl orthosilicate (TEOS) $Si(C_2H_5O)_4$ was used as the precursor for fabrication of the silica matrix. Starting sol was prepared from TEOS diluted in absolute ethanol (EtOH) (molar ratio TEOS/EtOH: 1/1) and 0.1 M HCl acidulated water (molar ratio TEOS/water: 4/1).

Hydroxyl-functionalized multi-walled carbon nanotubes (OH-MWCNTs), provided by Nanocyl Company, with 9.5 nm average outer diameter and about 1 μm average length, were used as nanoreinforcement of the sol–gel silica coatings in a proportion of 0.005 wt.% using two different mixing techniques.

The first mixing technique consisted in forming a suspension of ethanol in which the OH-MWCNT were added and dispersed using an ultrasonic probe; the suspension was stable for long times, as it has been previously reported by the authors [14]. Subsequently, this suspension was added to the solution containing the rest of the precursors required, i.e. TEOS and acidulated water. This solution was mechanically mixed using a magnetic stirrer for 2 h at room temperature and, finally, it was allowed to age for 30 min. The coatings fabricated using this process will be denoted as MM (mechanically mixed).

The second mixing technique used consisted in adding directly the nanoreinforcement to the precursors solution with the same proportions previously mentioned and dispersing them via ultrasonic probe processing for 45 min. The sol so obtained was stable for days when the mixture was prevented from evaporation. The coatings fabricated using this process will be denoted as UM (ultrasonic mixed).

Coatings were obtained by dipping the magnesium alloy substrates in the sols and using a controlled extraction speed of 35 cm/min. Coatings were dried at room temperature for 30 min to allow the evaporation of water and constrained ethanol, and subsequently sintered at 400 °C for 2 h. After this time, samples were air quenched. Considering the volume and weight reduction in the coating during evaporation and consolidation stages, the final OH-MWCNT content in the final coating was 0.1 wt.%. This percentage is consistent with the observed in the TEM micrographs of the reinforced coatings [14].

For both mixing processes, sols without nanoreinforcement addition were also fabricated for comparative purposes using the same procedures. Finally, other set of samples were fabricated without coating but submitted to the same heat treatment of the coated samples, i.e. heated at 400 °C for 2 h; these samples will be denoted as HT.

All the coated samples, as well as the heat treated substrates, showed a reduction of their hardness to 72 ± 2 HV_2; i.e. 11% hardness reduction.

2.3. Samples characterization

Scanning Electronic Microscopy (SEM), using a Hitachi S-3400 N with 15 kV as accelerating voltage and in high vacuum conditions, equipped with a Bruker Energy Dispersive X-ray spectroscopy (EDX) detector (XFlash 5010), each spectrum obtained at with a primary energy of 15 kV, tilt angle of 0º and working distance of 10 mm, was used to determine the influence of the sol–gel fabrication process (UM or MM) and the influence of the addition of CNT reinforcement in the final coatings. SEM was also used to analyze the worn tracks and the debris formed during the wear tests in order to determine the main wear mechanisms and to find out the coating with the highest wear protection. For a better SEM characterization, some the coatings were metalized with Pt using the sputtering technique.

To determine the reinforcement integration in the sol–gel silica MM + CNT coatings were studied by Transmission Electron Microscopy (TEM) (FEI Tecnai 20 T) using 200 kV as operating voltage.

2.4. Wear tests

Wear tests were carried out on a pin-on-disc tribometre (MT/10/SCM from Microtest) under unlubricated conditions and room temperature. The counterbody was a 6 mm diameter steel ball. The tests were carried out with 1 N load and a rotating speed of 0.1 m/s for a total wear distance of 60 m. Mass loss was measured with a 10^{-5} g analytical balance before and after the tests. Four different tests were carried out for each coating condition.

Volume loss after the wear test was determined in each specimen from the mass loss measurements considering the real density of the material or of the coating. From it, the specific wear rate (mm^3/N m), as defined by Friedich et al. [15], was calculated by dividing by the normal applied load and the total wear length as the following equation indicates:

$$\frac{V}{L} = kW \quad (1)$$

In this equation V is the wear volume, L is the sliding distance, being the coefficient V/L the wear rate, W is the applied load and k is the specific wear rate. This equation can be used to evaluate the wear behaviour of the substrate/coating systems due to the very similar densities between magnesium alloy WE54 (1.86 g/cm^3) the multiwall carbon nanotubes used (1.9 g/cm^3) and sol–gel silica density (2.2 g/cm^3).

3. Results and discussion

3.1. Coatings microstructure

The surface of the silica coated magnesium substrates was observed by SEM and only marks of the grounding process on the surface substrate could be seen (Fig. 1a). The coating copies the surface roughness and the absence of any defect on it avoids distinguishing its presence. However, EDX analysis shows the presence of silicon and oxygen at the surface (peaks at 1.7 and 0.5 keV, respectively, inset in Fig. 1a) proving the existence of a silica layer on the substrate surface. The addition of CNTs to the sol–gel silica matrix of the coating did not change the morphology of the coating (Fig. 1b).

When ultrasonic mixing technique was used, clear differences were observed in the final silica layers (Fig. 2). The unreinforced coating seemed to be free of cracking at low magnifications, although detachment of the coating in some small zones was observed at high

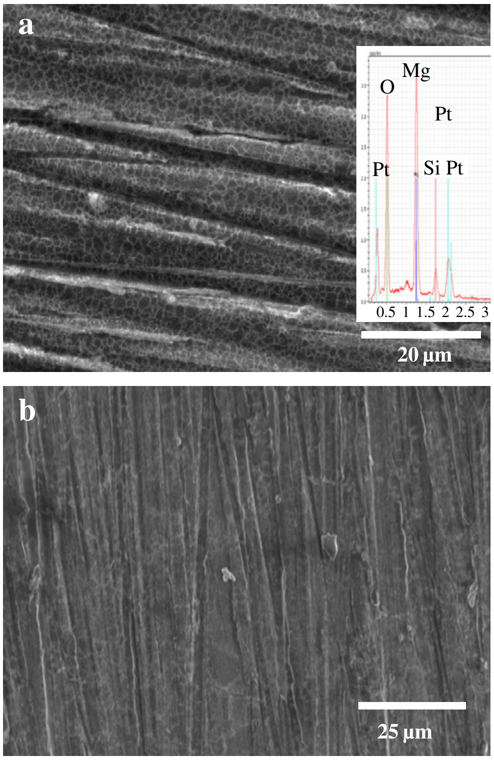

Fig. 1. SEM micrographs of the mechanical mixed coatings (MM): (a) unreinforced condition, general view; (inset) EDX analysis of the surface; (b) reinforced coating (MM + CNTs).

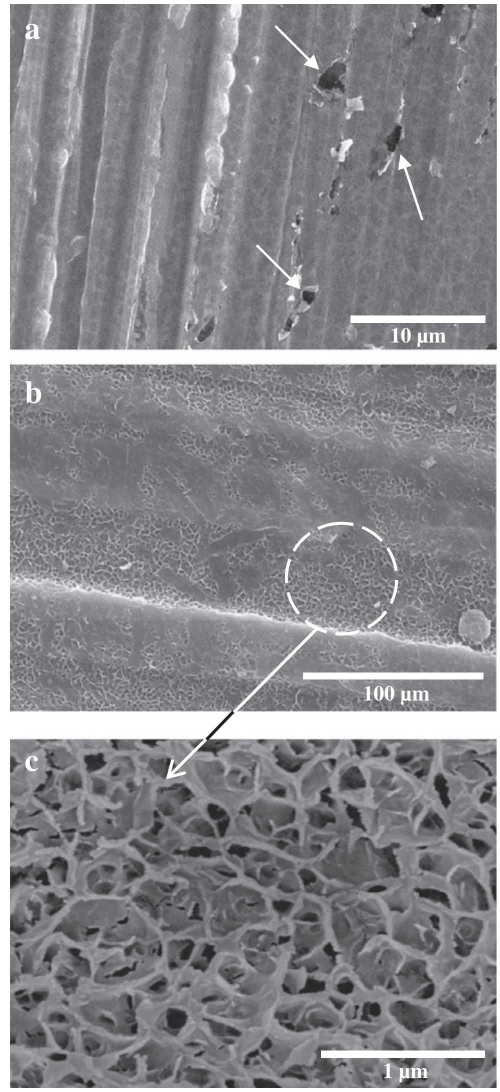

Fig. 2. SEM micrographs of the ultrasonically mixed coatings Pt coated: (a) unreinforced condition; (b) CNT-reinforced coating; (c) detail of (b).

magnifications (arrowed zones in Fig. 2a). When this UM coating was reinforced with OH-MWCNTs extensive zones of the coatings with high porosity were obtained (Fig. 2b). The morphology observed at higher magnifications (Fig. 2c) evidences a sponge-like structure in different zones of the substrate.

The thickness of the coatings was 3 µm ± 0.4 µm for all the fabrication techniques (MM or UM) independently of the addition of the CNTs [11]. In this previous work [11] it was also evaluated by atomic force microscopy the roughness of the different tested specimens. In terms of root mean square (RMS) the ultrasonically mixed coating reinforced with CNTs had the largest roughness (369.9 nm) because of its great porosity, followed by the grounded bare substrate (340 nm), the unreinforced (220.6 nm), the reinforced mechanically mixed layer (213.4 nm) and finally the unreinforced ultrasonically mixed one (173.9 nm). All the coatings, with the exception of the ultrasonically mixed reinforced with CNTs, reduce the roughness of the bare substrate.

3.2. Wear testing

The wear rate of the different samples in dry sliding conditions has been plot in Fig. 3. The friction coefficient (circles) of all the samples was in the range 0.40–0.46, and differences between similar samples were very small. For the uncoated samples, there was a small increase for the heat treated one which may be related with the slight hardness decrease observed during the heat treatment. Among the coated specimens, the friction coefficient of the mechanically mixed coating was smaller than that of the ultrasonically mixed ones, possibly due to its higher compaction. For each system (MM or UM), the incorporation of the CNTs in the coating caused a small reduction in the friction coefficient.

The wear rate observed strongly varied for the different systems (columns in Fig. 3). The highest wear rates were observed for the uncoated systems, particularly for the heat treated one which showed 23% increase as compared with the as-received sample (AR). As it was mentioned in the Experimental section, the heat treated substrates experimented a hardness reduction of about 11%, due to an overaging process of the as-received substrate, The high temperature used for

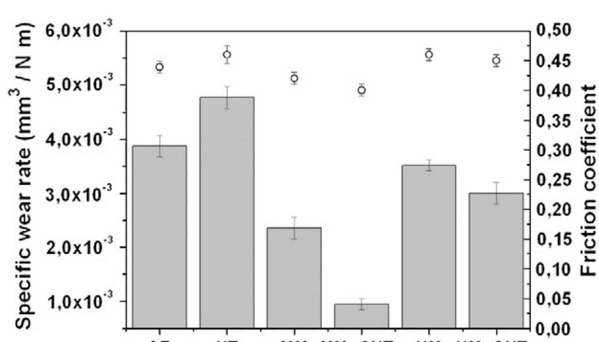

Fig. 3. Specific wear rate (columns) and friction coefficient (circles) of the samples tested (AR: as-received magnesium alloy; HT: heat-treated magnesium alloy; MM: mechanically mixed coating; MM + CNTs: mechanically mixed coating reinforced with carbon nanotubes; UM: ultrasonic mixed coating; UM + CNTs: ultrasonic mixed coating reinforced with carbon nanotubes).

the sintering of the sol–gel coatings cause the coarsening of the hardening precipitates, β-phase particles (Mg_7Zn_3(RE) and Mg_{12}RE) of nanometric size and finely dispersed in the magnesium matrix during the T5 treatment [16], and the subsequent lost of hardness and other mechanical properties such as tensile strength and yield strength. On the other hand, the deposition of the sol–gel coating caused a significant reduction of the wear rate. With MM coatings were obtained reductions of 39% as compared with the AR sample, and of 51% as compared with a substrate in the heat treated state, i.e. the HT one. The ultrasonically mixed coating caused a reduction of the wear rates of 9.3% and 18.9% as compared with the as-received and the heat treated substrates, respectively.

Wear rates reduced further when CNTs were added to the coatings with values that were 59.4% for the mechanically mixed coatings reinforced with CNTs and of 14.5% for the ultrasonically mixed coatings reinforced with carbon nanotubes as compared with the unreinforced mechanically mixed and ultrasonically mixed coatings and, respectively. The results show that the global reduction in the wear rate was 80% for the mechanically mixed coatings reinforced with CNTs as compared with the substrate in the same heat treated conditions and of 76% respect to as-received condition.

3.3. Wear mechanisms

3.3.1. Uncoated samples

The SEM image of the worn track of the WE54 in the as-received state showed many aligned grooves in the sliding direction (Fig. 4a) and, in some zones, detached material from the surface was also observed (Fig. 4b). These two morphologies evidenced the simultaneous action of abrasive and surface fatigue wear mechanisms. For the heat treated sample, the size and number of the abrasion lines strongly increased (Fig. 4c) and deformation and detachment of material from the surface was more frequent and with bigger size (Fig. 4d). In addition, a strong peak of oxygen appeared in EDX spectrum of the worn surface (inset in Fig. 4d) indicating the presence of an oxidative mechanism, which contributed further to the wear deterioration of the HT sample. It is important to state that the role played by oxidation in these samples was less important than in many other magnesium alloys such as ZE41A [17] or AZ91 [18].

Wear debris of the as-received WE54 magnesium alloy was also analyzed by SEM and a mixture of particle morphologies was observed. There was ribbon-like strip debris (Fig. 5a) indicating the presence of cutting abrasion, and also lathy strip debris indicating the presence of a delaminating mechanism by surface fatigue, with the crack propagation in the detached particle can be clearly seen (Fig. 5b).

3.3.2. Coated samples

At low magnifications, the SEM image of the wear track of substrate coated with the mechanically mixed layers showed the presence of very thin grooves (Fig. 6a), revealing that the abrasive wear mechanism contribution decreased. At higher magnification, the coating was still visible and it was nearly not degraded, as its presence could be only demonstrated by the presence of cracks in it (Fig. 6b). Two types of cracks were visible: big delaminated ones elongated in the sliding direction in zones where the deepest grooves concentrated (arrow in Fig. 6b) and small cracks at its vicinity (circled zone). From its morphology, it seems that the growth and coalescence of these small cracks gave rise to the big detachments. On the other hand, the silica coating present after the wear test was still protecting the magnesium alloy substrate from the action of the counterbody. This indicates that, although silica is a brittle ceramic coating, it still presents good inner compaction, and that high adherence to the substrate of the MM coating was achieved. In the wear debris of the MM coating (Fig. 6c) only a small number of particles were observed and EDX spectrum confirmed that they were silica platelets (inset in Fig. 6c). These platelets corresponded in size with the delaminated silica parts of the coating.

The wear track of the substrate coated with the mechanically mixed layers reinforced with carbon nanotubes revealed a milder wear process (Fig. 7a). Minor detachment of the coating was observed. The most of the sol–gel remained in the wear track, as the presence of the cracks in

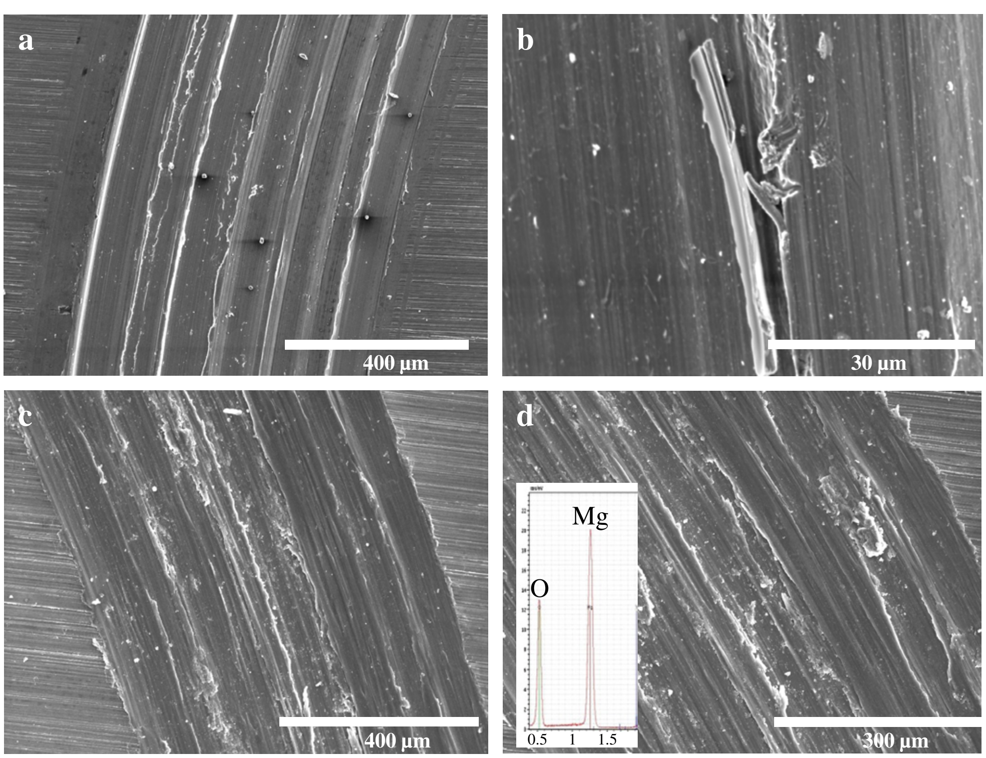

Fig. 4. SEM micrographs of the wear track of: (a) as-received WE54 alloy general view; (b) detail.; (c) wear track of heat treated WE54 substrate; (d) detail; (inset) EDX of the worn track.

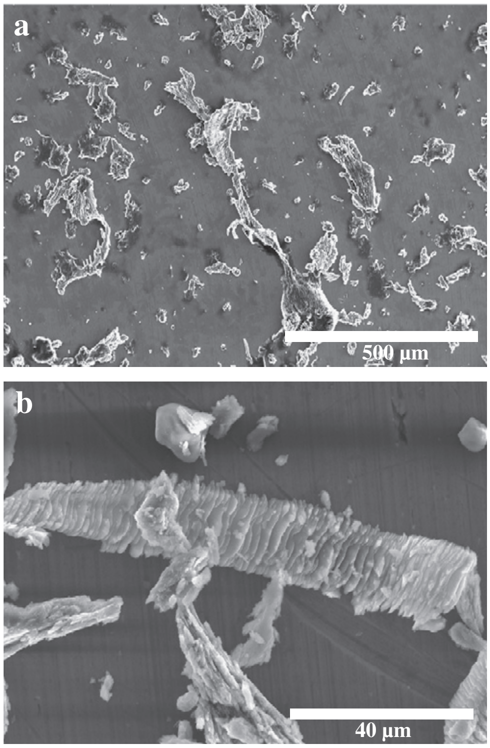

Fig. 5. Wear debris of the as-received WE54 alloy; (a) general view; (b) detail.

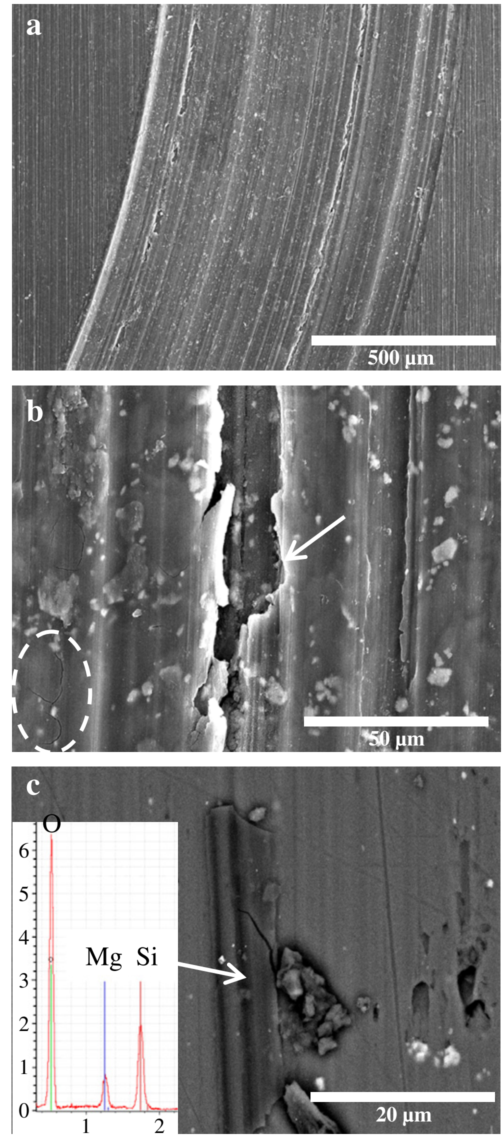

Fig. 6. SEM micrographs of the unreinforced MM sol–gel coating: (a) general view of the wear track; (b) detail of the wear track with coating cracking arrow marked; (c) wear debris and its EDX inset.

the coating suggests (Fig. 7b) and as it has been verified by EDX (inset in Fig. 7b). At higher magnifications it can be appreciated that there were many CNTs in the surface of the coating (Fig. 7c). They were clearly visible in some parts of the worn coating, suggesting that some of the coating has been removed although many CNTs have remained in the non-detached part of the coating. This indicates that a pull-out mechanism took place but that the CNTs were adequately joined to the remaining coating (Fig. 7d).

The diameter of the CNTs at the surface was ~70 nm, while its diameter in the as-received condition was 9.5 nm. This indicates the formation of a SiO_2 layer around the CNTs, facts also seen in the TEM images and EDX analyses (Fig. 7e) of the MM + CNT coatings. This silica promoted by the –OH functionalization of the CNTs, may have helped to the integration of the CNTs to the silica matrix of the coatings and allowed the load transfer between the CNTs and the silica layer.

Fig. 7d shows the presence of some CNT that are connecting two parts of the worn ceramic coating in which a crack was formed. This indicates that bridging mechanisms were taking place in the coating and that a good load transfer from the matrix to the nanoreinforcement is also occurring.

The nanoreinforcement was well distributed in the ceramic coating and was locking the cracks propagation by bridging mechanism and avoiding subsequent spalling of the coating caused by mechanical fatigue processes. The reduction in the friction coefficient suggested that the CNTs would also probably bear some part of the cyclic load because of its sliding and rolling capability in response to shear forces [19] as well as the CNTs would also reduce the strength of the interaction with the contacting couple during the wear process because of the closed tubular structure of the graphene sheet [20].

SEM analyses of the wear debris of the substrate coated with the reinforced mechanically mixed layers revealed silica platelets which were smaller than for the unreinforced MM coating and which were also in a smaller number (Fig. 7f). This confirms the higher toughness of the CNT-reinforced coating, which provides higher wear protection to the magnesium substrate.

The unreinforced and reinforced ultrasonic mixed coatings presented worse wear resistance and higher friction coefficient than the other coatings tested, with values only slightly better that those of the bare magnesium alloy (Fig. 3). Fig. 8 collects the wear track of these two coatings. The coatings were not present in the surface of the worn track at the end of the test presumably by their lower fracture toughness [11,14], which eased the removing of the coating after the first instants of the wear test and exposing the substrate to the wear action of the pin. Therefore, abrasive, delaminating and oxidative (oxidized zone arrowed in Fig. 8b) were again the predominant wear mechanisms, as in the case of the as-received and of the heat treated substrates.

The wear behaviour of the coatings correlates well with other works that have evaluated that the incorporation of CNTs to the MM coatings increases the fracture toughness of the coatings by 24%, mainly by the bridging mechanism of the CNTs [11] as those observed in the SEM micrographs of the wear track. In the unreinforced MM coatings, previously discussed, it was observed that the main mechanism for the progressive loss of coating during the test was brittle fracture. The addition of the CNTs resulted in the reduction of the specific wear rate in 30% respect to the unreinforced MM coatings

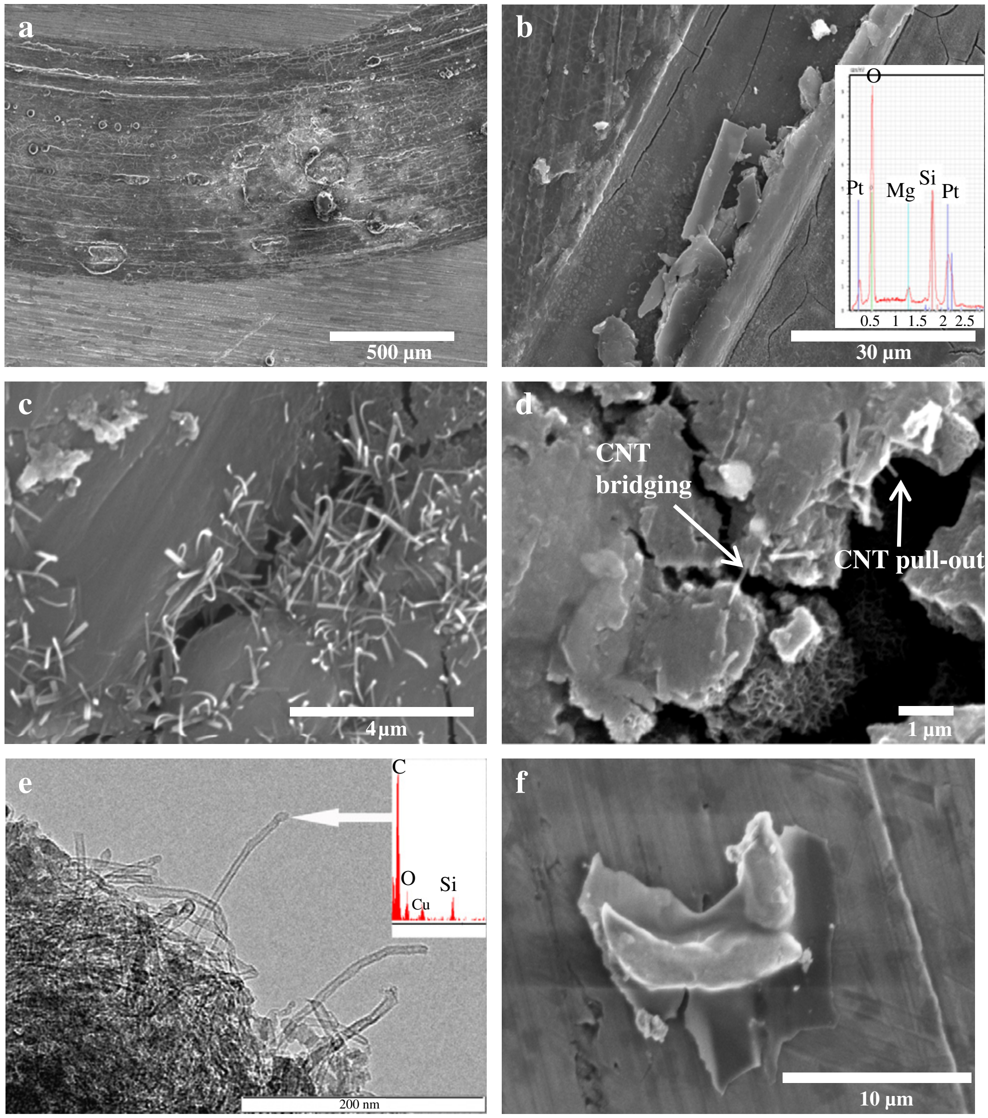

Fig. 7. SEM micrographs of mechanically mixed CNT-reinforced sol–gel coating: (a) general view of the worn track; (b) general view of the coating and EDX spectrum inset; (c) and (d) details of the worn track with the break of the coating and the presence of the carbon nanotubes ; (e) TEM image of the coating and EDX spectrum of a CNTs; (f) wear debris.

and a total reduction of 76% and 80% respect to AR and HT magnesium substrates, respectively.

On the other hand, the fracture toughness of the ultrasonically mixed coatings hardly increased [11] and was in all cases below that of the unreinforced mechanically mixed coatings. In this case, this allowed the removing of the coating from the sample surface and avoided wear protection but for the first metres of the test, causing only a small reduction of the wear volume for the tested length.

The fabrication method of the *sol*, mechanical mixing or ultrasonic mixing, has been proved to have an extremely influence in the final mechanical properties – elastic modulus, hardness and toughness as presented in [11] and also in the wear resistance – of the unreinforced and CNT-reinforced sol–gel silica coatings. This fact is due to the differences in the inner consolidation of the coatings obtained by both fabrication methods. The mechanical mixing of the *sol* lead to well consolidated coatings (Fig. 1). But, as it is clearly seen in Fig. 2, the ultrasonication of the *sol* leads to coatings with low inner densification, especially in the case of the CNT-reinforced ones, with high level of porosity and a sponge-like structure [11]. The lack of consolidation of the silica matrix in the ultrasonically mixed coatings may have been caused by the acoustic cavitations' bubbles formed by the ultrasonic treatment that speeds up hydrolysis and condensation reactions during the *sol* formation [21]. In the absence of CNTs, ultrasonic treatment could have only accelerate the gelification of the coating, lead to some lack of densification in the UM coatings (Fig. 2a). But in the presence of CNTs, it seems that the nanotubes have acted as nuclei for the gelification of the sol–gel, accelerating the formation of a silica layer around them and causing the formation of voids in the zones of the gel around the coated nanotubes. Afterwards, the subsequent sintering step cannot form a dense ceramic layer, giving rise to the observed UM + CNT morphology of the coating (Fig. 2c). In the case of the mechanically mixed coatings, the low energy introduced in the *sol* makes that the hydrolysis and condensation reactions take place at the proper speed and as a consequence a final coating, unreinforced or CNT-reinforced, with high inner consolidation is obtained.

4. Conclusions

The sol–gel route is a suitable technique to fabricate dense and free of defects silica coatings reinforced with carbon nanotubes on the surface of WE54 magnesium alloy. The main wear mechanisms revealed in the case of the bare magnesium alloy were abrasion and delamination. All the sol–gel silica coatings studied in this work led to a decrease in the

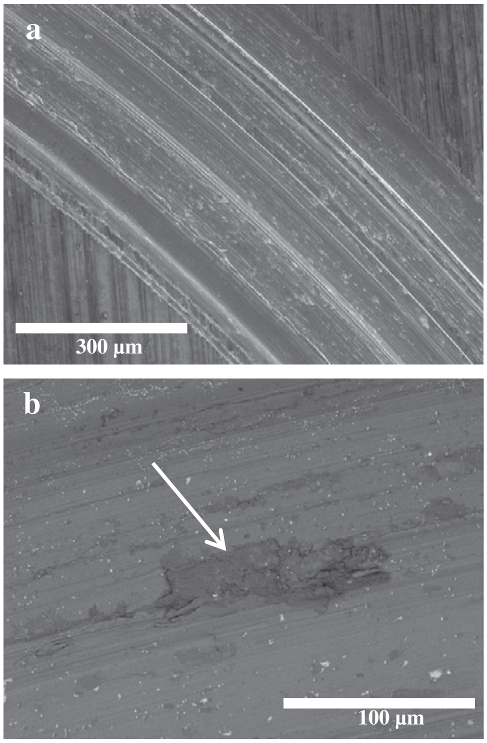

Fig. 8. SEM micrographs of ultrasonically mixed and CNT-reinforced sol–gel coating: (a) general view of the worn track; (b) Backscattered micrograph of a detail of the worn track.

specific wear rate because of a softened of the previously mentioned wear mechanisms.

The wear resistance of the silica coatings depended of the fabrication route, because this conditioned the inner densification of the coatings, and also of the addition of the carbon nanotubes, especially when mechanical mixing procedure was used. UM coatings slightly reduced the wear rate, but this reduction was not as important as in the case of MM coating because lack of inner compaction of the layer. The addition of CNTs to some extent (0.1 wt.%) improved the wear resistance of the coating.

Mechanical mixing is the most appropriated process for the formation of protective wear sol–gel coatings, obtaining a reduction in the specific wear rate of 39% over the bare substrate and of 51% over the heat treated magnesium alloy. Addition of 0.1 wt.% of CNTs to the MM coatings slightly reduces the friction coefficient, but reductions of 76% and 80% over the bare and heat treated WE54, respectively, were obtained. Crack bridging and pull-out of the CNTs were the mechanisms responsible for the toughening of the MM + CNT ceramic coating and, therefore, for the improvement of the dry sliding wear resistance.

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