Thin Solid Films 519 (2011) 7904–7910

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

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

A.J. López *, A. Ureña, J. Rams

Dept. de Ciencia e Ingeniería de Materiales, ESCET, Universidad Rey Juan Carlos, C/ Tulipán s/n, Móstoles 28933 Madrid, Spain

ARTICLE INFO

Article history:
Received 11 November 2010
Received in revised form 17 May 2011
Accepted 28 May 2011
Available online 6 June 2011

Keywords:
Sol–gel coating
Carbon nanotubes
Ceramic matrix composite
Magnesium alloys
Wear

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

---

* Corresponding author. Tel.: +34 4888083; fax: +34 914888150.
E-mail address: antoniojulio.lopez@urjc.es (A.J. López).

0040-6090/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2011.05.076

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 $22\times22\times2\ \mathrm{mm}^3$. 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 $72\pm2\ \mathrm{HV}_2$; 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:

$$\frac{V}{L} = kW \tag{1}$$

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