Surface & Coatings Technology 352 (2018) 411–419

Contents lists available at ScienceDirect

Surface & Coatings Technology

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

Preparation and tribological properties of graphene oxide doped alumina composite coatings

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ARTICLE INFO

Keywords:
Graphene oxide
Al_2O_3
Coating
Electro-deposition
Wear resistance

ABSTRACT

In this paper, nickel matrix composite coatings incorporated with graphene oxide (GO) and graphene oxide doped alumina (GO-Al_2O_3) particles were fabricated through electro-deposition. Given the excellent mechanical properties of GO and Al_2O_3, excellent anti-wear properties are expected when embedding GO-Al_2O_3 particles in Ni matrix. For this purpose, nano-Al_2O_3 particles were first grafted on GO surfaces to fabricate the GO-Al_2O_3 particles. The structure, composition and morphology of the GO and GO-Al_2O_3 were characterized by XRD, FT-IR, SEM, TEM and BSE, respectively. The results revealed that nano-Al_2O_3 particles were successfully doped on GO surfaces. The tribological performances of the coatings were studied under dry sliding condition. It was found that the wear rate of Ni/GO composite coating declined by 20.9% compared to pure Ni coating. The results also indicated that the Ni/GO-Al_2O_3 coatings with higher amount of Al_2O_3 content presented the lower friction coefficients and better anti-wear behaviors. The superior tribological properties of the Ni/GO-Al_2O_3 coating were attributed to the synergistic effects of GO and Al_2O_3.

1. Introduction

Failure of most engineering components occurs at the surface, corrosion begins from the surface, fatigue cracks propagate inwards from the surface and wear also occurs on the surface [1]. Surface coating is a typical method of surface engineer, and it plays an important role to improve the service performance of components.

Composite electroplating, as a coating technology, is a method by which fine particles are co-deposited with a metal or alloy matrix [2]. During the fabrication process, insoluble particles are suspended in a conventional plating electrolyte and captured into the growing metal coatings. The micro-hardness, yield strength tensile strength [3], anti-corrosion [4,5] and oxidation [6] of the coatings are improved by the presence of the second-phase particles. Wear resistance is another important application for the co-deposition coatings. The traditional dispersed phase can be hard oxide (SiO_2 and Al_2O_3), carbides (SiC and WC), diamond or polymer (PTE and PTFE) [7–9]. The incorporation of hard particles act as a load-bearing element [10] and the polymers usually work as lubrication phase [8].

Recently, graphene has attracted tremendous interests in tribological area [11–13]. However, it contains rare surface functional groups with limited dispersibility in solvents [14]. The hydrophilic graphene oxide (GO) is an oxygenated derivative of graphene and it can be easily dispersed in polar solvents, which made it a facile material to fabricate composite coatings by the electrochemical technology [15]. Similar to graphene with the layer structure, GO is expected as a good solid self-lubricant. The composite coatings, co-depositing GO as a second-phase, exhibit excellent tribological performances. Liu et al. [16] found that the incorporating GO greatly improves the friction reduction and wear resistance of the Co/GO composite coating. Algul et al. [17] reported that the increment of GO content in the Ni/GO coatings result in significant increase in the micro-hardness and the wear resistance, as well as a decrease in friction. Xue et al. [18] introduced Ni/GO composite coatings produced by electro-deposition under supercritical carbon dioxide. This Ni/GO film presents lower surface roughness and smaller grain size. Meanwhile, the incorporations of GO in the coating improve the wear resistance and friction reduction. The tribological performances of electroless Ni−P coatings are improved when embedding GO [19] and the subsequent research found that appropriate heat treatment can also enhance the micro-hardness as well as wear resistance of Ni-P-GO coatings [20]. Usually, the wear rate of the composite coatings decreases with the enhancing of GO content.

In this paper, combined with the excellent lubricity of GO and load bearing capacity of hard particle, attempt has been made to develop GO doped nano-Al_2O_3 powder (GO-Al_2O_3) as co-depositing particles. The properties of the GO and GO-Al_2O_3 were characterized. Composite

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https://doi.org/10.1016/j.surfcoat.2018.08.042
Received 2 October 2017; Received in revised form 11 August 2018; Accepted 13 August 2018
Available online 14 August 2018

coatings of Ni/GO and Ni/GO-Al_2O_3 were prepared via electro-deposition and the tribological performances of the coatings were evaluated. The effect of the ratio relation between the GO and Al_2O_3 hard particle in the composite coatings was also discussed.

2. Experimental section

2.1. Synthesis of GO and GO-Al_2O_3

GO was prepared from purified natural graphite by a modified Hummer's method that involves a strong oxidation of graphite powder with H_2SO_4/$KMnO_4$ and exfoliation process in solution. The specific procedure can be found in ref. [21, 22]. The GO-Al_2O_3 powder was obtained through a self-assembling process under the effects of electrostatic interaction. Briefly, 0.1 g of GO was dispersed in 50 mL deionized water. And 1.0 g of commercial Al_2O_3 powder with the size of about 50 nm was added to 100 ml acetic acid solution with the concentration of 0.5 mol/L and the pH value was about 3–4. The solutions were both dispersed using ultrasonic treatment for 1 h. Subsequently, the GO suspension was slowly added to the Al_2O_3 under continuous stirring. Then, the mixture was moved to oil bath and heated to 120 °C for 24 h. After that, the suspension was filtered and washed with purified water to remove by-products. The dried GO-Al_2O_3 powder was ground by ball-milling in vacuum for 12 h at the speed of 80 rpm. During the experiment, the ratio of GO: Al_2O_3 was reached by changing the mass ratio of GO and Al_2O_3 in the suspension. Produced GO-Al_2O_3 composites in this paper are characterized with the following mass ratio (GO: Al_2O_3) of 1:1, 1:2, 1:5 and 1:10, respectively.

2.2. Electro-deposition

Nickel (Ni), composite (Ni/GO) and (Ni/GO-Al_2O_3) coatings were fabricated using the electro-deposition method. The volume of the deposition bath is about 500 mL and the distance between anode and cathode is controlled at 5 mm. And the pure Ni plate is used as anode. The composition of Watts bath and specific experimental conditions are shown in Table 1. Prior to the deposition, GO and GO-Al_2O_3 powders respectively, were ultrasonically dispersed in the plating bathes for 15 min. A copper plate with Φ30 × 3 mm was used as the substrate and its surface was mechanically polished to Ra 0.1–0.15 μm. The substrate was then activated for 20 s in a mixed acidic bath followed by ultrasonic cleaning with acetone and deionized water for 5 min, respectively. All electroplating times were fixed at 120 min. After that, the final coatings were ultrasonically cleaned in acetone and washed with running water.

2.3. Characterizations

The structures of the GO and GO-Al_2O_3 powders were detected via X-ray diffraction using an X'Pert Pro diffractometer (Panalytical) at a scan rate of 2°/min. Fourier transform infrared (FT-IR) spectra of the samples dispersed in KBr pellets was recorded on an infrared spectroscopy (NEXUS870, NICOLET). The morphology of the powder samples were determined using a transmission electron microscope (TEM, JEOL JEM-200CX) and a scanning electron microscopy (SEM, Hitachi S3400). EDS and BSE were used to further confirm the component and distribution of GO-Al_2O_3 powder.

The cross-sectional microstructures and surface morphology of the coatings were observed by a scanning electron microscopy (SEM, JSM-6480LV) and the EDS analysis was performed to detect the element content. The elementally X-ray maps from the cross-section of Ni/GO-Al_2O_3 composite coating were detected using an energy dispersive X-ray spectrometer. The micro-hardness of the coating surfaces was determined using a Vicker's microhardness indenter with a load of 100 g for 10 s. At least ten points along the radius direction were tested and the final hardness was an average of the ten points.

Ball-on-disc tests were performed to determine the anti-wear properties of the coatings under dry condition. A standard 304 stainless steel ball with a diameter of 4.0 mm was used as the upper specimen. All tests were carried out under a 2 N load with a sliding speed of 0.1 m/s. The wear topography of the coatings was observed by SEM. The volumetric loss of the coatings after friction test was measured using a surface profilometer (Bruker, ContourGT-K) and the wear rates were calculated based on the volumetric loss.

Table 1
Experimental condition for the electro-depositions.

Compositions and conditions	
Nickel sulfate, $NiSO_4·6H_2O$ (g/L)	300.0
Nickel chloride, $NiCl_2·6H_2O$ (g/L)	45.0
Boric acid, H_3BO_3 (g/L)	40.0
Sodium dodecyl sulfate (g/L)	0.5
Saccharin sodium (g/L)	1.0
Particle concentration (g/L)	0, 0.5
Temperature (°C)	45
pH	4 ± 0.5
Current density (A/dm^2)	2
Magnetic stirring speed (rpm)	200

3. Results and discussion

3.1. XRD analysis

Fig. 1 shows the XRD patterns of GO and GO-Al_2O_3 powders. The GO depicts a strong and broad diffraction peak at 2θ of 9.62° and a corresponding d-spacing of 0.91 nm, which is due to the presence of oxygen functionalities in the basal plane of natural graphite [23]. A mild and broad peak at around 20° suggests the thorough graphitic crystal structures. According to the XRD pattern of GO-Al_2O_3 powder, the crystalline structure of alumina is corundum and the peak at 10° belongs to GO. Apart from corundum and GO, no other phase was detected.

3.2. FT-IR analysis

Fig. 2 shows the FT-IR data of GO-Al_2O_3 composite powders, and the pure alumina powder without GO was also given for comparison. The spectrum of GO-Al_2O_3 shows the representative groups of Al_2O_3 and GO. The characteristic absorption of Al—O bond at 640 cm^{-1} was observed for both GO-Al_2O_3 and Al_2O_3 [24]. The presence of oxygen-containing functional groups at 1230 cm^{-1}, 1567 cm^{-1} and 1720 cm^{-1}

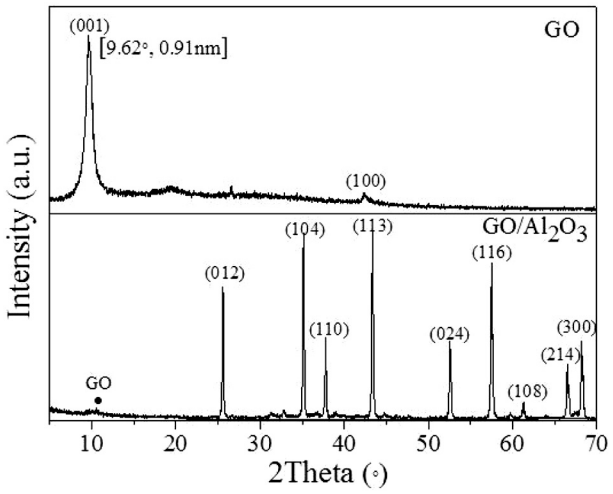

Fig. 1. X-ray diffraction (XRD) patterns of GO and GO-Al_2O_3 powders.