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Microstructure and properties of duplex (Ti:N)-DLC/MAO coating on magnesium alloy

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ABSTRACT

Ti and N co-doped diamond-like carbon ((Ti:N)-DLC) film was deposited on the MAO coated substrate using a hybrid beam deposition system, which consists of a DC magnetron sputtering of Ti target and a linear ion source (LIS) with C_2H_2 and N_2 precursor gas. The microstructure and properties of the duplex (Ti:N)-DLC/MAO coating were investigated. Results indicate that the (Ti:N)-DLC top film with TiN crystalline phase was formed. Ti and N co-doping resulted in the increasing I_D/I_G ratio. The significant improvement in the wear and corrosion resistance of duplex (Ti:N)-DLC/MAO coating was mainly attributed to the increased binding strength, lubrication characteristics and chemical inertness of (Ti:N)-DLC top film. The superior low-friction and anti-corrosion properties of duplex (Ti:N)-DLC/MAO coating make it a good candidate as protective coating on magnesium alloy.

1. Introduction

Magnesium and its alloys are increasingly used in the automotive industry because of the flexibility in fabrication and high strength-to-weight ratio [1]. Unfortunately, their practical applications have been limited due to the poor wear and corrosion resistance [2]. One of the effective ways to overcome these drawbacks is to coat a protective layer with high wear and corrosion resistance. Recently, microarc oxidation (MAO), a simple and novel surface technique, has been widely used to prepare ceramic oxide coatings, having relatively high hardness and excellent adhesion strength, on the surfaces of valve metals and their alloys, e.g., Al, Mg, Ti, etc. [3–6]. However, such MAO coatings on magnesium alloy often exhibited a relatively high friction coefficient against many counter materials during the dry sliding processing, and also suffered from corrosion failure due to the micropores distributed on the coating surface [7–10]. Therefore, a design of duplex treatment combined MAO and a low friction layer was considered in this work.

As diamond-like carbon (DLC) film is well known for its high hardness, low friction, excellent wear resistance and chemical innerness, it may be able to counterbalance the disadvantages of magnesium alloy [11,12]. For such DLC film/substrate system, the key breakthrough is its weak adhesion to the soft substrate because of the mechanical incapability and high internal stress [13–15]. The previous study has proven that metal film as an interlayer or metal doping could significantly improve the adhesion of DLC film to the magnesium substrate [16–19]. However, these coatings had a poor corrosion resistance due to the existence of through-thickness defects in the films and the large difference between interlayer and the Mg substrate in galvanic series [20–22].

Our previous work demonstrated that the MAO coating as a interlayer of DLC film could significantly improve the corrosion and wear resistance of the Mg substrate, which was attributed to the restrained corrosion process between the interlayer and substrate for the thick MAO coating and a low friction coefficient of DLC top thin film [23]. Meanwhile, metal doping seems a potential method to further improve the properties of DLC film efficiently [21].

Based on the above consideration, in this work, Ti and N co-doping is employed to form the DLC film with TiN crystalline phase on the MAO coating surface, which is expected to increase the binding force. Otherwise, the corrosion process induced by the doping metal (such as Ti) may be restrained due to the formation of TiN crystalline phase in the DLC film. In addition, it is known that TiN has the high thermal stability. If the microstructure of DLC film with TiN crystalline phase was formed, it might increase the thermal stability of the coating, which could further improve its tribological properties [24]. Subsequently, in this study, the microstructure, tribological and corrosive properties of the duplex (Ti:N)-DLC/MAO coated AZ80 Mg alloy are systematically investigated.

2. Experimental procedure

The AZ80 Mg alloy substrate (mass fraction: Al 7.8–9.2%, Mn 0.15–0.5%, Zn 0.2–0.8%, Mg balance) discs (Φ20 mm × 5 mm)

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Table 1
Surface roughness and thickness of the coatings.

Films	Thickness/nm	Ra/nm
DLC	480.4	0.92
Ti-DLC	556.4	1.87
(Ti:N)-DLC	500.6	2.69

were mechanically polished to an average surface roughness of Ra ≈ 23.5 nm, followed by ultrasonic cleaning in acetone for 20 min. The fabrication of the duplex MAO/(Ti:N)-DLC coatings on AZ80 Mg alloy discs was performed by two steps including MAO and ion beam deposition technique. In MAO preparation, the ceramic coating was fabricated in an aqueous solution containing 5 g/L sodium silicate (Na_2SiO_3), 10 g/L potassium hydroxide (KOH), and 8 g/L potassium fluoride (KF), by a constant voltage mode on a direct-current (DC) pulsed electrical source with the frequency of 500 Hz and the duty cycle of 5%. The oxidation time was 3 min and the thickness of ceramic coating was 5 μm. The DLC, Ti-DLC and (Ti:N)-DLC top films were prepared on the MAO coated samples and Si substrates by a hybrid ion beam deposition system (including a linear ion source (LIS) and a magnetron sputtering source) as shown in the literature [25]. The base pressure was evacuated to a vacuum of 2×10^{-5} Torr. Hydrocarbon gas (C_2H_2) and N_2 (C_2H_2/N_2 ratio 8 sccm:7 sccm) were introduced into the linear ion source to obtain the hydrocarbon ions for (Ti:N)-DLC deposition. The Ar sputtering gas was supplied to the magnetron sputter for Ti doping, as the sputtering current of 2.5 A and Ar flux of 70 sccm. Typical values of LIS voltage and current were 1100 ± 20 V and 0.15 A, respectively. The DC power supplied to the sputtering gun was about 1050 W (420 V, 2.5 A). The C_2H_2/Ar ratio was controlled at 15 sccm:70 sccm as the Ti-DLC film was deposited. The DLC film was deposited as the C_2H_2 gas flux was 15 sccm. A negative pulsed bias voltage of −100 V was applied to the substrate. The deposition time was 40 min. The surface roughness and thickness of the films are summarized in Table 1.

The surface morphology of the duplex coating was examined using atomic force microscopy (AFM) and field emission scanning electron microscope (FESEM). Energy dispersive X-ray spectrometer (EDS) was used to test the element distribution of the coatings after friction tests. Raman spectroscopy with an incident Ar^+ beam at a wavelength of 514.5 nm was used to measure the atomic bonds of films. An X-ray photoelectron spectroscopy (XPS) with Al (mono) Kα irradiation at pass energy of 160 eV was used to characterize the chemical bonds of the films. The binding energies were referenced to the C 1s line at 285.0 eV. High-resolution transmission electron microscopy of the films was performed on Tecnai F20 electron microscope operated at 200 keV with a point-to-point resolution of 0.24 nm. The TEM specimens were prepared by peeling off the films from the NaCl crystalline substrates, which were dissolved in deionized water. The adhesion of the films to the AZ80 substrates was assessed by a scratch tester performed on a Rockwell diamond indenter with a conical tip of 0.2 mm in radius. The normal load of the indenter was linearly ramped from the minimum to the maximum during scratching. Here, the minimum load and the maximum load were 1 N and 15 N, respectively. In the test, the scratch length was 3.00 mm and the scratch speed was 0.2 mm/s. The wear resistance of the coated samples was assessed using ball-on-disk wear tests. During the tests, a 1 N contact load was applied on the samples through a steel ball (SUJ-2, HRC60) with a diameter of 6 mm. The samples (discs) were tested when they rotated at a constant speed of 0.1 m/s. The diameter of the sliding track was 2 mm. For the electrochemical investigation, the experiments were performed on an Autolab Pgstat302 advanced electrochemical system, using the conventional three-electrode technique. The coated sample was masked by epoxy resin with the surface area of 0.5 cm^2 exposed in 3.5 wt.% NaCl solution. These tests were carried out at 1 mV/s at room temperature.

3. Results and discussion

3.1. Coating characteristics

The bonding natures of samples were investigated using XPS analysis. Fig. 1(a) shows the deconvolution of N 1s peak of the (Ti:N)-DLC top film, giving two peaks at 396.6, 398.3 and 400.4 eV, which are assigned to TiN, —N= and C—N bonds, respectively [26,27]. The deconvolution of Ti $2p_{3/2}$ and Ti $2p_{1/2}$ peaks of (Ti:N)-DLC top film was shown on Fig. 1(b), which gives four peaks at 455.481, 457.581, 461.20 and 463.46 eV. For the deconvolution of Ti $2p_{3/2}$ peak, it gives two peaks at 455.481 and 457.581 eV, which are assigned to TiN and TiO_2 bonds. The deconvolution of Ti $2p_{1/2}$ peak also gives two peaks at 461.20 and 463.46 eV, which are also assigned to TiN and TiO_2 bonds. So it can be deduced that TiN was formed in the (Ti:N)-DLC film. Furthermore, the microstructure of this film is analyzed by TEM. Fig. 2 shows the plan-view TEM images and corresponding sectional area electron diffraction (SAED) patterns of the (Ti:N)-DLC film. It is different from the pattern of the pure DLC film representing the typical amorphous structure [21]. The crystalline diffraction ring-like are observed in Fig. 2(b), which is different from the pattern of pure DLC film representing the typical amorphous structure [21]. Those rings could be identified to be the (2 0 0) and (2 2 0) reflections of the face-centered (FCC) titanium nitride structure with the interplanar spacings of 0.213 nm

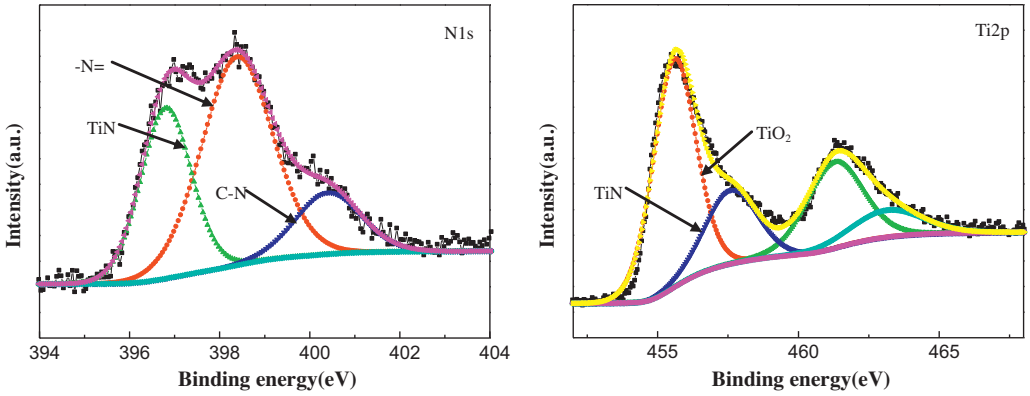

Fig. 1. Typical N 1s and Ti 2p high-resolution XPS spectras of the (Ti:N)-DLC film. (For interpretation of the references to color in figure legend, the reader is referred to the web version of the article.)