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Oleylamine/graphene-modified hydrotalcite-based film on titanium alloys and its lubricating properties

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ABSTRACT

A novel structured hydrotalcite-based film was synthesized on TC4 titanium alloy by facile hydrothermal method, and then modified with graphene and oleylamine. The structure, morphology, composition, wetting and lubricating properties of the as-prepared films were investigated. The oleylamine/graphene-modified hydrotalcite-based film (HT-OAm/GN) exhibited lower friction coefficient and longer wear life. The enhancement of wear properties was attributed to the synergistic effects of the hard and lubricating graphene layer and oleylamine molecules.

1. Introduction

Environment-friendly and economic lubricants have attracted great concerns in the field of tribology. The research for novel materials and lubricants can potentially reduce friction and wear. In the past few years, a wide variety of layered materials, including MoS_2 [1,2], WS_2 [3] and multilayer graphene [4], were reported as solid lubricants owing to their layered structure and relatively weak van der Waals force between layers. The platelets in such structures are easy to shear and transfer to the worn surfaces to decrease friction and wear.

Hydrotalcite-like (HT) compounds as a new lubricant additive, are a family of attractive laminate-structure clays, and contain positively charge-balancing exchangeable anions in the interlayer [5,6]. HT compounds have a hexagonal layered crystal structure which are similar to graphite and MoS_2, leading to easy shear of crystal platelets. In the previous investigations, HT compounds exhibited excellent tribological properties as lubricant additives [7,8]. Two possible friction reducing mechanisms of HT compounds are the formation of tribochemical reaction film [9] and structure distortion of hydrotalcite during the friction process [10]. The benefits of HT compounds are the large numbers of hydroxyl groups existing on the surface of HT platelets, making it possible for surface organic modification [6].

Titanium alloys are widely applied owing to their distinguished properties such as high strength-to-weight, excellent corrosion resistance and good biocompatibility [11]. However, the high friction coefficients of titanium alloys result in poor wear resistance, thus decreasing the service life of machine components [12]. However, the conventional surface treatments such as hard coatings are limited in application because of their relatively high friction coefficient [13]. This work offers an effective and eco-friendly way to improve the tribological properties of titanium alloys. A novel structured HT-based film was fabricated by a facile hydrothermal method, and subsequently modified with graphene and oleylamine, aiming to reduce the friction coefficient and wear rate of TC4 titanium alloy.

2. Experimental

A 60 ml mixed solution of $Zn(NO_3)_2{\cdot}6H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$ ($[Zn^{2+}] = 0.15$ M, $[Al^{3+}] = 0.05$ M) was added 12 mmol NH_4F and 30 mmol $CO(NH_2)_2$ under stirring for 15 min, and then transferred into a 100 ml autoclave. A cleaned TC4 plate was vertically immersed in the solution and heated at 120 °C for 12 h (HT-based film was obtained). Subsequently, a graphene suspension was prepared by the mixed solvent (50 ml deionized water and 50 ml ethanol) with 0.03 g graphene under ultrasonic treatment for 24 h. Then the HT-based film was immersed vertically in the solution for 5 min and dried in an oven at 60 °C for 2 h (Graphene-modified HT film was obtained). Afterward, the as-prepared film was immersed in a mixture of oleylamine and

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ethanol (1:1) and heated at 45 °C for 2 h, and drying at 60 °C overnight (Oleylamine/graphene-modified HT film was obtained). The oleylamine-modified HT film, as those above, was additionally prepared as reference.

3. Results and discussion

Fig. 1a-b shows the SEM images of the HT-based film and the graphene-modified HT (HT-GN) film. Interestingly, two types of structures are clearly observed on the HT-based film: (a) on the bottom of the film, a nest-like structure is composed of interconnected hexagonal hydrotalcite nanosheets, which oriented almost vertically to the substrate surface; and (b) a flower-shaped structure, consisted of needle-like crystals, is formed on the top of the HT film. GAXRD pattern of the HT-based film is presented in Fig. 1c. Well-resolved reflections of typical HT phases are observed along with the reflections intrinsic to the titanium. The (003), (006), (009) and (110) characteristic reflections occur at around 10°, 20°, 35°and 60° respectively, attributed to the flower-like structure on the bottom of the film [14]. In addition, the reflections at 18.9°, 34.4° and 38.3° are attributed to the formation of $Zn(OH)_2$ [15]. This results indicate that the flower-shaped structure as observed in the SEM image is composed of $Zn(OH)_2$ crystals. Note that graphene nanoplatelets are observed on the surface of HT-GN film, as confirmed by Raman spectroscopy (Fig. 1d). The Raman spectrum of HT-GN film shows D band and G band at about 1358 cm^{-1} and 1586 cm^{-1}, respectively. The 2D band originating from second-order Raman scattering process appears at 2716 cm^{-1} [16]. The results demonstrate that the graphene is absorbed on the surface of HT-based film.

Fig. 2a-b shows the SEM images of the oleylamine-modified HT (HT-OAm) film and the oleylamine/graphene-modified HT (HT-OAm/GN) film. It is clear that an oleylamine layer is formed on the HT film. Compared with the HT-OAm film, the HT-OAm/GN film is more uniform and compact. In order to evaluate the surface modification of the HT films, ATR-IR spectroscopy was applied as shown in Fig. 2c. The spectra of all the films show typical absorption peaks of LDHs. The stretching vibration (ν_{O-H}) at 3435 cm^{-1} and the bending vibration (δ_{O-H}) around 1620 cm^{-1} are visible, which can be attributed to the water molecules and hydroxide groups in HT films [5]. As for the HT-OAm samples, the hydrocarbon stretching vibration at 2858 cm^{-1} and 2927 cm^{-1} (ν_{C-H}), and the bending vibration of methyl group at 1465 cm^{-1} (δ_{C-H}) are ascribed to the characteristic peaks of oleylamine molecules [6].

In Fig. 2d, the water contact angles of HT, HT-OAm, HT-GN and HT-OAm/GN films are 0°, 59.9°, 22.7° and 135.7°, respectively. The results illustrate that the HT-based film is superhydrophilic. Interestingly, the modification of oleylamine or graphene alone is limited to improve the hydrophobic property of the HT-based film, while the HT-OAm/GN film is much more hydrophobic owing to the more uniform and compact film.

The friction coefficient and wear rate of TC4 alloy and the specimens covered with HT-based films were measured under a load of 2 N with a fixed rotating speed of 200 rpm and a spin semidiameter of 3 mm, as shown in Fig. 3. HT-base films have low friction coefficient at the beginning of friction process along with suddenly increasing. It is indicated that the covered HT film is broken and the measured friction coefficient belongs to substrates. Oleylamine-modified samples appear friction coefficient lower

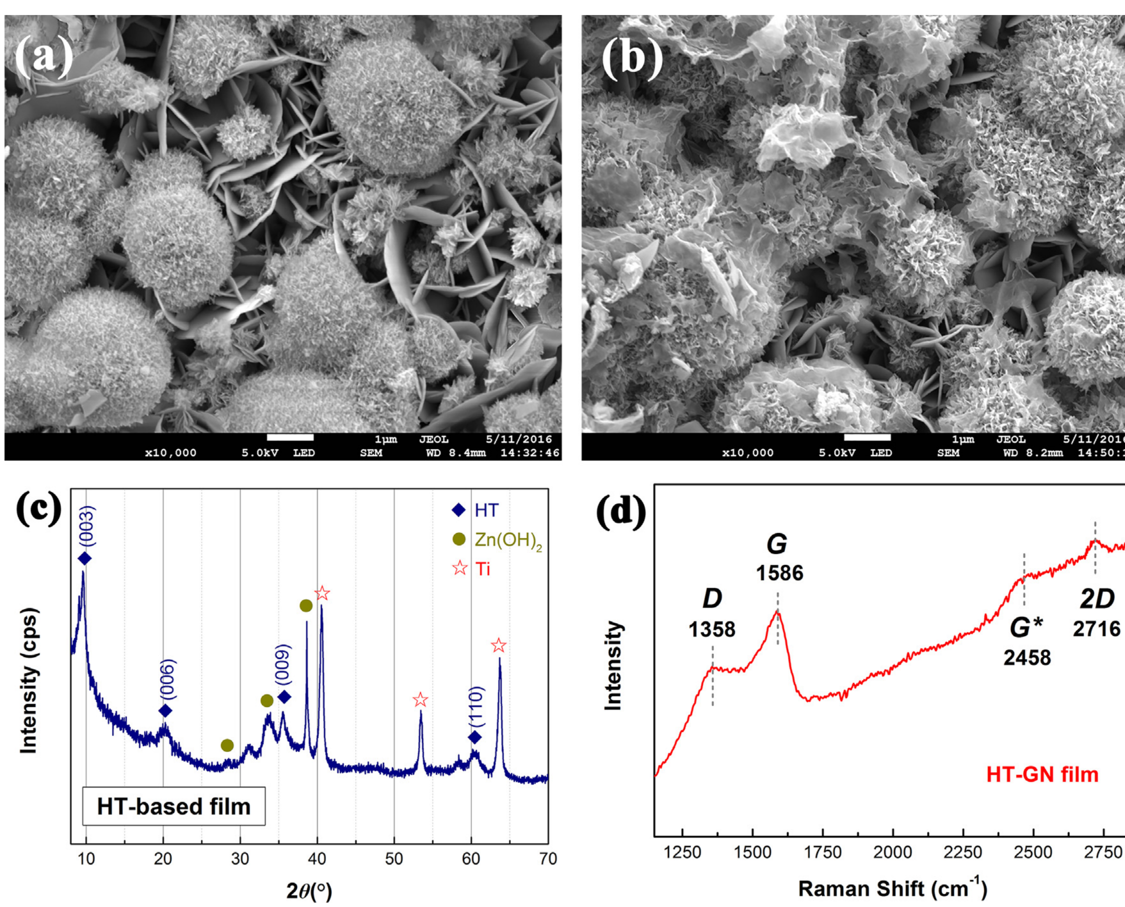

Fig. 1. SEM images of the HT-based film (a) and the HT-GN film (b); (c) The GAXRD pattern of the HT-based film; (d) Raman spectrum of the HT-GN film.