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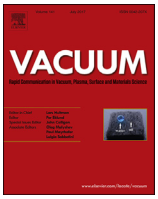

Microstructures and nano-mechanical properties of multilayer coatings prepared by plasma nitriding Cr-coated Al alloy

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ABSTRACT

A novel surface treatment combined with depositing Cr films followed by plasma nitriding was carried out on the surface of the 2024 Al alloy. Nano-grained Cr films were firstly deposited on the substrate surface by using magnetron sputtering, then plasma nitrided at 490 °C for 8 h under a gas mixture of 25% N_2+75% H_2. Microstructures and mechanical properties of the as-obtained coatings were characterized by using X-ray photoelectron spectrometer (XPS), X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM) and nanoindentation. Results showed that a nitride/aluminide multilayer coating was obtained due to N-Cr and Cr-Al diffusion reaction. The outside nitride layer consisted of mainly CrN with nano crystals. The inner aluminide layer was composed of Al_4Cr with nano lath-shaped structure and $Al_{18}Cr_2Mg_3$ with large rectangle crystals. The nitrided surface showed a remarkable increase in hardness (15.4 GPa) than that of the untreated Cr film (5.2 GPa). The high valves of H/E ratio (0.078) and H^3/E^2 ratio (0.094) indicated the better wear resistance and plastic deformation resistance for the nitride surface.

1. Introduction

Aluminum alloys are widely used in the aerospace and automotive industries for lightweight manufacturing, owing to their high specific strength and good mechanical formability [1,2]. However, the lack of surface hardness and wear resistance limits the extensive applications for aluminum alloys. Ceramic coatings like nitrides (TiN, CrN and their multi-component nitrides) and oxides (Al_2O_3) were mostly used to enhance the surface properties of Al alloys by various methods [3–6]. Due to the large difference of mechanical properties between the hard coating and the relative soft Al alloy, the coating/substrate match needs to be considered.

The transition layer design could be an efficient way to resolve the mismatch problem of hard/soft coating systems. Especially for the sputtering nitride coatings (TiN and CrN) by PVD method, soft pure metal, i.e., Ti or Cr was usually deposited as intermediate layer [7,8]. Similar method was also used for the diamond-like carbon (DLC) coating on the surface of pure Al alloy, with Ti as interlayer [9]. The adhesion is improved, but another problem occurs, that the inner stress increases with increasing the thickness of the deposited hard coatings. Thus, material researchers propose the composition-gradient coating to reduce the inner stress. Thick TiAlN coatings are fabricated on surface of Al-Si alloy by adjusting the nitrogen flow during deposition, gradient distribution of elements, hardness, and stresses across the coating thickness is achieved [10]. Thus, the transition layer with composition gradient may be a good choice to produce hard ceramic coatings on soft substrate.

As for Al alloys, surface alloying with transition metals (TM) like Cr, Ti, Ni and Fe could generate Al-TM based intermetallics such as Al_7Cr, Al_3Ti, Al_3Ni, and Al_5Fe_2 [11–13]. These intermetallics have relatively high hardness (300–500 HV), compared with the soft Al substrate, which can be used to improve the surface mechanical properties of Al substrate. In addition, these compounds show moderate modulus between ceramics and Al alloys. Thus, it provides an inspiring choice to use Al-TM based intermetallics as transition layer for nitride coatings on surface of Al. In our previous studies [14], combining thermo-diffusing titanium and plasma nitriding was conducted on the surface of 2024 Al alloy to produce

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$TiN_{0.3}$/Al-based intermetallic gradient coatings. Similar method was also employed on surface of Cu alloy to obtain TiN/Cu-Ti intermetallic coatings [15,16]. Both TiN and CrN has high hardness, but TiN exhibits a relatively high friction coefficient and high brittle tendency [17,18]. While Cr-based nitride coatings show good coating-to-substrate adhesion and relatively low wear, thus superior than Ti-based nitrides to be used on soft substrate such as aluminum and copper.

In the present study, gradient Cr-based nitrides/Cr-Al intermetllic coatings with high hardness are expected to enhance the surface properties of 2024 Al alloy. Due to the high affinity to nitrogen, pure Cr film is pre-deposited on surface of Al alloy, following by plasma nitriding treatment. Cr-N and Cr-Al reaction diffusion could be motivated simultaneously to produce nitriding and Cr-alloying layer on surface of 2024 Al alloy. The aim of the present study is to analyze the microstructure, chemical composition and phase structure of Cr-N and Cr-alloyed duplex coating. The detail microstructure and nanoindentation behavior of the duplex layers on the surface of 2024 Al alloy were investigated.

2. Experimental

2.1. Materials and coating process

The substrate material is 2024 Al alloy with chemical composition of 3.81 Cu, 1.40 Mg, 0.40 Mn, 0.40 Fe, 0.14 Zn, 0.22 Si, Ti < 0.05, Cr < 0.05 (in wt.%), and Al balance. Samples were cut to the dimensions of 20 mm in diameter and 4 mm in height, ground up to 2000 grid with silicon carbide paper, polished with diamond pastes and ultrasonically cleaned in acetone.

The duplex surface treatment involves two sequential procedures. Fig. 1 illustrates the schematic of the coating process. Firstly, pure Cr film was deposited onto the 2024 Al alloy disk by using a magnetron sputtering ion plating system (UDP-450, Teer Coatings Ltd, UK) [19] with a high quality Cr target (purity, 99.999%). The substrates were placed on a rotary holder in the vacuum chamber (base pressure, 4×10^{-3} Pa), with a target-substrate distance of 80 mm. Prior to deposition, the substrates were sputter cleaned for 40 min in an Ar plasma discharge (sputtering pressure, 0.2–0.3 Pa) at a bias of −400 V. Then, the Cr film deposition was conducted under the following conditions: target power E = 1.0 kW, substrate bias voltage U = −70 V, deposition pressure P = 0.4–0.5 Pa, holding time t = 2 h. Secondly, the Cr-coated samples were plasma nitrided in a nitriding unit (LDMC-30, 30 kW). Before the application of a glow discharge, the chamber was evacuated to below 8 Pa by a rotary pump. Then, the nitriding treatments were conducted in a gas mixture (N_2 0.1 L/min + H_2 0.3 L/min) at 490 °C for 8 h. The voltage and the working pressure during nitriding were 650 V and 230 Pa, respectively. After the treatment, the samples were cooled down slowly inside the chamber with a nitrogen gas flow.

2.2. Characterization

The phase structure of the Cr film and the multilayer coating were characterized by grazing incidence X-ray diffraction (GIXRD, Bruker D8 Advance) at an incident angle of 1.5° and Bragg-Brentano X-ray diffraction (BBXRD) by employing Cu-Kα radiation (λ = 0.15406 nm), respectively. X-ray photoelectron spectroscopy (XPS) analysis of the Cr film before and after nitriding was conducted on a PHI 5700 system with high resolution X-ray photoelectron spectrometer (XPS). The microstructure of the surface layer was studied using a scanning electron microscope (SEM, FEI QUANTI 200F), with the energy dispersive X-ray spectrometer (EDS). The fine microstructures of the Cr film and the as-obtained layers after nitriding were characterized by transmission electron microscope (TEM, TECNAI G2 FEG, 200 kV). Nanoindentation tests were conducted to assess the hardness and elastic modulus of the as-obtained coatings by using an Anton Paar nanoindenter equipped with a Berkovich diamond tip (triangular based pyramid).

3. Results and discussions

3.1. Microstructures of the as-obtained coating

Fig. 2 shows the chemical bonds of the as-deposited Cr film and the nitrided surface by using XPS analysis. As seen from Fig. 2a, the as-deposited Cr film exhibits mainly Cr-Cr metal bonds (peaks located at 573.8 and 583.1 eV) [20,21], with minor contaminant Cr-O bond (peaks located at 576.3 and 586.3 eV) due to the residual oxygen in the chamber. After plasma nitriding, the peaks shift to high binding energies due to the formation of Cr-N compounds. As described in Fig. 2b, the Cr2p spectrum is fitted into six peaks referred to metallic Cr-Cr bonds (574.3 and 583.5 eV), Cr-N bonds (575.6 and 584.5 eV) and Cr-O bonds (576.9 and 586.5 eV) [22,23]. Fig. 2c shows the N1 s spectrum of the nitride surface, which is illustrated by N-Cr-N bond at peaks of 396.9 eV and N-Cr-O bond at 397.2 eV [24]. Thus, it can be inferred that the as-deposited Cr film can be transformed into nitrides under present nitriding condition.

Fig. 3 shows the XRD patterns of the Cr-coated samples with and without nitriding. As for the deposited Cr film, three typical peaks located at 44.37°, 64.7° and 81.7° are referred to (110), (200) and (211) plane of pure Cr [25,26], respectively. However, the peaks of Al substrate are detected due to the thin thickness of the Cr film. As can be seen from Fig. 3, newly formed phases were observed after plasma nitriding at 490 °C for 8 h. The surface layer mainly consists of CrN phase and Al-Cr based intermetallic phase (Al_4Cr and $Al_{18}Cr_2Mg_3$). The formation of the ternary intermetallic phase $Al_{18}Cr_2Mg_3$ indicates that intense diffusion occurs between the Cr film and Al alloy substrate with Mg element. According to the XPS and XRD analysis, the surface of Al alloy substrate can be successfully alloyed with Cr and N with the help of plasma nitriding.

Fig. 4 displays the surface morphologies of the Cr film and the as-obtained coating after plasma nitriding. As seen from Fig. 4a–b,

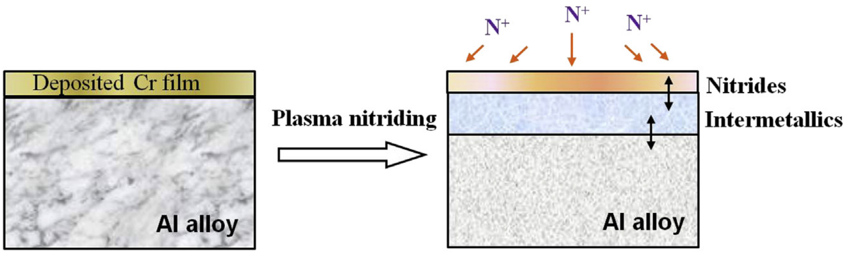

Fig. 1. Schematic showing the duplex treatment with Cr-deposition and plasma nitriding.
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