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Structural and tribological properties of CrTiAlN coatings on Mg alloy by closed-field unbalanced magnetron sputtering ion plating

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ABSTRACT

In this paper, a series of multi-layer hard coating system of CrTiAlN has been prepared by closed-field unbalanced magnetron sputtering ion plating (CFUBMSIP) technique in a gas mixture of Ar + N_2. The coatings were deposited onto AZ31 Mg alloy substrates. During deposition step, technological temperature and metallic atom concentration of coatings were controlled by adjusting the currents of different metal magnetron targets. The nitrogen level was varied by using the feedback control of plasma optical emission monitor (OEM). The structural, mechanical and tribological properties of coatings were characterized by means of X-ray photoelectron spectrometry, high-resolution transmission electron microscope, field emission scanning electron microscope (FESEM), micro-hardness tester, and scratch and ball-on-disc tester. The experimental results show that the N atomic concentration increases and the oxide on the top of coatings decreases; furthermore the modulation period and the friction coefficient decrease with the N_2 level increasing. The outstanding mechanical property can be acquired at medium N_2 level, and the CrTiAlN coatings on AZ31 Mg alloy substrates outperform the uncoated M42 high speed steel (HSS) and the uncoated 316 stainless steel (SS).

1. Introduction

The Mg alloy has been widely applied in many different areas due to the properties of high specific strength and specific elastic modular ratio, such as automobile, aviation and military industry, and has been already an important light alloy structure material. Several different techniques, such as micro-arc oxidation, chemical conversion, anode oxidation and laser surface treatment [1–3], have been developed for the Mg alloy, and the corrosion-resistant and wear-resistant properties were improved due to the surface coatings. Although the modification treatments for different methods enhanced service performance of Mg alloy, the need for coatings of higher property should be developed by physical phase deposition protective coatings, which can be deposited at lower temperature.

Magnetron sputtering has been applied successfully in hard coatings many years, and has improved the workpiece life due to excellent mechanical and wear-resistant properties. The initial research was focused on binary nitride and carbide coatings, while the transitional metal had spread well beyond the other due to high hardness and tribological property. Before long, the ternary nitride and carbide coatings gradually replaced the former, such as CrAlN [4], CrTiN [5], TiAlN [6], etc., this can remarkably improve the wear-resistant and mechanical properties. In the past decade, the quaternary nitride coatings, such as CrTiAlN and TiZrAlN [7,8], etc., have been developed and successfully applied in tool and die. For the multi-layer and multi-phase hard polycrystalline coatings, after the modulation period was optimized, the biggest mechanical property was exhibited when the modulation period ranged from 5 to 10 nm due to the biggest difference of shear modulus [9].

In recent years, Altun and Hollstein prepared hard coatings on the Mg alloy by magnetron sputtering system, such as AlN, CrN, TiN and AlN/TiN [10–12], to improve the corrosion-resistant and mechanical properties. The CrN and TiAlN coatings showed the best performance due to the improvement of corrosion-resistance, adhesion and hardness, but the capability of protecting the Mg alloy is limited due to structure and composition. In the paper, the CrTiAlN coatings on the Mg alloy were prepared by the closed-field unbalanced magnetron sputtering ion plating (CFUBMSIP) system to research the effect and application of CrTiAlN coatings on AZ31 Mg alloy. Several check and analysis methods were used to characterize the mechanical and structure property, and the research result was described below.

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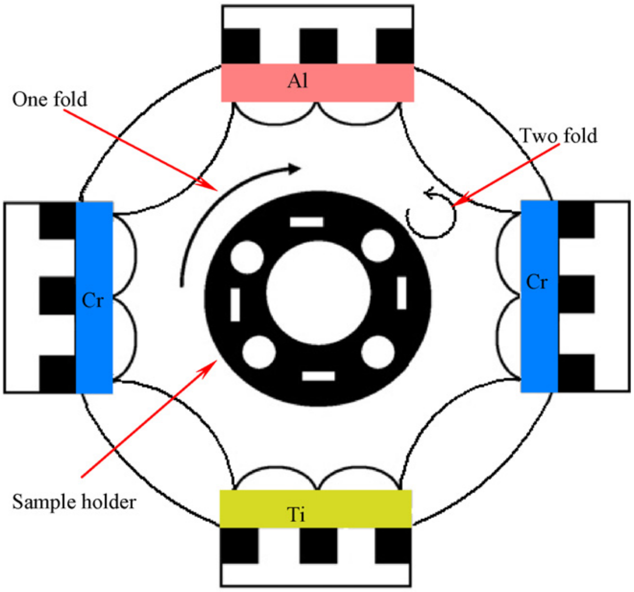

Fig. 1. Cross-section schematic drawing of arrangement plan of magnetron targets and substrate holder in CFUBMSIP system.

2. Experimental details

2.1. Deposition apparatus

The CrTiAlN coatings were deposited on AZ31 Mg alloy by the CFUBMSIP, which is a small industrial coating equipment (type UDP450). The vacuum chamber with internal size Ø 450 mm × 570 mm is a double wall, vertical axis, stainless steel cylinder which is water cooled. Edwards E2M40 backing pump and main chamber Diffstak oil diffusion pump comprise vacuum pumping system. The advanced energy pinnacle 6 × 6 dc power and plus 5 kW pulsed power comprise power supplies system. Fig. 1 is the schematic illustration of magnetron arrangement; four magnetrons were arranged at 90° intervals around stainless steel chamber. It belongs to a type of unbalanced magnetron in an arrangement whereby neighboring magnetrons are of opposite magnetic polarity which was configured in a closed-field arrangement for adjacent magnetrons, which are an industrial rectangle target with a size 133 mm × 330 mm. The centered sample holder is a disc whose rotation speed can be adjusted by a geared motor with triaxial planetary rotation.

2.2. Deposition procedure

After machining to size of Ø 25 mm × 3 mm, the AZ31 Mg alloy substrates were polished by 6 μm diamond abrasive paper and ultrasonically cleaned in acetone for 30 min, and then the substrates were fixed on vertical rod of sample holder with biaxial and triaxial rotation. Before depositing, the base pressure of vacuum chamber was pumped to 4×10^{-4} Pa. The deposition procedure was pre-sputtered cleaning at 5 min to improve the adhesion force of CrTiAlN coatings, followed by the deposition of a metallic adhesive layer about 8 min. The CrTiAlN coatings were deposited by the element target with 99.95at.% in a mixture atmosphere with Ar + N_2. The N_2 flow rate gradually increased to appropriate rate, which meets the constant multi-layer CrTiAlN coatings, and was controlled by a plasma optical emission monitor (OEM) with feedback control. The modulation period Λ, of the multi-layer was controlled by the current density of target and rotation speed of onefold. The relative concentration of the metals in the coating was controlled by the relative sputtering current density on each target. Under this condition, the technological temperature was about 180 °C. During deposition step, the rotational speed of sample holder was controlled at 4 cycles/min, and total pressure was 0.3–0.4 Pa.

2.3. Coating evaluation

A Nova400 type field emission scanning electron microscope (FESEM) was used to observe the high-resolution scan on the surface and fractured cross-sectional morphlogies of CrTiAlN coatings, and an INCA energy 350 type X-ray energy dispersive spectrometer (XEDS) equipped was used to check the chemical bulk composition of coatings. The chemical state on the top of CrTiAlN coatings were checked by a VG ESCALAB 250 type XPS. The analyzer was operated by a monochromator in the constant analyzer energy (CAE), Al Kα source (1486.84 eV) radiation and large area XL lens mode, the energy step size 0.1 eV and the pass energy 50 eV. The calibration of the binding energy scale was performed according to a standard procedure as the following standards: Au $4f_{7/2}$ (84.0 eV), Ag $3d_{5/2}$ (368.3 eV) and Cu $2p_{3/2}$ (932.7 eV). The cross-section morphology of CrTiAlN coatings was studied by a type H-9000NAR high-resolution field emission transmission electron microscope (TEM); the line scanning of composition was detected by XEDS under scanning transmission electron microscope (STEM) mode.

The morphologies of scratch tests and wear tests were observed by the metallographic microscope with the function of image collection and analysis. The thickness of CrTiAlN coatings was measured by a WC–6% Co ball crater (POD-1), adhesion and wear-resistant properties were tested using a multi-function ball-on disc (type ST3001) with the acoustic emission (AE) signal monitor, which showed the increasing signal due to crack of coatings. The scratch tests were operated by variable load up to 10 N. During wear-resistant test step, multi-pass bi-directional wear test was applied, total sliding distance and linear velocity was 4 mm and 150 mm/min, respectively. Micro-hardness and Young's modulus of CrTiAlN coatings were measured using a Vicker's ultra micro-hardness tester (Fischer scope H100) which a load on the indentor increased to 5 mN in 20 steps to maintain the indentation depth is lower than 10% of total thickness of coatings.

3. Results and discussion

3.1. Composition and adhesion property

The CrTiAlN coatings were deposited under different N_2 level conditions, which were adjusted by OEM with feedback control, at the same time the substrate temperature and relative concentration were subject to the targets power, which in turn were around 320 W for two Cr targets, 975 W for Ti target and 642 W for Al target during deposition step. The total thickness of CrTiAlN coatings is shown in Table 1. Although the CrN- and TiN-based coatings were applied at high-speed steel with excellent adhesion property, abundant metal Cr and Ti decreased the adhesion because of less compatible property with Mg alloy, the need for higher Al content in adhesion layer can increase the sticking property. At first the Al target was increased to normal power, and then the Cr and Ti target were increased to normal power. The AZ31 Mg alloy substrates in most cases did not provide adequate "load support" for the hardness and scratch tests with similar coatings on steel, so a need for lighter load is to measure the micro-hardness and adhesive force.

Composition was analyzed by the XEDS and the change of relative concentration of element in CrTiAlN coatings can be found,