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Microstructure, Interface, and Properties of Multilayered CrN/Cr_2O_3 Coatings Prepared by Arc Ion Plating

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There has been much interest in developing multilayered or nanolayered physical vapor deposition (PVD) coatings identified as a group of promising protective coatings for their excellent mechanical properties and corrosion resistance. In this study, the multilayered CrN/Cr_2O_3 coatings with different bilayer periods (Λ) were synthesized on the polished high speed steel substrates from a Cr target with the alternative atmosphere of pure nitrogen and pure oxygen by arc ion plating (AIP) technique. The results revealed that the microstructure, morphologies and properties of the multilayered coatings were strongly influenced by the bilayer period (Λ). There were two kinds of interfaces in the multilayered CrN/Cr_2O_3 coatings: the sharp ones and the blurry ones. With reducing the value of Λ, the macro-particles densities decreased gradually, whereas the coating microhardness, adhesive strength and wear resistance first increased, and then decreased slightly or remained stable as the bilayer period $\Lambda < 590$ nm. The multilayered CrN/Cr_2O_3 coating with the bilayer period Λ of 590 nm possessed the best comprehensive properties, namely the highest microhardness, the strongest adhesion, and the lowest wear rate.

KEY WORDS: Cr_2O_3/CrN; Multilayered coating; Arc ion plating; Interface; Mechanical properties; Wear

1. Introduction

CrN and Cr_2O_3 being two kinds of typical Cr-based protective coatings, have been widely used in many industrial fields due to their attractive properties, such as strong adhesion, good toughness and corrosion resistance, chemical inertness, mechanical strength, optical characteristics, high hardness and low friction coefficient[1–4]. However, the hardness of CrN coatings needed to be further improved for its wide industrial applications. On the other hand, the chipping and radical brittle failures of Cr_2O_3 coatings on the tool steel substrate often happened due to its brittleness and high residual stress level[5].

In order to improve the poor adhesion of Cr_2O_3 coating to substrate and to further improve the hardness of CrN coating, CrN/Cr_2O_3 composite coatings, mainly in the form of double-layered or duplex coatings, have been developed using arc[6–10] or sputtering[11,12] methods in recent years. The CrN/Cr_2O_3 duplex coatings have exhibited better performances than the single CrN coatings and the Cr_2O_3 coatings, such as higher hardness and stronger adhesion, as well as excellent wear resistance. These advantages resulted in some possible industrial applications of such “duplex” coatings (e.g. as release mold coatings for aluminum die casting or injection applications)[7,12].

During the past several years, many composite coatings in the form of multilayered, nanolayered or super lattice have been developed rapidly due to their excellent mechanical properties and corrosion resistance[13–17], such as multilayered Cr/CrN coatings[14], multilayered f-TiN/h-AlSiN films[16], CrN/Mo_2N multilayers[18], nanolayered TiN/AlN coatings[19], and CrN/AlN super lattice films[20]. The advantages of two components in these multi- or nano- layered coatings were shown, even beyond their individual strengths, which resulted from the reduction of scale or size.

Similarly, the multilayered CrN/Cr_2O_3 coating would combine the merits of the CrN and Cr_2O_3 layers more effectively, which can be used as a potential protective coating with better performances. However, there are few studies on the preparation, microstructure and properties of the multilayered CrN/Cr_2O_3 coatings. The aporia could be attributed to the control of the broadening interface between the oxide layer and the nitride layer, which resulted from the high activity of oxygen. In this

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work, the multilayered CrN/Cr_2O_3 coatings with various bilayer periods (Λ) but the same total thickness were prepared by arc ion plating (AIP) technology in an alternative atmosphere of nitrogen and oxygen from a Cr target. And the effects of bilayer period (Λ) on the microstructure, interface, morphologies, as well as mechanical and tribological performances of multilayered CrN/Cr_2O_3 coatings were investigated systematically.

2. Experimental

2.1. Deposition of multilayered CrN/Cr_2O_3 coatings

The multilayered CrN/Cr_2O_3 coatings with various bilayer periods (Λ) were deposited on high-speed-steel (HSS) (W6Mo5Cr4V2-M2 HSS: 0.9% C, 6.1% W, 5.0% Mo, 4.1% Cr, 1.95% V, Fe balance (in wt%); 64–66 HRC at room temperature) discs (20 mm × 20 mm × 3 mm) by AIP system from a Cr target (99.9% purity) with a diameter of 64 mm. The substrates were mirror-polished to Ra < 0.05 μm, followed by wet cleaning in an ultrasonic bath of acetone and alcohol for 15 min each, then were dried and fixed onto the rotating substrate holder at a distance of 130 mm from the target in the vacuum chamber. With the alternative atmosphere of pure nitrogen and pure oxygen (99.99% in purity) controlled by mass flowmeters, the deposition procedures of CrN and Cr_2O_3 layer were repeated to prepare multilayered CrN/Cr_2O_3 coatings following the Ar^+ bombardments and Cr interlayer depositions. During the whole deposition procedure, no additional heating was applied to the specimens. The temperature near the substrates rose up to ~210 °C from room temperature during the Ar^+ bombardments, and then decreased to ~175 °C in the coating deposition. In view of the insulativity of the Cr_2O_3 phase at low temperature, once the arc was extinguished, it was very difficult to be re-generated. The CrN layer of next period was deposited continuously on top of the former Cr_2O_3 layer to maintain the arc. In addition, the interface adhesion between the Cr_2O_3 layer and CrN layer would be enhanced by the existence of small amount of residual oxygen, which participated in forming the Cr–O–N bonds. By adjusting the deposition time of CrN and Cr_2O_3, respectively, the monolayer thickness was controlled. All the deposition process of the multilayered CrN/Cr_2O_3 coatings was started from the CrN layers after the deposition of the Cr interlayer, which was used to improve the adhesion with the HSS substrates, and ended at the Cr_2O_3 layer. The total thickness and the thickness ratio of CrN vs Cr_2O_3 layer of all the coatings were kept about 3.5 μm and 1:1, respectively. The deposition details are summarized in Table 1.

Table 1 Details of deposition parameters of the multilayered CrN/Cr_2O_3 coatings by arc ion plating technique

Parameters	Value
Distance from target to substrates (cm)	130
Rotation speed (r/min)	25
Base pressure (Pa)	6.5×10^{-3}
Arc current (A)	60
Ar^+ bombardment	0.2 Pa, −800 V × 30% pulsed bias superposed by −50 V DC bias for 10 min
Interlayer deposition	Cr, 0.2 Pa, −300 V × 30% pulsed bias for 7 min
CrN layer deposition	0.8 Pa, −150 V × 45% pulsed bias
Cr_2O_3 layer deposition	0.4 Pa, −50 V × 45% pulsed bias superposed by −50 V DC bias
Thickness ratio of CrN vs Cr_2O_3 layer in each period	~1:1
Total thickness of multilayered coatings	~3.5 μm

2.2. Microstructure and morphology analysis

The as-deposited multilayered CrN/Cr_2O_3 coatings were analyzed by X-ray diffraction (XRD; D/MAX-RA of Rigaku, Japan) with monochromatic Cu$K\alpha$ (λ = 0.154056 nm) radiation operated at 50 kV and 300 mA. The diffraction angle (2θ) of the scanning scope ranged from 20° to 85° with a 0.02° step size and 4°/min scanning speed. Scanning electron microscopy (SEM; INSPECT F, FEI) was used to observe the cross-sectional and surface morphologies, and to measure the thickness and bilayer period (Λ) of each multilayered coating. The densities and the diameters of the macro-particles on the surface of the multilayered coatings were counted using a metallographic image analysis software (SISC IAS V8.0, Beijing KYKY Comp. Technol. Ltd. Co, China). X-ray photoelectron spectroscopy (XPS; ESCALAB250 of Thermo VG, USA) was used to analyze the depth profile of a typical multilayered coating (Λ = 590 nm). Cross-sectional morphologies and high-resolution (HR) images of the interface in the typical sample were observed by transmission electron microscopy (TEM; Tecnai G^2 F30).

2.3. Mechanical property measurements

A Knoop diamond microhardness tester (LM 247_{AT}, LECO Co. Ltd., US) was used to evaluate the microhardness of all the as-deposited multilayered coatings under a load of 25 g and a dwelling time of 15 s. The adhesive strength of all the specimens were evaluated via scratch tests using a multifunctional test instrument of materials surface properties (MFT-4000, Lanzhou ICP, CAS, PR China) with a Rockwell C diamond stylus (cone apex angle: 120°; tip radius: 0.2 mm). The loading rate, translation speed, termination load and scratch length were 100 N/min, 0.083 mm/s, 100 N and 5 mm, respectively.

2.4. Tribological tests

Rotating sliding wear tests against alumina balls (4 mm in diameter) in the form of the traditional ball on disk were performed on a classical rotating friction tester (MS-T3000, Lanzhou ICP, CAS, PR China) to characterize the tribological behaviors of all the multilayered coatings under ambient atmospheric conditions (25 ± 5 °C and 40 ± 5% RH). The normal load, rotating speed, rotating radius and the testing time for each sample were 5 N, 200 r/min, 6.5 mm and 60 min, respectively. The average friction coefficients were calculated from the steady-states (from 10th to 60th min in this work) in the frictional coefficient curves. The specific wear rate k can be calculated according to Archard's classical wear equation[21]:

$$k = \frac{V}{SL} \tag{1}$$

where V is the wear volume calculated by the cross-area of wear tracks, which was measured by using a Stylus Profiler tester