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Ru-induced microstructural change in ion-plated TiN coating and its tribological properties

Bowen Li[a], Quan Liu[b], Minghui Chen[a,*], Yunsong Niu[c,*], Shenglong Zhu[c], Fuhui Wang[a]

[a] Corrosion and Protection Division, Shenyang National Laboratory for Materials Science, School of Material Science and Engineering, Northeastern University, Shenyang 110819, China
[b] Shenyang Dongchuang Precious Metals Material CO., LTD, Shenyang 110819, China
[c] Corrosion and Protection Division, Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China

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ABSTRACT

TiN and Ti(Ru)N (3 wt%, Ru) coatings were deposited on Ti6Al4V substrate by arc ion plating method. Ti(Ru)N coating exhibits golden luster as the TiN coating does. From XRD, XPS and TEM investigations, Ru addition refines the TiN grains and Ti(Ru)N coating can be concluded as a kind of composite layer, which is mixed by Ru-containing amorphous part and crystalline TiN phases. The related hardening mechanism of Ru addition in TiN coating is fine grain strengthening. Wear resistance of Ti(Ru)N coating is significantly better than that of TiN coating, due to its higher hardness, higher H/E value and lower COF value. Improved wear performance of Ti(Ru)N coatings is mainly contributed to the mechanism of fine grain strengthening, which delays the occurrence of pitting of large-scale peel-off behavior like TiN coating.

1. Introduction

Over the past years, TiN coating has been widely used on cutting tools, bearing gears, extrusion dies and jewelries due to its low friction coefficient, good chemical stability, high hardness and attractive golden color [1–5]. However, with the development of industry, the requirement of hard coating becomes increasingly higher. It is quite necessary in some special mechanical industries to further improve their hardness and wear resistance.

Hardness improvement happens through microstructure modifications, such as point defect increment, increase of internal stress, grain boundary densification and crystalline refinement. Firstly, from the aspect of point defect increment, the defects can act as obstacles for dislocation movement, drastically increasing the hardness thereby [6]. They can be formed by adding certain alloying elements to form a plural nanostructured composite coating. For the Al addition, $Ti_{1-x}Al_xN$ ternary nitrides crystallize in metastable NaCl face-center-cubic (fcc) structure for the low Al contents and in ZnS hexagonal wurtzite structure for the high Al content ($x \geq 0.65$) [7]. However, the coating, deposited on comparatively soft substrates, is apt to the brittle nature and has low crack resistance. Addition of yttrium results in extensive grain refinement and a more equiaxed structure owing to the continuous nucleation process [8,9]. Rare metal Zr can enter into the fcc TiN lattice and form substitutional solid solution lattice, which refines grains as well and increases the hardness of the TiN coating and wear resistance [9–11]. Secondly, the increase of internal stress can be caused by the high-energy bombardment of plasma flux, which are resulted from high negative bias, leading to atom rearrangement and diffusion to cumulate exotic and imposed energies. Moreover, the high-energy bombardment can also bring about the increase of point defects. Unfortunately, the annealing during service can induce defect recovery, lattice defect diffusion and relaxation of the ion-induced bombardment effect (internal stress), leading to hardness reduction. TiN, TiN/NbN and TiN/CrN are the cases that they will lose their properties and are thermally unstable [12–14]. Thirdly, for the grain boundary densification, Veprek et al. reported a TiSiN coating with super hardness of 80–105 GPa [15]. It is argued that the hardness enhancement can be attributed to the binary nanocrystalline/amorphous phase structure. Si_3N_4 amorphous phase grows along the TiN grain boundaries, forming the amorphous encapsulated nanocrystalline structure. The amorphous Si_3N_4 at grain boundaries refines the TiN grains, and effectively prevents dislocation slip, thereby increasing the hardness and wear resistance of the TiSiN coating. Finally, for the crystalline refinement, the small (~nm) grain size can hinder the dislocation movement which increase hardness [16]. The hardness increasing according to the 'Hall–Petch' relationship ($H_{(d)} = H_0 + Kd^{-1/2}$) is the result of a well-

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[*] Corresponding authors.
E-mail addresses: mhchen@mail.neu.edu.cn (M. Chen), ysniu@imr.ac.cn (Y. Niu).

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cohesive interface among the nanosized small grain, which prevents crack propagation during boundary sliding. Moreover, segregation of a second nanocrystalline phase can generate the strengthening effect on grain boundaries, and thus prevents grain growth [17]. Although this nanocomposite design can increase hardness, it may not improve toughness because dislocation movement is prohibited, inducing crack initiating and then propagation, which become the main mechanism of relieving strain if the cohesive strength of phase segregation is not sufficient to withstand the local tensile stress. TiN in Ni [17], TiN in Ag [18], ZrN in Ni [19], ZrN in Cu [20], CrN in Cu [21] can solve this problem. In these coatings, the host elements Ti, Zr, and Cr are compounded with N in the manner of hard nitride phase, while the other one remains unreacted in the growing film. In addition, just the existence of the metal matrix makes the coating toughness improve. Hence, the hardness can be enhanced by the nanocomposite structure, as well as toughness improvement simultaneously.

It should be pointed out that such the above improvements in hardness of the TiN coating by adding a third element is at the expense of its golden luster, ruining its application in decoration and sometimes sacrificing coating toughness. By now, efforts on enhancing mechanical properties of the TiN coating and meanwhile maintaining its golden luster have been rarely made. In this study, we investigate a third element effect of Ru addition in TiN coating. From previous studies, it can be found that Ru was added into the single crystal superalloys to possess higher creep resistance [22–24]. Therefore, the purpose of this experiment is an attempt to elucidate the effect of Ru additions in wear properties of TiN coatings, on the premise of keeping the golden luster and extending the lifetime owing to the Ru-induced high creep resistance, so that it can satisfy the decoration and harsher requirements.

2. Experimental

2.1. Coating preparation

Titanium alloy Ti6Al4V was used as the substrate material, whose nominal composition was given in Table 1. Specimens of 15 × 10 × 2 mm were machined from the Ti6Al4V ingot by wire cut electrical discharge machining, and their surfaces were ground with a final 2000# SiC paper, then mechanically polished with 2.5 μm diamond (Ra = 1.60 μm, measured by Alpha-step IQ surface profiler). Before coating deposition, all of the specimens were degreased by an ultrasonic cleaner in acetone and ethanol.

TiN and Ti(Ru)N coatings were deposited by using the Ti target (99.9%, size: Φ70) and Ti-Ru target (3 wt% Ru, size: Φ70) respectively in a DH-7 type arc ion plating (AIP) machine. The distance between the target and the substrates is about 200 mm. AIP parameters were listed as follows: base pressure 5×10^{-3} Pa; Ar partial pressure 1×10^{-1} Pa; N_2 partial pressure 14×10^{-1} Pa; arc current 70 A; bias voltage −600 V; deposition time 120 min; the chamber temperature was heated to 200 °C. For further cleaning, the substrates were etched using metal ion bombardment at a bias of −900 V for 3 min prior to the coating deposition.

2.2. Characterization methods

Phase composition was determined by X-ray diffraction (XRD, X' Pert PRO, PANalytical Co., Almelo, Holland, Cu Ka radiation at 40 kV). X-ray photoelectron spectroscopy (XPS) was acquired using ESCALAB250 photoelectron spectrometer, and was deconvoluted by the XPSPEAK software. Binding energies were calibrated using carbon contamination with C1s peak value of 284.6 eV. Scanning electron microscopy (SEM, Inspect F 50, FEI Co., Hillsboro, OR) equipped with energy dispersive spectroscopy (EDS, INCA, XMax, Oxford instruments Co., Oxford, U.K.) and transmission electron microscopy (TEM, JEM-2100F, JEOL, Tokyo, Japan) were used for microstructure and composition analysis. HSR-2M microTribo Tester was used to investigate the coefficient of friction (COF) and dry sliding wear properties of the coating. A GCr15 steel ball with a diameter of 4 mm was used as the stationary pin. During the test, the sliding speed, applied normal load and total wear time were 0.1 m/s, 10 N and 10 min, respectively. Nano-indentation test was performed on a nano-indentation apparatus with a Berkovich diamond indenter (Agilent G200 Nano indentor). Continuous stiffness measurement (CSM) mode was used to get hardness and elastic modulus of the coatings at different indentation depths. Hardness was analyzed using the Oliver-Pharr method [25]. Ten positions were selected for each sample. Poisson's ratio was set as 0.27, and the average maximum indentation depth was 600 nm. In order to eliminate the influence of substrate and surface roughness on the measurement results, the final hardness and elastic modulus were calculated from data obtained only between 100 nm and 200 nm indentation depth.

Table 1
Nominal composition of Ti6Al4V alloy (wt%).

Ti	Al	V	Fe	Si	C	O	H	N
Bal.	6.00	4.00	0.03	0.15	0.1	0.15	0.015	0.05

3. Results and discussion

3.1. Phase and microstructure

Fig. 1 shows macroscopic morphologies of the TiN and Ti(Ru)N coatings. The as-deposited TiN coating presents beautiful golden color. With the addition content of 3 wt% Ru, its color keeps almost unchanged, only turns a little dark, but also presents the golden color as expected. In addition, both coatings have a mirror surface. No spallation or cracks can be detected even at the sides and corners. The coating thickness of are about 12 μm by the cross-sectional SEM morphologies in Fig. 2, and the interfaces between the coating and the substrate of both coatings are well bonded.

XRD patterns of the TiN and Ti(Ru)N coatings are shown in Fig. 3. Phase constituents and orientation of the diffracting planes were calibrated by standard PDF cards. It can be seen from Fig. 3 that both coatings are composed exclusively of TiN phase, but the diffraction peak at plane (220) of the Ti(Ru)N coating shifts to the lower angle direction as compared to that of the TiN. Hao Du et al. added lanthanum to the TiAlN film, which caused the diffraction peak at plane (111) to shift to the low angle and increase lattice parameters [26]. The reason for the change of the diffraction peak of the Ti(Ru)N coating is the same as that of the TiAl(La)N film, due to the lattice distortion, induced by the dispersion of Ru element in the solution manner. However, no reflection peak containing Ru or RuN phase can be observed for the Ti(Ru)N coating in Fig. 3. The existing Ru is considered as the metallic phase or a tiny amount of Ru nitride in the films. The first reason may be that the content of ruthenium in the Ti(Ru)N coating is too few to detect, and the second one is that Ru phase may be in amorphous state or Ru is scattered in the form of very small grains that exceed the detection range of the XRD analysis system [27]. It results in peak broadening, accompanied with a decrease in peak intensity, in comparison with the TiN diffraction peaks.

To validate the compound state of Ru in Ti(Ru)N coating, a detailed XPS study was performed on the Ti(Ru)N coating. Argon sputtering of the sample surface for 20 s was explored before the XPS analysis. The presence of X-ray photoelectrons and X-ray-excited Auger electrons bands is related to titanium, ruthenium and nitrogen. Ti 2p, Ru 3d and N 1s XPS spectra of Ti(Ru)N sample after 20 s of argon sputtering are shown in Fig. 4. The peaks in the Ti 2P spectra centered at 454.7 eV and 460.7 eV are corresponds to the Ti 2p 3/2 and Ti 2p 1/2 in TiN_x ($0.72 < x < 1.19$) compounds, respectively. The binding energy positions of Ru 3d 5/2 and Ru 3d 3/2 bands are centered at 284.4 eV and 279.5 eV, respectively. The binding energy value near 285 eV is usually