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Residual stress analysis of TiN film fabricated by plasma immersion ion implantation and deposition process

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ABSTRACT

Titanium nitride (TiN) films were fabricated on AISI52100 bearing steel surface employing a hybrid plasma immersion ion implantation and deposition (PIIID) technique. The chemical composition, morphology and microstructure of TiN films were characterized by atomic force microscope (AFM), energy dispersive spectrometer (EDS), scanning electron microscope (SEM) and X-ray diffraction (XRD), respectively. The residual stress of TiN films under different deposition parameter conditions were measured by means of glazing incidence angle X-ray diffraction (GIXRD) method. The influence of film thickness and X-ray glazing incidence angle on residual stress were investigated. AFM observation reveals that the TiN films have extremely smooth surface, high uniformity and efficiency of space filling over large areas. XRD analysis results indicate that TiN phase exists in the surface modified layer and exhibits a preferred orientation with the (200) plane. The GIXRD data shows that the residual stress in as-deposited TiN films is compressive stress, and the residual stress value decreases with the film thickness and increases with the glazing incidence angle. The compressive stress reduces from 2.164 GPa to 1.163 GPa, which corresponds to the film thickness from 1.5 μm to 4.5 μm, respectively. Reasonably selecting PIIID process parameters for TiN films fabrication, the residual stress in the film can be controlled effectively.

1. Introduction

Titanium nitride (TiN) thin film has been widely applied in industry fields as anti-wear, anti-corrosion and decorative coatings or as diffusion barriers for years. The significant and widespread availabilities of TiN film is mainly due to its remarkable physical and chemical properties including high melting point, good chemical inertness, excellent thermodynamic stability, high hardness, low friction coefficient, superior wear and corrosion resistance [1–5].

At present, TiN film is mainly fabricated by physical vapor deposition (PVD) or chemical vapor deposition (CVD) [6–11]. Plasma immersion ion implantation and deposition (PIIID) technique has also been proved to be a promising method. PIIID technique has several advantages, such as low temperature treatment, none line-of-sight restriction and potential for sophisticated-shape components [12–15]. It is believed that sputter deposition combined with ion implantation is effective at depositing TiN films with high hardness and good tribological properties, because of the non-equilibrium characteristics in the physical process of sputter deposition and simultaneous energetic ion bombardment during film growth. In addition, ion implantation and film deposition can cause a high residual stress. Under normal circumstances, the residual stress in film includes intrinsic stress and thermal stress, and the stress is parallel to the film and substrate interface. The intrinsic stress results from the film growth process and primarily depends on the deposition parameters, whereas the thermal stress is caused by the differences in temperature, cooling conditions and thermal expansion coefficients between the film and the substrate material [16]. Large residual stress seriously affects the physical and mechanical performances of TiN film. Therefore, residual stress control is essential to fabricate TiN film with excellent physical and mechanical properties.

However, the investigation of plasma immersion ion implantation and deposition TiN film mainly focused on its microstructure, chemical composition, friction and wear behaviors, mechanical property and corrosion resistance [17–20]. According to our knowledge, seldom studies have been reported on the residual stress of TiN films directly fabricated onto bearing steel surface by PIIID technique. In this paper, TiN films were prepared by PIIID, and the residual stress in TiN films was measured using glazing incidence angle X-ray diffraction (GIXRD) method. The influence of TiN film thickness and glazing incidence angle were also discussed.

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2. Experimental procedures

2.1. Sample and TiN film preparation

Samples of AISI52100 commercial bearing steel in quenched and tempered state (HRC6165) were used in this study. The flat samples were machined to a diameter of 15 mm and thickness 3 mm. Before ion implantation and deposition, one side of each coupon was ground with SiC abrasive paper No. 400, 800, 1200 and 1500 grits sequentially, then polished with fine diamond paste (average size 0.5 μm) to a surface roughness of approximately 0.08 μm (measured by a stylus profilometer), followed by an ultrasonic clean 20 min in acetone and alcohol, and then kept in an electric-dryer to prevent the surface from pollution again.

TiN film was fabricated in the multi-function PIIID facility [21]. The vacuum chamber was evacuated to a base vacuum of 5.0×10^{-3} Pa, and then Ar ion sputtering was introduced into the chamber to remove undesirable oxide and other contamination layers. Titanium plasma was generated by pulsed cathodic arc plasma source with an S-shape curved magnetic duct. Nitrogen plasma was produced by radio-frequency glow discharge. The flow rate is 50 sccm, working gas pressure 0.4 Pa. The implantation pulse width is 60 μs, main arc current 120 A and main arc pulse width 1000 μs. The ion implantation and titanium nitride film deposition time is 2 h, 3 h, 4 h and 5 h, corresponding to the TiN film thickness 1.5 μm, 2.5 μm, 3.5 μm and 4.5 μm, respectively.

2.2. Characterization of the TiN film

After PIIID, microstructure and mechanical properties of the treated samples were evaluated and compared with the AISI 52100 bearing steel substrate. The as-deposited films were characterized by X-ray diffraction (XRD) on Philips X'pert diffractometer with Cu Kα (λ = 0.154056 nm) excitation radiation. The accelerating voltage was 40 kV and current 30 mA. The scan angle (2θ) varied from 20° to 90°. The surface topography and root-mean-square (RMS) roughness was obtained by atomic force microscopy (AFM) (NanoscopeIIIA, America) over sampling areas of 5 μm × 5 μm. TiN film residual stress at incidence angles of 1°, 5°, 10°, 15° and 20° was measured by grazing incidence X-ray diffraction (GIXRD) method, respectively.

2.3. Residual stress evaluation

Generally, residual stress in thin film deposited on substrate surface can be measured by different means such as X-ray diffraction, acoustic-wave detection, and curvature measurement using a laser profilometer and electrical resistance or capacitance method. In all of these methods, stresses are measured through the measurement of strain, and the strain is measured by different "strain gages". In XRD, the "strain gages" is the *d*-spacing of a series of planes: the residual stresses cause a change of the spacing of crystal planes, reflected as the shift of the diffraction peak to higher or lower angle depending upon the nature of the stress. Measuring the peak shift or the lattice parameter change enables measurements of residual stresses. GIXRD is a powerful method for investigating the depth profile of microstructural parameters in the implantation affected zone because of the small penetration depth of X-rays. Moreover, GIXRD is a non-destructive method that can be advantageously applied if a material has to be studied after a repeated post-treatment. In this study, we apply X-ray diffraction using "$\sin^2\psi$ method" to determine the residual stress in PIIID TiN film. The $\sin^2\psi$ technique is chosen because it can be used to quickly measure the average biaxial stress in film from a liner fit of d_{hkl} vs. $\sin^2\psi$ data, with as few as two ψ method tilts.

Because the film is too thin to use normal $\sin^2\psi$ method, we slightly improve the $\sin^2\psi$ method for its limitation. For simplification, the following assumptions are used [22–26].

(1) For a very thin film, the residual stress is assumed to be independent on the depth from surface.
(2) For a polycrystalline film, the residual stress in the plane paralleled to the surface is isotropic, i.e. the stress is axisymmetric about the normal direction of film surface.

The diffraction pattern was obtained with 2θ scan under a certain grazing incidence angle. Fig. 1 shows a schematic diagram of the relationship among directions of the incidence X-ray, the diffraction X-ray and the normal of the diffraction plane. It is clear that

$$\psi = \left[\frac{\pi}{2} - \left(\frac{\pi}{2} - \theta\right) - \omega\right] = \theta - \omega \quad (1)$$

where ω is the angle between incidence X-ray and the TiN film surface; θ is the Bragg's angle and ψ the angle between the normal direction of diffraction plane and the normal direction of the film surface.

The strain along ON direction (normal direction of diffraction plane) can be determined by the shift of diffraction peak corresponding to the stress-free sample, which can be described as Eq. (2)

$$\varepsilon_\psi = \frac{d_\psi - d_0}{d_0} = -\cot\theta_0 \Delta\theta_\psi \quad (2)$$

where d_ψ is the interplaner spacing measured in the diffraction peak, θ_ψ the corresponding Bragg's angle, θ_0 and d_0 are the Bragg's angle and interplaner spacing of stress-free sample, respectively. The d_0 value used in here is d_n value, d_n is the interplaner spacing measured at $\psi = 0$.

When the residual stress in the film is assumed as axisymmetric about the normal direction of TiN film surface, we have

$$\varepsilon_\psi = \cos^2\psi\varepsilon_z + \sin^2\psi\varepsilon_x \quad (3)$$

According to Huker's law, the following equation can be obtained:

$$\varepsilon_x = \frac{\sigma_x}{E} - \frac{\nu}{E}(\sigma_y + \sigma_z) = \frac{(1-\nu)}{E}\sigma_x$$

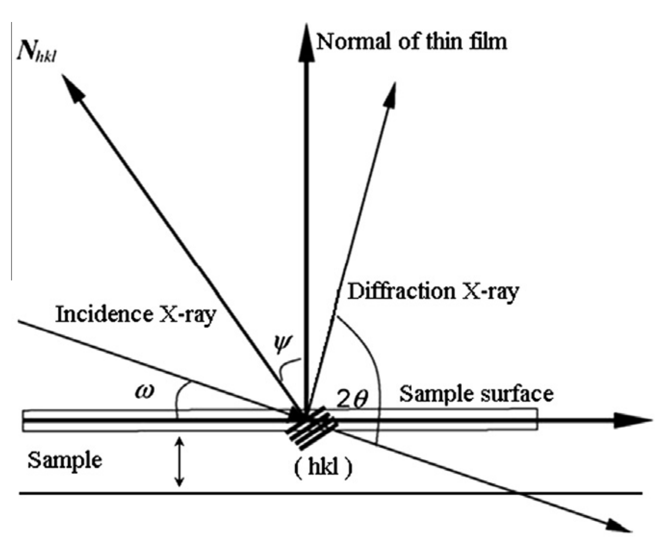

Fig. 1. Scheme of grazing incidence angle X-ray diffraction of thin film.