ADHERENT NANO-SUPERHARD TITANIUM NITRIDE FILM AND ITS FORMING MECHANISM IN MULTI-ARC ION-PLATING SYSTEM

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An adherent nano-superhard titanium nitride (TiN) film on the substrate of Cr12Mo4V high speed steel was prefabricated in a vacuum cathode multi-arc ion-plating system. Microhardness, film-to-substrate adhesion, and microstructure of the film were investigated typically using Vickers hardness meter, scratch tester, and X-ray diffractometer. Results show that: (i) the achievable film microhardness is in the range of 35–45 GPa; (ii) the critical load (Lcr) of the superhard TiN film is approximately 64 N; (iii) the nm scale mean main grain sizes of the film are approximately of 12.7 nm for TiN(111), 19.7 nm for TiN(200), and 9.6 nm for TiN(220); and (iv) compared with the standard TiN film with the hardness of 22 GPa, the accomplishment of the nano-superhard TiN film may be due to (a) the ion bombardment induced residual stress within the film, and (b) the combined effect of the decrease of crystalline size and preferred orientation in the plane (111).

Keywords: Superhard TiN film; mechanical property; crystalline size; preferential orientation.

1. Introduction

TiN film has been extensively studied and successfully used for decades due to its favorable properties of high melting point, high hardness, and high thermal conductivity. Its application ranges from hard and protective coating on mechanical tools to decorative coating, and diffusion barriers in microelectronic components.1,2 Currently, the rapid development of engineering and high technologies brings strict demand on the quality of TiN film, and therefore the performances of the film still need to be further improved. Multi-arc ion plating (AIP) with features of high ionization rate, ion kinetic energy, and deposition rate has rapidly developed in the last two decades. Macroparticles and neutral particles are usually accompanied with the ions in the
vicinity of cathode arc sources, during the deposition of AIP TiN film, which subsequently roughens relatively the TiN film structure in the presence of columnar grains and other defaults. Microhardness of this type of films is normally in the order of 20–30 GPa, which lowers the erosion and corrosion resistance and reduces the brightness.

The conventional approach to improve the hardness and wear resistance is to increase the film thickness, which may not be so effective. Approach to improve the film intrinsic and/or extrinsic properties like grain size, morphology, texture, etc., can also enhance these performances. Recent interest in nanotechnology further stimulates the studies of films for understanding the formation and growth mechanism at the atomic level. The ever-growing demand for superior protective coatings for withstanding severe operating conditions drives the development of novel hard and superhard coatings.

This study was initiated to synthesize an adherent superhard TiN film on the substrate of Cr$_{12}$Mo$_4$V high-speed steel using multi-arc ion-plating coater. Moreover, the relationship among the deposition parameters, the mechanical properties, and the nanostructure was also investigated so as to facilitate the understanding of the forming mechanism.

2. Experimental Procedures

2.1. Coating equipment and sample preparation

Post of polishing of substrate surfaces of Cr$_{12}$Mo$_4$V high-speed steel to an average surface roughness of $Ra=0.08 \mu$m, the steel substrate was thoroughly cleaned in an acetone ultrasonic bath for 15 min and then blow-dried with nitrogen. The so-prepared steel coupons were vertically hung on steel racks of the rotational substrate holder in the center area of the vacuum coater with cross-sectional view, as shown in Fig. 1. There were eight round Ti targets set around the vacuum chamber. Ar gas was injected from the 1 mm diameter holes uniformly arranged on a double-layer steel bar directing to each of two arc evaporation sources vertically collocated, and nitrogen gas was injected from the two ion sources toward the substrate so as to improve its efficiency of ionization. The flow of Ar and N$_2$ gas was controlled by two different mass flowmeters. Controlling of the bias voltage and the bias current to the substrate was achieved by a unipolar pulse DC bias power supply. The duty ratio of the pulsed bias voltage in Ar ion cleaning was 70% and that during the deposition was 50%. Prior to deposition, the temperature of vacuum chamber was gradually raised up to 300°C. Then, the coupon surfaces were further cleaned for 15 min by Ar ion bombardment at a bias voltage of $-1200$ V in a 4 Pa argon atmosphere. The depositing pressure was maintained at $2 \times 10^{-1}$ Pa in the argon atmosphere. After Ti ion etching for 5 min under the $-1000$ V bias voltage, Ti interlayer of about 0.2 $\mu$m was therefore pre-deposited for 10 min using the eight Ti targets with 80 A arc current and under $-300$ V. Then, TiN layer deposition was initiated so as to accomplish a TiN film thickness of 3 $\mu$m, approximately, by introducing nitrogen gas with the target voltage stabilized at 20 V. PLC (Programmable Logical Controller) system was used to control automatically the process parameters in each coating. TiN layers were deposited with individual bias voltages, varying in steps of $-100$ V, from the range of $-100$ V to $-600$ V under the depositing pressure of $2 \times 10^{-1}$.

2.2. Surface analysis methods

MH-6 microhardness tester with a Vickers indenter under a load of 20 g was used to measure the film hardness. MS-S3000 scratch tester with an initial load 3 N, loading rate 100 N/min, and transverse
speed 4 mm/min was used to investigate the adhesion between the steel coupons and the TiN films. Optical microscope with a video camera was used to observe the wear traces in the scratch testing. Toughness was evaluated by a ball-pressing test with a Φ12 SiC ball pressing and dwelling onto a TiN-filmed disc coupon for 5 min under a vertical force of 100 kg. X’pert Pro X-ray diffractometer (XRD) was used to investigate the crystallographic structures of the TiN film. CuKα radiation operated at 40kV and 40 mA was used to record the scanning results in a 2θ range from 20° to 75° of the XRD detection with a step size of 0.02° and a dwell time of 4 s. Degree of preferred orientation (POD) of films was determined by formula (1):

$$[POD]_\alpha = \frac{\sum k \frac{I_{0\alpha}}{I_{s\alpha}}}{\sum k}$$

where $I_{0\alpha}$ is the relative intensity measured at an orientation angle of $\alpha = 0°$, $I_{s\alpha}$ is the relative intensity in the same plane of the standard PDF card, and $n$ is the total number of reflection peaks obtainable from the film.

3. Results and Discussions

3.1. Microhardness

To measure accurately the Vickers microhardness of micron-scale thick TiN films the mathematical mean of five measurements, taken with same measuring conditions, at four different points was sampled as the experimental value. Relationship of the bias voltages and the microhardness of the TiN films are shown in Fig. 2 in which there are also micrographs to illustrate: (i) the intended superhard TiN film of 45 GPa, as shown in micrograph (1) and (ii) the pressing-ball used to perform the indentation, shown in micrograph (2). The achievable values, indented under a load of 20 g, of microhardness for the TiN film coupons deposited with a bias voltage in the range of −100 to −600 V were ranging between 35 and 45 GPa that was beyond 40 GPa, which was about twofold of that for the arc-ion-plated TiN films. The micrograph for the ball-pressing test suggested the high toughness of the film that was beneficial in achieving the good adhesion. As the ion current in the deposition of the TiN films was high, it thus resulted in a high substrate bias current, typically in the range of 6–14 A that was almost fourfold that in the magnetron sputtering. Furthermore, the low deposition pressure in the scale of $10^{-1}$ Pa would provide purer space and longer mean free path for the film-forming ions than that in several-Pascal scale as in the ordinary arc-ion-plating process. This also activated the high-energy ion bombardment in the scale of several-hundred volts for forming fine and dense structure of the films that enhanced their microhardness. Since biasing the substrate increases the density of excited radicals and brings a suitable high energy for ion bombardment onto the substrate, it also strengthens the microhardness of the films. However, the overlarge bias voltage, typically beyond −350 V, may enlarge residual stress in the TiN films that results in the degradation of the mechanical properties. Hence, the achievement of superhard TiN films requires the adequate optimization of the process parameters. Following analyses were performed on a 45 GPa TiN film deposited with a −200 V substrate bias voltage and 0.2 Pa gas pressure.

3.2. Film-to-substrate adhesion

The surface of the specifically deposited superhard TiN film was drawn across by a diamond stylus for scratch test with an ever-increasing normal load. During the loading process, noise signals and images
Fig. 3. Curves of changes of friction forces and acoustic signals during scratching test and typical morphology.

of friction force in the scratch test were monitored and plotted (Fig. 3). The variation of the curves for friction forces and noise signals along with the images of typical morphologies allows the determination of critical load \( L_c \) and the evaluation of the scratch history from the images of typical scratch traces (Fig. 3). The scratch trace for image 1 gave a flat trend with very mild variation, and the relative strength of the friction force and the friction noise was low. When the loading was increased, the morphology for image 2 illustrated signs of some visible scratch traces but with only a few wear cracks to be observed. However, the cracks were neither large enough to propagate through the film thickness range of the TiN layer, nor too small to break the film. It tended to increase the friction force and noise gradually. Further increasing the loading would lead to the commencement of forming chip in the film, as seen in image 3. When the applied load was approaching a critical value \( L_c = 64 \text{N} \) which was likely to break the film, some visible peeling traces were detected on the film surface, which subsequently caused a sudden raise in the friction force and noise. Increasing applied load beyond this value, brought about some enlarged cracks and chips along the scratch trace (see image 4 in Fig. 3) that led to a sharp fluctuation on the curves of friction forces and noise. The film illustrated peeling off at the end stage with a large load of 100N.

3.3. Microstructure

The microstructure characteristics of the superhard TiN film were investigated using the XRD technique so as to compare with those of the standard TiN films in PDF card 6-642. The XRD spectrum of the superhard TiN film (Fig. 4) illustrated a strong preferred crystalline orientation on the \((111)\) orientation plane and weak ones on the orientation planes of \((200)\) and \((220)\), differing from the standard TiN film in PDF card 6-642 that its \( I/I_o \) value of the relative intensity showed (i) the maximum characteristic peak of 100 for the \((200)\) plane at the \( 2\theta \) of 42.4°, and (ii) the intensities of the other two characteristic peaks decreases from 75 of the \((111)\) plane to 55 of the \((220)\) plane; the relative intensity of the maximum characteristic peak for the superhard TiN film was 100 for the \((111)\) plane at \( 2\theta \) of 36.5° and its minimum characteristic peak was 2.5 for the \((200)\) plane. This obviously illustrates that for the superhard TiN films deposited using the AIP system: (i) it gives a preferred orientation of the \((111)\) plane; (ii) its maximum characteristic peak is moved to the \( 2\theta \) of 73.7° \((111)\) plane instead of being on the \( 2\theta \) of 42.4° \((200)\) plane for the standard TiN film; and (iii) its intensity difference between the maximum and minimum characteristic peaks obviously becomes more striking.

As the structure of TiN material belongs to NaCl type face-centred cubic one in which Ti atoms constitute mainly to the skeleton of the crystal lattice with N atoms filling into its interspaces, TiN films hence share the densest structure at the \((111)\) plane rather than in the planes of \((200)\) and \((220)\). The formation of the preferred orientation and preferred growth at \((111)\) plane for the superhard TiN film may thus be due to the crystalline grains concentrating at the plane \((111)\) that subsequently constitutes orderly and uniform arrangement, whereas...
their lesser uniform arrangement occurs at planes of (200) and (220). Such orderly and preferred orientation greatly contributes to the super-hardness. The measured POD on the (111) plane of this film was 3.59 that is much higher than the value reported for the other sputtered TiN films.\textsuperscript{10}

When the deposited TiN films have crystal sizes below $10^{-5}$ cm, their broadened diffraction peaks tended to be sensitive with the decreasing crystal sizes as these sizes are below $10^{-5}$ cm. Under such circumstances, the crystal sizes can be calculated using the Scherrer formula\textsuperscript{11}:

$$D_{hkl} = \frac{K \lambda}{B_{1/2} \cos \theta},$$

(2)

where $D_{hkl}$ is the crystal size along the direction normal to the plane; $K$ is Scherrer constant; $\lambda = 0.154$ nm is the X-ray wavelength of CuK$_{\alpha}$ radiation; $B_{1/2}$ is the full-width at half maximum of a Bragg peak; and $\theta$ is the Bragg angle. Calculation gave the values of the mean nm-scale grain-sizes of the film as 12.7 nm for TiN$_{111}$, 19.7 nm for TiN$_{200}$, and 9.6 nm for TiN$_{220}$. All these values are smaller than that of the other AIP TiN films as reported in Ref. 12.

4. Conclusion

An adherent nanocrystalline superhard TiN film was deposited on the substrate of Cr$_{12}$Mo$_4$V high-speed steel using a multi-arc ion plating system that was operated under (i) a low depositing pressure of 0.2 Pa and (ii) the energetic bombardment of the high ion flux and ion energy. The nanocrystalline superhard TiN film so deposited possesses a microstructure characteristic of nanometer scale preferred crystalline orientation on the plane (111), which subsequently induces superhardness of the film.

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References