Effects of Substrate Pulse Bias Duty Cycle on the Microstructure and Mechanical Properties of Ti–Cu–N Films Deposited by Magnetic Field-Enhanced Arc Ion Plating

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Received: 30 October 2016/Revised: 19 November 2016/Published online: 6 February 2017
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Abstract Ti–Cu–N films were deposited on 316L stainless steel substrates by magnetic field-enhanced arc ion plating. The effect of substrate pulse bias duty cycle on the chemical composition, microstructure, surface morphology, mechanical and tribological properties of the films was systemically investigated. The results showed that, with increasing the duty cycle, Cu content decreases from 3.3 to 0.58 at.%. XRD results showed that only TiN phase is observed for all the deposited films and the preferred orientation transformed from TiN(200) to TiN(111) plane with the increase in duty cycle. The surface roughness and deposition rate showed monotonous decrease with increasing the duty cycle. The residual stress and hardness firstly increase and then decrease afterwards with the increase in duty cycle, while the variation of critical load shows reverse trend. Except for the film with duty cycle of 10%, others perform the better wear resistance.

KEY WORDS: Magnetic field; Arc ion plating; Ti–Cu–N film; Residual stress; Hardness

1 Introduction

TiN hard films have been successfully used in the cutting and forming tool industries due to their superior wear resistant and corrosion-resistant properties. With the development of industry, mechanical and tribological properties of TiN films cannot meet requirements of difficult-to-cut material [1, 2], so hard nanocomposite protective films have attracted considerable attention in recent years [3, 4]. The hard nanocomposite films are generally

divided two types. One is nc-MeN/hard phase nanocomposite, such as nc-TiN/a-Si₃N₄ and nc-TiN/a-TiB₂, and the other is nc-MeN/soft phase (such as Cu, Ni, Y and Ag.) [5]. Here nc- and a- stand for the nanocrystalline and amorphous phase, respectively, and Me = Ti, W, Zr, Cr, Mo, Al, etc., are elements synthesizing hard nitrides. Ti–Cu–N nanocomposite films as a typical nc-MeN/soft phase film have been widely investigated due to their excellent mechanical properties [6]. Recent reports also pointed out Ti–Cu–N nanocomposite films exhibited very good antibacterial properties [7].

Various physical vapour deposition (PVD) techniques have been used to prepare Ti–Cu–N nanocomposite films [8–10]. Arc ion plating (AIP) technique is one of the most prospective PVD techniques for large-scale industrial application of Ti–Cu–N films because of the high degree of ionization in the target material, the easy control of the parameters and the high deposition rate. However, some problems of conventional DC-biased AIP are universally recognized, such as droplet contamination, high substrate temperature and large residual stress, due to continuous ion bombardment on the substrate during the deposition.

Available online at <http://link.springer.com/journal/40195>

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Pulsed bias was then introduced into AIP to solve the problems and improve film quality [11–13].

In previous work, we also successfully deposited the Ti–Cu–N nanocomposite films on high-speed-steel substrates by pulse bias arc ion plating (PBAIP) [14] and designed a magnetic field-enhanced arc ion plating system with pulse bias (MFE-AIP) [15, 16]. The system, keeping all the merits of conventional AIP, brings new features such as macro-particle cleaning due to faster arc spot movement speed, film compactness promoting due to higher ionic charge density, as well as increased deposition rate due to more focused ion beam. As is well known, the properties of films can be optimized by selecting proper pulse bias parameters, e.g. voltage amplitude, duty cycle or pulse frequency [17–20]. The pulse bias duty cycle is the fraction of time that a pulse bias voltage is in an “active” state during one period and decides the quantity of plasma accelerated by bias electric field. However, there is little research for the effects of substrate pulse bias duty cycle on the microstructure and mechanical properties of Ti–Cu–N films.

In this present work, Ti–Cu–N films were deposited on 316L stainless steel by MFE-AIP. And then, the influence of the pulse bias duty cycle on surface morphology, microstructure and mechanical properties of the films was systematically investigated.

2 Experimental

2.1 Deposition of Ti–Cu–N Films

The Ti–Cu–N films were deposited on commercial mirror-polished 316L stainless steel sheets (30 mm × 30 mm × 0.8 mm and 50 mm × 10 mm × 0.8 mm) by the magnetic field-enhanced arc ion plating system [15]. The modulus of elasticity E_s and Poisson ratio ν_s of the substrates is 195 GPa and 0.3, respectively. The schematic

Fig. 1 Schematic view of the magnetic field-enhanced arc ion plating system used to deposit Ti–Cu–N films

diagram of this vacuum system is shown in Fig. 1. The target material was TiCu alloy (Ti/Cu-90:10 at.%) with purity of 99.99%. The axial magnetic field can be produced by an adjustable electromagnetic coil located outside and twined around the chamber. By regulating the coil current, the magnetic field strength can be controlled. And the magnetic induction was determined by a SHT-V magnetometer. The work gas was high-purity nitrogen (99.99 at.%) and high-purity argon (99.99 at.%), respectively. Prior to the film deposition, the base pressure of chamber was 5.0×10^{-3} Pa, and then Ar (gas pressure 0.3 Pa) was introduced to etch the substrate. Subsequently, Ti and Cu ions bombardment at a -600 V dc bias voltage was applied for 5 min with 70 A target arc current to improve the film/substrate adhesion.

During deposition, the pulse bias duty cycles were set as 10%, 30%, 50%, 70% and 80%, respectively, in order to study their influence on film properties. The other deposition parameters were kept constant: N_2 pressure 1.0 Pa, the pulsed bias amplitude -100 V with 40 kHz frequency, the arc currents 70 A, the distance between the target and substrate 300 mm, the magnetic field intensity 10 mT, the substrate temperature T_s about 300 °C and the total deposition time 40 min.

2.2 Characterization of Ti–Cu–N Films

The chemical composition was examined by X-ray photoelectron spectroscopy (XPS, ESCALAB250), with Ar^+ of sputtering voltage of 2 kV for 10 min. The microstructure analysis was carried out by X-ray diffraction (XRD, Rigaku, Japan, D/max2400 with $CuK_\alpha = 0.154056$ nm). The cross-sectional images and diffractions were obtained by a Tecnai G2 F20 S-Twin transmission electron microscope (TEM). The surface morphology and cross-sectional images of Ti–Cu–N films were characterized by a Zeiss Supra 55 scanning electron microscopy (SEM). The deposition rate was calculated according to the SEM cross-sectional images. The surface roughness R_a was determined by a KLA-Tencor Alpha-Step IQ surface profiler.

Hardness (H) and elastic modulus (E^*) measurements were taken by using a nanoindenter (Nano Indenter G200, Agilent Technologies) with a Berkovich diamond tip, the maximum applied load was 20 mN, and the indent depth was lower than 10% of film thickness. The residual stresses of the films were determined by substrate curvature technique [21]. The adhesion between the film and substrate was tested using a WS-2005 Automatic scratch tester with a loading speed of 100 N min^{-1} . The critical loads were determined from the acoustic signal.

The sliding wear resistance was tested using a MS-T3000 ball-on-disc tribometer. During the test, an alumina ball (4.0 mm in diameter) was used as the counter face.

The tests were carried out with a sliding speed of 0.06 m s^{-1} with a normal load of 5 N. The total testing time was 20 min (6 mm in diameter of wear track). The test temperature was about $(25 \pm 3) ^\circ\text{C}$, and the relative humidity was about 30%. The friction coefficient was directly obtained from measurement record. The dimensions of wear tracks were tested by a KLA-Tencor Alpha-Step IQ surface profiler. The wear rate k can be calculated by the following formula [22]:

$$k = V/(SL). \quad (1)$$

where V is the wear volume calculated according to the dimensions of wear tracks, and S and L are the total sliding distance and the imposed load, respectively.

3 Results and Discussion

3.1 Chemical Composition

Negative pulse bias is usually used to produce an electric field with pulse mode (not d.c. mode) and to increase the energy and quantity of plasma reaching substrates. When the pulse is “on”, a pulse sheath can be produced and all the positively charged ions entered into the pulse sheath will be accelerated to obtain more energy. The duty cycle is a ratio of pulse duration to a complete cycle period. The bigger is the duty cycle, the more quantity of plasma will be accelerated, at the same time the higher is the average energy of plasma reaching substrates. The atomic content in the Ti–Cu–N films is shown in Fig. 2. The result showed that the content of Cu appeared to decrease from 3.3 to 0.58 at.% with substrate pulse bias duty cycle increasing from 10% to 80%. The content of Ti and N appeared to slightly decrease and remarkably increase, respectively, with increasing duty cycle. Sundgren’s study already pointed out that the energy of the charged particle

impinging on the substrate increased as the bias voltage increased [23]. Because the sputtering yield increased with energy, more materials were resputtered with the increase in pulse bias duty cycle. It is shown that the sputtering yield of Cu is higher than that of Ti [24]. Therefore, the decrease in the atomic fraction of Cu was attributed to the discriminatory resputtering of Cu atoms. Meanwhile, the decrease in the atomic fraction of Ti would also be related to the resputtering effect with increasing the duty cycle, and in comparison with the results of Ti and Cu content, N content would be therefore increased.

For further understanding the phase composition and the possible chemical bonding states of Cu in the Ti–Cu–N films, Cu2p XPS spectra for the film with duty cycle 50% are presented in Fig. 3. The Cu2p peaks appear at 932.4 eV and 933.1 eV for Cu2p_{3/2} and 952.4 eV for Cu2p_{1/2}. Tian et al. [25] observed the peaks of Cu2p_{3/2} at 932.7 eV and 933.8 eV, and Wang et al. [26] surveyed the peaks of Cu2p_{3/2} at 931.8 eV and Cu2p_{1/2} at 951.9 eV. Both of them attributed these results to pure metallic Cu. Therefore, in this present work we suggest that Cu exists mainly in the form of free copper in the films.

3.2 Microstructure

For the evaluation of microstructures of the Ti–Cu–N films under different pulse bias duty cycles, XRD spectrum tests were performed. Figure 4 shows XRD patterns of the Ti–Cu–N films. It is clear that all results only show the diffraction peaks that can be allocated to cubic TiN. There is not any diffraction peak from copper to be observed, excluding the possible superposition of TiN(200) with Cu(111). It is extremely hard to distinguish them due to their similar crystalline interplanar spacing [6]. In addition, it is also the possible reason that fairly low content and very fine grain size of Cu in the films. As shown in the figure, the films exhibited a relatively strong TiN(200)

Fig. 2 Chemical compositions (at.%) of Ti–Cu–N films plotted as a function of duty cycle

Fig. 3 X-ray photoelectron spectral details collected from the Ti–Cu–N film with duty cycle of 50%

Fig. 4 X-ray diffraction patterns of the Ti–Cu–N films prepared under different bias duty cycle

orientation plane at pulse bias duty cycle of 10%, and the texture of the films transformed from TiN(200) preferred orientation to TiN(111) with pulse bias duty cycle increasing from 30% to 50%. Specially, for the films with 70% and 80% duty cycles, the (222) diffraction peak also occurred. Conclusively, the enhanced pulse bias duty cycle is beneficial for TiN(111) preferred orientation of the Ti–Cu–N films. The intensity of peak of Fe from the substrates gradually increased with duty cycle, which implied that the thickness of the films decreased.

As we know, for PVD deposition, in order to minimize the films' total energy (includes surface energy and strain energy) during their growth, preferred orientation of the films will be formed [27, 28]. For films with both fcc- and NaCl-type structure, the surface energy (S_{hkl}) changes with the preferred orientation as $S_{111} > S_{220} > S_{200}$ [29], while the strain energy (U_{hkl}) converts with the preferred orientation as $U_{200} > U_{220} > U_{111}$ [30]. In this study, for minimizing the total energy in the Ti–Cu–N films during their growth, the (200) orientation was dominant for the lowest surface energy when bias duty cycle (i.e. lower ions energy) lowered. With bias duty cycle increasing (i.e. ions energy increasing), the (111) orientation got stronger and became dominant for the lowest strain energy.

In addition to the XRD analysis, the microstructures of the Ti–Cu–N films were evaluated using TEM observation. Figure 5 shows the diffractions and the cross-sectional TEM images of the films at pulse bias duty cycle of 10%, 50% and 80%, respectively, and a high-resolution image from the film with 50% duty cycle. Regions A, B and C showed some results of the selected area electron diffraction (SAED). From the bright field image, the microstructure shows almost equiaxed grains whose size could be estimated to be about 10–50 nm, similar to the results of our previous work [14]. According to the morphology and diffraction pattern, the grain size increased

firstly and then decreased with the pulse bias duty cycle increasing, which could be related to the next reasons. One reason is grain refining due to bias duty cycle increasing, and the other is grain refining owing to increasing the copper content [6, 31]. Some researchers had concluded by means of theoretical analysis that the Cu exists as the very tiny grains dispersing around the TiN nanocrystallites [6, 11]. According to some high-resolution images, we can clearly observe that the Cu survives as amorphous particle around the TiN crystallites, and one of them is shown in Fig. 5. Because the Cu cannot wet TiN, it is too difficult for Cu to form amorphous layer surrounding the TiN crystallites [9, 31, 32]. In this present work, we suggest that the Ti–Cu–N films are the nanocomposite films formed with Cu amorphous particle and TiN nanocrystallites. Anders put forward to an extended structure zone diagram used to understand the relation between energy flux and growth structure [33]. In his model, when the normalized energy flux exceeds a certain amount, the growth structure will be transformed to nanocrystalline with preferred orientation, which can be used to explain our experiment results. Due to the application of axial magnetic field, the ion quantity and energy increased compared to the conventional AIP technique. Furthermore, both the ion quantity and energy increased with duty cycle, which are favourable for the formation of nanocrystalline structure with preferred orientation.

3.3 Morphology

The SEM surface and cross-section images of the Ti–Cu–N films are shown in Fig. 6. Many macroparticles (MPs) were observed on the surface of the films. With the duty cycle increasing, the number and size of MPs and the sputtered craters obviously decreased. In general, the change in bias voltage amplitude will lead to variety of the sheath thickness and the quantity of particle accelerated. However, the duty cycle only affected the quantity of particle accelerated when the bias amplitude was fixed. The MPs with weak negative charges would be repeatedly charged in the pulse sheath under pulse electrical field and then were repelled by the substrate with negative bias [34]. Therefore, the higher the duty cycle, the less the MPs on the film surface. In addition, some long rod MPs were observed on the surface of the films under lower duty cycle, which were originated by mutual collision and concentration of the MPs. According to the cross-sectional images in Fig. 6, there is no obvious defect in the films and deposition rate can be calculated based on the thickness of the films.

The surface roughness (Ra) and deposition rate of the Ti–Cu–N films as a function of duty cycle are shown in Fig. 7. It can be seen that the surface roughness decreases with the duty cycle increasing, which attributes to the less

Fig. 5 A cross-sectional TEM micrographs and electron diffraction patterns of the Ti–Cu–N films with duty cycle of 10%, 50% and 80%, and a high-resolution photograph of the Ti–Cu–N film with duty cycle of 50%

Fig. 6 SEM images of Ti–Cu–N films deposition with different duty cycles

MPs and sputtered craters on the film surface (see Fig. 6), similar to the results of Wei and Gong [17]. The deposition rate also decreases with the duty cycle increasing, probably because the increase in duty cycle could enhance ion

bombardment [35], which causes more intensive resputtering during film deposition. The variation trend of deposition rate is consistent with the results from XRD

Fig. 7 Surface roughness and deposition rate of Ti–Cu–N films as a function of bias duty cycle

with the fact that the diffraction peaks of substrate increases with the duty cycle.

3.4 Mechanical Properties

Figure 8 shows the variations of the residual stress and the critical load of the films as a function of duty cycle. The residual stress firstly increased and then decreased with duty cycle increasing, while the critical load showed almost opposite trend. It was mentioned that the ion energy would be enhanced with duty cycle in the previous paragraph. The compressive stress increased when the film was bombarded by ions with energies of tens or hundreds of eV through a process of “atomic peening” [36, 37]. However, further increasing the energies of bombarding ion could cause lattice relaxation and recrystallization. The residual stresses can be relaxed by the thermal spikes, which results in the release of strain caused by the atomic peening effect [38]. Therefore, in this present work, the residual stress increases initially and decreases afterwards with duty cycle

Fig. 8 Residual stress and critical load of Ti–Cu–N films as a function of bias duty cycle

increasing. It is easy to find the correlation between the critical load and residual stress. The critical load rises when the residual stress declines, and vice versa.

The values of hardness H and elastic modulus E of the films measured by nanoindentation are presented in Fig. 9a as a function of duty cycle. They were obtained by using Oliver and Pharr’s method [39]. It seemed that both the H and E showed almost relevant tendency as the residual stress. With the increase in duty cycle, the density of plasma and the ion bombardment were improved. The “atomic peening” effect probably dominates variation tendency of the hardness and elastic modulus. Toth’s study pointed out that the texture can play a role for the film hardness when the same compositions are applied [40]. In this present work, the maximum hardness was achieved at duty cycle of 50% owing to higher stress and stronger preferred orientation. Veprek *et al.* [3] reviewed the origin of hardness enhancement in the nanocomposite films. It has been reported that the strengthening mechanism of the hardness of the nanocomposite film is a combination of many factors, such as chemical bonding, solution hardening, Hall–Petch strengthening and formation of a stable nanostructure. As is well known, the hardness of the common ternary nitrides (e.g. TiAlN, CrAlN, TiCN) is originated from solution hardening, but the hardness of the transition metal nitride based on nanocomposite films depends on grain boundary hardness [41]. In general, Hall–Petch effect is used to explain the grain boundary hardness of nanocomposite films. However, in this case, our results might be not entirely consistent with the effect. Argon and Yip provided an analytical model that explains in detail the physics of the competition between decreasing dislocation activity and increasing grain boundary shear, which results in the so-called strongest size [42, 43]. For smaller grain size, the hardness will decrease due to grain boundary shear. In this present work, the grain size of the film with

Fig. 9 Hardness, elastic modulus and H^3/E^2 value of Ti–Cu–N films as a function of bias duty cycle

50% duty cycle may be more close to the “strongest size” of the Ti–Cu–N films, and then it has the highest hardness. In addition, Myung *et al.* [6] reported that the Ti–Cu–N film containing approximately 1.5 at.% Cu achieved maximum hardness of 45 GPa, and the hardness value will reduce no matter copper content increase or decrease. The research of Zhang *et al.* [44] showed that the Ti–Cu–N films reached a maximum hardness of 37 GPa with the Cu content of about 0.6 at.%. Their works indicated that the hardness of the Ti–Cu–N film was strongly correlated with Cu content. In our experiments, from 30% to 70% duty cycle, the Cu content of the Ti–Cu–N film was closed to 1.5 at.% (see Fig. 2). Meanwhile, Li *et al.* [45] pointed out that the Ti–Cu–N film with strong TiN(111) texture will exhibit higher hardness. The interaction of Cu content, the grain size and the growth texture in the films determines the variation tendency of the hardness of the films with duty cycle.

The ratio H^3/E^{*2} is the parameter that can represent the plastic deformation resistance of materials [46]. The higher the ratio H^3/E^{*2} , the better the wear resistance is. It can be seen that the ratio H^3/E^{*2} increases with duty cycle and the ratio remained higher value when the duty cycle is higher than 50% (see Fig. 9b). This means that the Ti–Cu–N film with higher duty cycle might be better wear resistance.

3.5 Tribological Properties

Figure 10 reveals the wear rate and friction coefficient as a function of duty cycle. The wear resistance is related to the hardness of composite films. According to Archard’s law, the wear resistance of a material is proportional to its hardness [47]. The wear rate of the film was extremely high at duty cycle of 10%, because its hardness was obviously lower and its number of MPs was remarkably more. It seemed that, with the increase in the duty cycle from 30%

to 80%, the wear rate of the films did not depend on the hardness and they had little change, which is roughly corresponding to the variation of the ratio H^3/E^{*2} . In our previous work [15], the wear rate of the TiN films is $10^{-13} \text{ m}^3 \text{ N}^{-1} \text{ m}^{-1}$, which is higher two orders of magnitude than the Ti–Cu–N films in the present work. That indicates that the abrasive resistance of the films got significant improvement due to the addition of Cu in TiN films. As can be seen, the average friction coefficient of the films shows little difference with the different duty cycles. In some results, the friction coefficient of the Ti–Cu–N films is less than 0.5 [6, 26, 48]. However, in our tests, the friction coefficients of the films are almost close to 1.0 and even higher than of most TiN films, which is similar to the results from Ozturk *et al.* [49]. We considered that the “crystal chemical” approach put forward by Erdemir [50] can be used to explain the tribological behaviour in this case. According to this approach, those oxides or oxide mixtures with higher difference of ionic potentials are more likely to present low friction. Conversely, the presence of those oxides with lower difference of ionic potentials will cause high friction. In these experiments, the surface of the Ti–Cu–N films during friction will form titanium oxides and copper oxide and their ionic potentials difference is rather small, which caused high friction coefficients of the films. Guo *et al.* [51] reported that the friction coefficients of the AlCuN nanocomposite films are also close to 1.0 and the wear rate gets $1.3 \times 10^{-16} \text{ m}^3 \text{ N}^{-1} \text{ m}^{-1}$ due to the dense microstructure in the films. Our results are higher two orders than the results of Guo *et al.*, which may be related to higher residual stresses in the films.

Figure 11 shows the wear scars morphologies of the Ti–Cu–N films. It was easy to find that there is no crack and abscission in all the wear scars. For most of the tribological applications, the most commonly encountered wear types are: adhesive, abrasive, fatigue and chemical (or corrosive). Now that the micro-plough does not exist on the wear scars; the wear mechanisms of the Ti–Cu–N films should be belonging to abrasive wear. The review summarized by Homlberg *et al.* [52] pointed out that the hard films on softer substrate can make friction and wear decrease by preventing ploughing both on a macroscale and a microscale. By EDS measurement, the wear debris mainly originate from Al_2O_3 wear ball. In particular, for the film under the duty cycle of 10%, some debris adhered to the surface of the film, which led to larger wear scar and wear rate.

4 Conclusion

Ti–Cu–N films have been deposited on SS substrates by magnetic field-enhanced arc ion plating system. The pulse bias duty cycle had obviously influence on the

Fig. 10 Wear rate and Friction coefficient of Ti–Cu–N films as a function of bias duty cycle

Fig. 11 Wear scar morphologies of Ti-Cu-N film at different duty cycles

composition, structure and properties of Ti-Cu-N films. With the increase in substrate pulse bias duty cycle, the texture transformed from TiN(200) to TiN(111), and the grain size firstly increased and then decreased. Due to gradually enhanced ion bombardment, resputtering effect is more enhanced, and then surface roughness and deposition rate decrease. The residual stress and hardness increase initially and decrease afterwards with the increase in duty cycle, while the variation of critical load is reverse. Except for the film under duty cycle of 10%, the films show better wear resistance. The film with duty cycle of 50% showed the better comprehensive mechanical properties, including higher hardness, proper stress, better adhesion and lower wear rate. Such optimization process of duty cycle would be quite favourable for industrial application in the future.

Acknowledgements This work was supported by the National Natural Science Foundation of China (Grant No. 51401128) and Shenzhen Science and Technology Project (No. JCYJ20140508155916426).

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