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ARTICLE

Effect of Substrate Pulse Bias Voltage on the Microstructure and Mechanical and Wear-resistant Properties of TiN/Cu Nanocomposite Films

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Abstract: TiN/Cu nanocomposite films were deposited on high-speed steel (HSS) substrates by axial magnetic field-enhanced arc ion plating (AMFE-AIP). The effects of substrate bias voltage on chemical composition, microstructure, mechanical and tribological properties of the films were investigated by X-ray photoelectrons spectroscopy (XPS), X-ray diffraction (XRD), nanoindentation and wear measurements, respectively. The results show that the Cu content increases first and then decreases with the increase of the pulse bias voltage, being a low value in the range of 1.3 at%~2.1 at%. XRD results show that only the TiN phase appears in all the films, and no Cu phase is observed. The preferred orientation of the films changes significantly with the increasing pulse bias voltage. A maximum value of hardness of 36 GPa is obtained under a pulse bias voltage of –200 V, corresponding to the film containing 1.6 at% Cu. Compared to the pure TiN film, the Cu addition in TiN films significantly improves the wear resistance.

Key words: arc ion plating; magnetic field; pulse bias; microstructure; mechanical property

Hard nanocomposite films, including hard transition metal nitride phases (nc-*Me*N) and soft metal phases (*Me*′), have attracted much attention owing to their characteristics, such as high hardness (up to 40 GPa) [1], high toughness[2] and excellent wear resistance[3]. The elements *Me*=Ti, Zr, Cr, Al, etc form hard nanocrystalline metal nitrides, and the elements *Me*′ composed of Cu, Ni, Ag, Y, etc. form soft phases [4]. This kind of hard nanocomposite films were proposed by Musil et al[5] in 1998. Among all nanocomposite films, TiN/Cu nanocomposite films have been widely investigated by many researchers. In particular, the incorporation of Cu can increase the hardness of the TiN film, but the friction coefficient of the nanocomposite film can be increased or decreased depending on Cu content and other factors[5,6]. Arc ion plating has been widely used in the industrial fields of cutting tools, moulds and other mechanical components for at least forty years, greatly improving the mechanical and wear-resistant properties of these workpieces. But this technique suffers from severe macroparticles (MPs) pollution on the final film surfaces, and the film quality is conversely deteriorated by MPs [7]. In order to solve this problem, the steered arc method is developed based on the interaction between the external magnetic field and the arc spot[8]. It was shown that the speed of the arc spot movement is strongly increased with the increasing magnetic field intensity. More importantly, higher ion/plasma density [9], higher ion energy[10], and higher ion charge state[11] can be easily achieved when a strong axial magnetic field is applied to the cathode surface.

In our previous work[12,13], both TiN and CrN films were deposited by axial magnetic field-enhanced arc ion plating (AMFE-AIP). The hardness values of the films firstly increased and then decreased with increasing magnetic field intensity. The maximum value of hardness responds to a

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rather low magnetic field intensity (about 5 mT to 10 mT). In the present work, when applying a very low magnetic field intensity (10 mT), the effects of substrate bias voltage on the chemical composition, microstructure, mechanical and wear-resistant properties of TiN/Cu nanocomposite films were investigated.

1 Experiment

An axial magnetic field-enhanced arc ion plating system was used to deposit TiN/Cu films, which was described in our previous work[12]. The system has a vacuum chamber with an inner diameter of 350 mm and a length of 450 mm, and the cathode target (made of Ti90at%Cu10at% alloy prepared by a melting method with purity of 99.99%, and pure Ti cathode target prepared by the melting method with purity of 99.99%) was placed at one of the chamber walls. An electromagnetic coil was winded outside the vacuum chamber in order to produce the axial magnetic field. And the intensity of magnetic field can be adjusted by changing the coil current. The value of the magnetic induction was measured by a magnetometer (SHT-V type from China). The commercial M2 high speed steel (HSS) samples with a size of 20 mm × 14 mm × 3 mm was served as the substrates. Before the substrates were put on the substrate support in the vacuum chamber, they were mirror polished and ultrasonically cleaned in alcohol and then thermally dried. Before the film deposition, a base pressure of about 5×10^{-3} Pa was obtained, and the substrate surface was bombarded with a TiCu alloy target for 5 min with an arc current of 70 A, an Ar partial pressure of 0.3 Pa and a dc bias of −600 V. During film deposition, the following parameters remain unchanged: arc current I_{TiCu}=70 A, N_2 partial pressure P_{N2}=1.0 Pa, distance between cathode and substrate of 300 mm, magnetic field intensity on the substrate surface of 10 mT, total deposition time of 40 min. During the deposition, a pulsed bias was applied to the substrates, and the pulse bias voltages were set to −50, −100, −200, −300, −400 and −500 V. The pulse bias duty ratio of 30% and pulse frequency of 40 kHz were applied. The substrate temperature was about 300 °C. For comparison, a TiN film was also deposited by the substrate pulse bias voltage of −300 V.

The chemical composition was identified by X-ray photoelectron spectroscopy (XPS, ESCALAB250, Thermo VC, USA), with sputtering voltage of Ar^+ of 2 kV for 10 min. The microstructure analysis was carried out by X-ray diffraction (XRD, Rigaku, Japan, D/max2400 with Cu Kα λ=0.154 056 nm) and transmission electron microscopy (TEM, Tecnai G2 F20 S-Twin). Hardness (H) and elastic modulus (E*) were tested 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 to avoid the effects of substrates. In order to get rid of the non-uniformity of the films, the hardness values were averaged over more than 10 measurements.

The sliding wear behavior was measured using a ball-on-disk tribometer (MS-T3000, China). During the test, an alumina ball (4.0 mm in diameter) was selected as the counter material. The tests were carried out at a sliding speed of 0.06 m/s and a normal load of 5 N. The total testing time was 20 min (6 mm in diameter of wear track). The temperature was about 25±3 ºC and the relative humidity was about 30%. A computer was used to continuously record the friction coefficient during the whole testing processes. After each test, a surface profiler was used to calculate the worn volume from multiple profiles of the cleaned wear tracks. The specific wear rate K can be calculated by the following equation [14]:

$$K = V/(SL) \tag{1}$$

where V is the wear volume of the TiN/Cu films calculated by the dimensions of wear tracks, and S, L are the total sliding distance and the applied load, respectively. It should be noted that at least 3 samples were tested for each experiment to assure repeatability.

2 Results and Discussion

2.1 Chemical composition of the as-received coating

Fig. 1 shows the elemental content in the TiN/Cu films. It can be seen that the content of Cu decreases from 2.1 at% to 1.3 at% as the substrate bias voltage increases from −50 V to −300 V, and then slowly increases to 1.6 at% with the further increase of the substrate bias voltage. The content of Ti and N firstly increases and then slightly decreases with increasing substrate bias voltage. It could be related to the sputtering yield of species. The sputtering yield increases with the energy of the species impinging on the substrate surface. The sputtering yield of Cu is larger than that of Ti[15]. Therefore, the decrease of the atomic fraction of Cu also decreases with the increase of bias voltage from −50 V to −300 V. As the substrate bias voltage further increases, the decrease of Cu content will be caused by inward diffusion[15]. In this case, the atomic fraction of Cu gradually increases when bias voltage decreases from −300 V to −500 V. All the TiN/Cu films show a very small amount of impurities, such as oxygen.

2.2 Microstructure

Fig. 2 shows the XRD patterns of the pure TiN and Ti-Cu-N films deposited at different substrate pulse bias voltages. It can be seen that all the TiN/Cu films reveal only diffraction peaks that can be assigned to the cubic TiN (B1-NaCl type structure). A diffraction peak of TiN in preferential orientation (111) is observed when the substrate bias voltage is from −50 and −300 V, whereas the corresponding peak changes to preferential orientation (220) when the pulse bias voltages increases to −400 and −500 V. The pure TiN film also shows a pronounced TiN(111) pre-

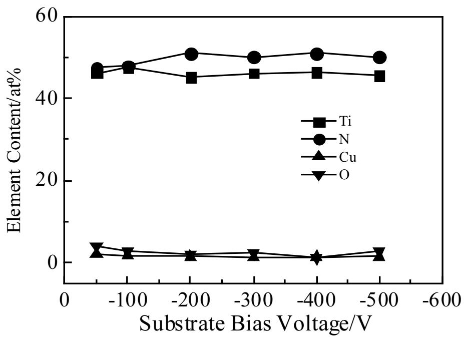

Fig. 1 Elemental content of the TiN/Cu films as a function of substrate pulse bias voltage

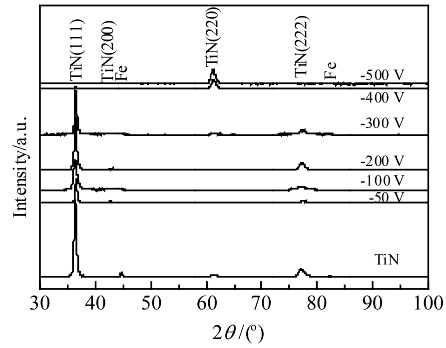

Fig. 2 XRD patterns of the pure TiN and Ti-Cu-N films deposited at different substrate pulse bias voltages

ferred orientation, and two weak diffraction peaks at about 61° and 74° are identified, corresponding to TiN(220) and TiN(222), respectively.

No reflection peaks of crystalline Cu are seen in all the films. This can be attributed to the low Cu content and the quite fine grain size of Cu crystals in the films. Moreover, no Cu nitride phase is formed, similar to our previous results[15].

Fig.3 shows the plan-view TEM observation of TiN/Cu films at different pulse bias voltages of −200 and −500 V. It can be clearly seen that small elongated crystals with an aspect ratio of about 5 (=150:30) are observed and no apparent porosity is found on the surface of the film. Under different pulse bias voltages, the grain size is almost the same, similar to the calculated results of Fig.3. The crystal structure of TiN/Cu films was also investigated by the selective area electron diffraction (insets) and TEM. A rock-salt structure (NaCl type) with (111) and (220) textured grain was determined for −200 and −500 V, respectively, similar to the results of XRD patterns in Fig. 2.

The increase of substrate pulse bias voltages will increase the ion energy arriving on the surface of the substrates, and the increased ion energy are possible to affect the thermodynamic and kinetic effects and as a result the preferred orientation and grain size of the films will be changed[16]. As for the small elongated crystals of the films, similar results of TiN/Cu films have been obtained by the same deposition technique [17]. At present, there is no evidence for the emergence of such structure, and much work needs to be done to analyze the reason in the future.

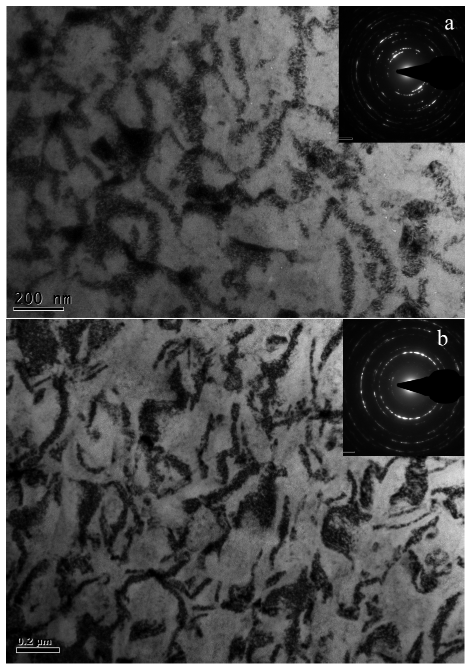

Fig. 3 TEM images and SAED patterns (inset) of TiN/Cu films at different pulse bias voltages: (a) −200 V and (b) −500 V

2.3 Mechanical properties

Hardness values of the TiN/Cu films measured by nanoindentation are shown in Fig. 4a as a function of substrate pulse bias voltage. It can be observed that the hardness increases from 19 GPa at −50 V, to a maximum of 36 GPa at −200 V corresponding to the film containing approximately 1.6 at% Cu. As the pulse bias voltage further increases, the film hardness decreases slowly and reaches 32 GPa at −500 V. Therefore, our results show that only 1at%~2 at% copper can significantly increase the hardness of TiN/Cu films.

Elastic modulus values of the films are also presented in Fig. 4b, showing a almost relevant difference in their values with hardness. As is well known, the resistance to plastic deformation of the films is proportional to the ratio of H^3/E^{*2}, and thus high hardness and low modulus are desirable [15]. A high H^3/E^{*2} value means a reduced contact pressure, because the applied load is distributed over a larger area[18]. The values of H^3/E^{*2} of TiN/Cu films are presented in Fig. 4c, which show a similar trend. It can be seen that higher values of H^3/E^{*2} are obtained at higher pulse bias voltages above −100 V, which suggests better mechanical properties.

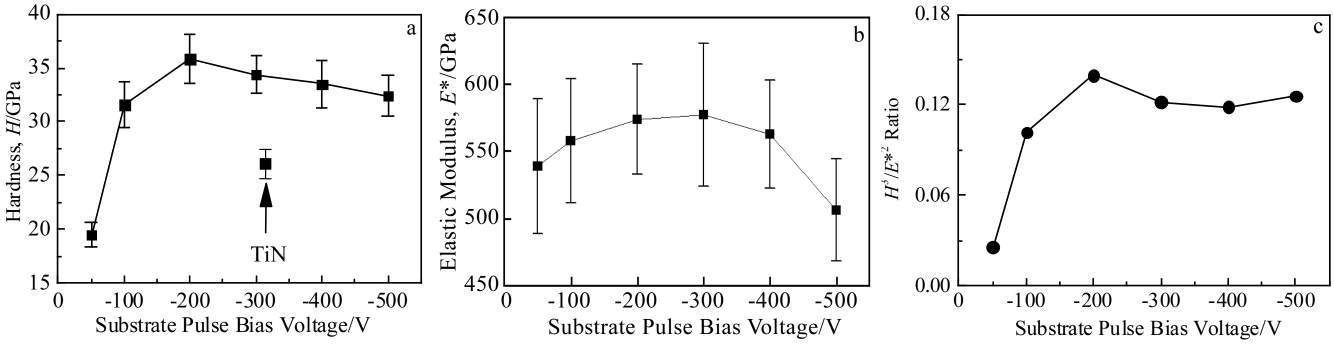

Fig.4 Hardness H (a), elastic modulus E^* (b) and H^3/E^{*2} ratio (c) of TiN/Cu films as functions of substrate pulse bias voltage

This increased ion bombardment caused by the increase in the substrate pulse bias voltages will increase the adatom mobility on the surface and enhance the displacement of surface atoms, which results in densification and changes of residual stresses of the growing films[6, 19]. Such structural change of the film can cause mechanical properties including hardness.

2.4 Wear resistance

Fig.5 shows the specific wear rate of the TiN/Cu films as a function of substrate pulse bias voltage. From the figure, one can see that the wear rate firstly increases with the substrate pulse bias voltage, reaches a maximum value at −100 V and then decreases, finally keeps almost unchanged when the pulse bias voltage becomes higher than −300 V. Moreover, it can be noted that the wear rate of the TiN/Cu films is much lower than that of TiN, which suggests that the addition of Cu can improve the wear resistance of TiN films.

The results of Ljungerantz et al[20] and Espinoza-Beltrán et al[21] show that the residual stresses of metal nitride films depend on substrate bias voltage, and the maximum value of residual stress can be found when the substrate bias voltage ranges from −80 V to −150 V. In this case, the higher wear rate at −100 V in this work may be related to the higher residual stress in the film. The plastic deformation

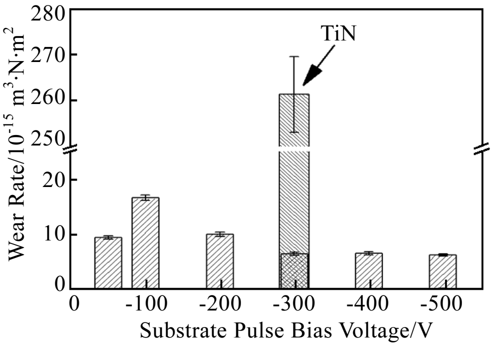

Fig.5 Wear rate of TiN/Cu films as a function of substrate pulse bias voltage

resistance (H^3/E^{*2}) of the films was verified to be an indicator for the wear resistance[18]. The higher the ratio of H^3/E^{*2}, the better the wear resistance. In this work, the ratio H^3/E^{*2} of the films has a high value when the substrate pulse bias voltage becomes higher than −200 V, which suggests that the films have a lower wear rate and better wear resistance.

3 Conclusions

1) TiN/Cu films are obtained by magnetic field-enhanced arc ion plating under different substrate pulse bias voltages. All films contain only TiN phase and no copper phase is observed.

2) The maximum hardness of 36 GPa is obtained for TiN/Cu film containing approximately 1.6 at% Cu under the substrate pulse bias voltage of −200 V.

3) A lower rate and better wear resistance are obtained when the substrate pulse bias voltage becomes higher than −200 V, which is related to the higher ratio H^3/E^{*2} of the films.

References

1 Musil J. *Surface and Coatings Technology*[J], 2000, 125: 322
2 Tian L H, Zhang Y, Ma Y *et al. Surface and Coatings Technology*[J], 2013, 228: S495
3 Lee J W, Kuo Y C, Chang Y C. *Surface and Coatings Technology*[J], 2006, 201: 4078
4 Musil J, Zeman P, Hrubý H *et al. Surface and Coatings Technology*[J], 1999, 120-121: 179
5 Musil J, Vlček J. *Materials Chemistry and Physics*[J], 1998, 54: 116
6 Zhao S S, Zhao Y H, Cheng L S *et al. Acta Metallurgica Sinica*[J], 2017, 30(2): 176
7 Zhao Y H, Lin G Q, Xiao J Q *et al. Applied Surface Science*[J], 2011, 257: 5694
8 Lang W C, Xiao J Q, Gong J *et al. Vacuum*[J], 2010, 84: 1111
9 Oks E M, Savkin K P, Yushkov S Yu *et al. Review of Scientific Instruments*[J], 2006, 77: 03B504
10 Anders A, Yushkov G Yu. *Journal of Applied Physics*[J],

2002, 91: 4824
11 Oks E M, Brown I G, Dickinson M R *et al. Applied Physics Letters*[J], 1995, 67(2): 200
12 Zhao Y H, Yang W J, Guo C Q *et al.* [J], 2015, 28(8): 984
13 Zhao Y H, Xu L, Guo C Q *et al. Acta Metallurgica Sinica*[J], 2016, 29(6): 546
14 Wang T G, Jeong D, Liu Y M *et al. Surface and Coatings Technology*[J], 2012, 206: 2638
15 Zhao Y H, Wang X Q, Xiao J Q *et al. Applied Surface Science*[J], 2011, 258: 370
16 Shen W J, Tsai M H, Chang Y S *et al. Thin Solid Films*[J], 2012, 520: 6183
17 Lu H C, Chen H Y. *Surface and Coatings Technology*[J], 2000, 130: 290
18 Galvan D, Pei Y T, Hosson J T M De. *Surface and Coatings Technology*[J], 2006, 200: 6718
19 Olbrich W, Kampschulte G. *Surface and Coatings Technology* [J], 1993, 61: 262
20 Ljungcrantz H, Hultman L, Sundgren J E *et al. Journal of Applied Physics*[J], 1995, 78: 832
21 Espinoza-Beltrán F J, Che-Soberanis O, García-González L *et al. Thin Solid Films*[J], 2003, 437: 170

基体脉冲偏压对 TiN/Cu 纳米复合薄膜组织结构、力学及耐磨性能的影响

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摘 要：采用轴向磁场增强电弧离子镀在高速钢基体上沉积了 TiN/Cu 纳米复合薄膜，研究了基体脉冲偏压幅值对薄膜成分、结构、力学性能及耐磨性能的影响。结果表明，薄膜中铜含量随着脉冲偏压幅值的增加先增加而后降低，在一个较低的范围内（1.3 at%~2.1 at%）。X 射线衍射结果表明所有的薄膜均出现 TiN 相，并未观察到 Cu 相。薄膜的择优取向随着脉冲偏压幅值的增加而改变。薄膜的最高硬度为 36 GPa，是在脉冲偏压幅值为−200 V 时得到的，对应了 1.6 at%的 Cu 含量。与纯的 TiN 薄膜相比，Cu 的添加明显增强了薄膜的耐磨性能。

关键词：电弧离子镀；磁场；脉冲偏压；显微结构；力学性能

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