Lifescience Global

Journal of Coating Science and Technology
http://www.lifescienceglobal.com/journals/journal-of-coating-science-and-technology

Reactive DC Magnetron Sputtering-Induced the Formation of Amorphous CuN Films Embedded Nanocrystalline WC Phase

Yue Lin and Shihong Zhang*

School of Materials Science and Engineering, Anhui University of Technology, Maanshan City, Anhui Province, 243002, P.R. China

Abstract: A novel amorphous CuN/nanocrystal WC (nc-WC/a-CuN) film synthesized by reactive dc magnetron sputtering is reported in this paper. The nc-WC/a-$CuN_{42\ at.\%}$ film which is composed of many WC dendrite crystals of 5~10 nm with (001) orientation embedded in amorphous CuN possesses ~55 GPa hardness. The high-temperature wear analysis shows that this novel film possesses the comparable excellent friction performance with DLC film which is attributed to self-lubricant function of a-CuN; simultaneously the film was still maintaining the higher hardness at elevated temperature.

Received on 07-04-2016
Accepted on 15-04-2016
Published on 24-05-2016

Keywords: Nanocomposite film; Reactive magnetron sputtering; CuN; WC; High-temperature wear behavior.

DOI: http://dx.doi.org/10.6000/2369-3355.2016.03.01.3

1. INTRODUCTION

It is generally accepted that microcrystal tungsten carbide (WC) synthesized by thermal spraying techniques has been widely used as hard wear-resistant coatings due to its high thermal stability and excellent wear resistance at elevated temperature. However, for all spraying WC systems at high temperature (>2000 ^{o}C), the loss of carbon (decarburization) caused by phase decomposition or oxidation during spraying deposition is very common. These phenomena directly resulted in the significant loss of carbide, which is detrimental since the decarburization-resulted phases, e.g., W_2C, W, are weaker than the original WC in wear resistance [1, 2]. Thus, preparing WC films by magnetron sputtering would be a better choice due to the low preparation temperature. Although some researchers synthesized nanocrystal WC/amorphous diamond-like carbon (DLC) nanocomposite films by physical vapor deposition (PVD) [3, 4], it is well known that the thermal stability of DLC film is poor because carbon would dissolve in most of metals when the temperature is above 500 ^{o}C [5, 6]. While, copper possesses excellent toughness and self- lubricious behavior at wide range of temperatures [7, 8]. And many hard nitrides such as TiN, AlN, CrN, Si_3N_4 and TaN are successfully introduced into superhard nanocomposites [9]. However, up to now, copper nitride phase in superhard films haven't been reported. In this paper, a novel amorphous CuN/nanocrystal WC (nc-WC/a-CuN) film was synthesized by reactive dc magnetron sputtering, and the microstructures, hardness and wear resistance at elevated temperature of nc-WC/a-CuN film were studied.

2. EXPERIMENTAL DETAILS

Three WC-CuN films incorporating different amounts of WC were deposited on Si(100) at 300 ^{o}C by a reactive dc magnetron sputtering system with dual targets of Cu and WC (including 5 at.% binder Co). The sputtering was carried out in Ar (20 sccm)-N_2 (40 sccm) gas mixture under a substrate biased voltage of −200 V and a substrate rotation speed of 15 rpm and a working pressure of ~0.25 Pa. Before sputtering, the background pressure was pumped down to 2.5×10^{-4} Pa. Cu target power and WC target power are 150 W and 200~400 W, respectively. Deposition time and film thickness are 60 mins and 200~800 nm, respectively.

The crystallographic structure of the films was determined by x-ray diffraction (XRD) using a Bragg-Brentano diffractometer in θ-2θ configuration. The elemental concentration and deposition rate was characterized by electron-probe microanalysis (EPMA) and field emission scanning electron microscopy (FESEM). The nanostructure was analyzed by high-resolution transmission electron microscopy (HRTEM) operated at 200 kV. A Fischer instrument with a four-sided diamond pyramid tip was applied to measure the

*School of Materials Science and Engineering, Anhui University of Technology, Maanshan City, Anhui Province, 243002, P.R. China; Tel: 86-555-2100919; Fax: 86-555-2100208; E-mail: tougaoyouxiang206@163.com

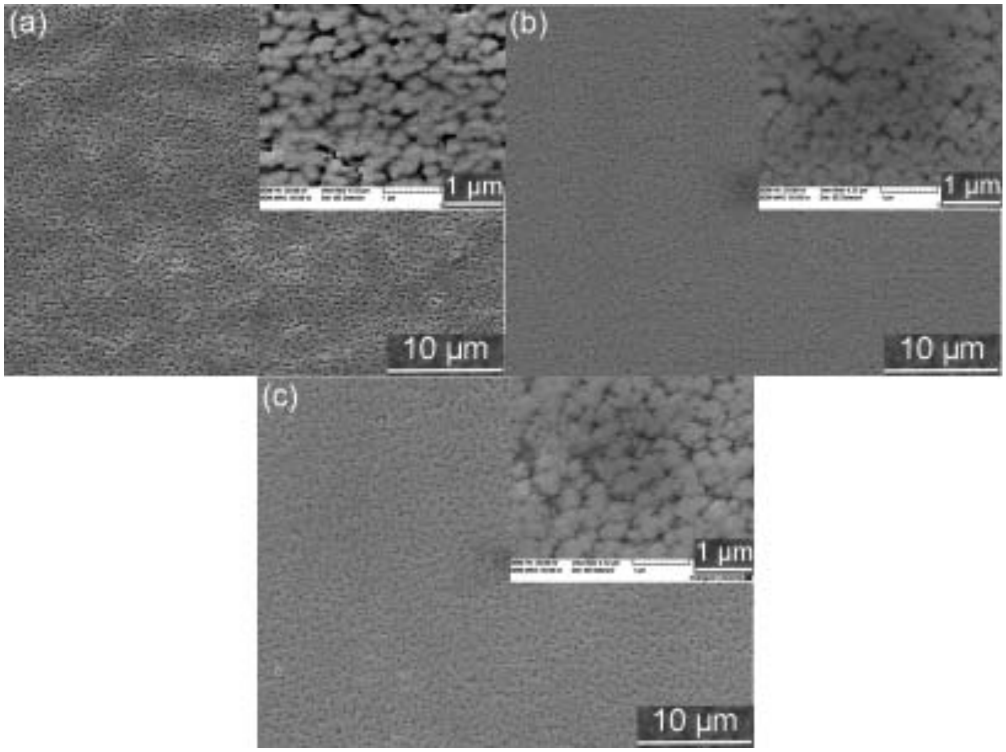

Figure 1: Typical FE-SEM surface micrographs of CuN-WC films deposited at various WC powers (**a**) 200 W, (**b**) 300 W and (**c**) 400 W.

microhardness using a single loading-unloading mode at a maximum load of 20 mN. And friction and wear properties were evaluated in sliding tests using a conventional ball-on-disc wear apparatus with ruby counter-ball at the conditions of 0.037 m/s sliding speed and 1 N load at 600 ^{o}C.

3. RESULTS AND DISCUSSION

Figure **1** shows the typical FESEM surface morphology of CuN-WC films deposited at various WC powers. It could be found that the surface morphology of CuN-WC films shows uniform and fine microstructures with grain size of 200~400 nm (Figure **1a-c**). Figure **2** shows the cross-sectional FE-SEM images of CuN-WC films at various WC target powers. As the WC target power increased, the microstructure changes from columnar crystallites separated by large and open grain boundaries to a fully dense structure with almost equiaxed grains. The calculated deposition rate of CuN-WC films is illustrated in Figure **3a**. As the WC target power increases to 400 W, the deposition rate is only 3 nm/min, which was due to that the movement of Cu atoms to substrate was blocked by large numbers of WC molecules. Figure **3b** illustrates the chemical compositions of CuN-WC films deposited at various WC target powers. It can be seen that increasing WC target power induced evident increase in W content and decrease in Cu content.

Figure **4** shows the XRD patterns of CuN-WC films at various WC target powers. Binder phase hcp-Co and hcp-WC phases with diffraction peaks of (001), (100), (110) and (002) planes could be identified in the films at different target powers. However, copper nitride phases were not detected by XRD technique, which might be due to the lower content in the film. As seen in Figure **4a**, **b** and **c**, with the WC target power

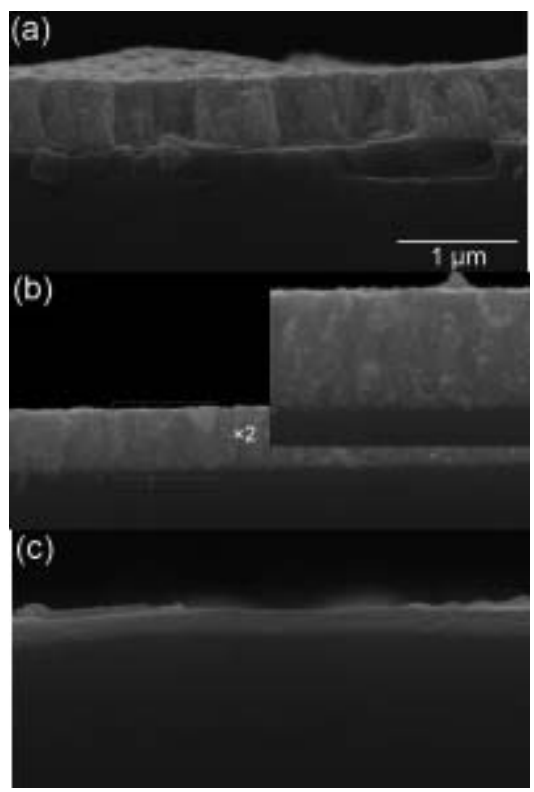

Figure 2: Typical cross-sectional FE-SEM images of CuN-WC films deposited at various WC powers (**a**) 200 W (**b**) 300 W (**c**) 400 W.

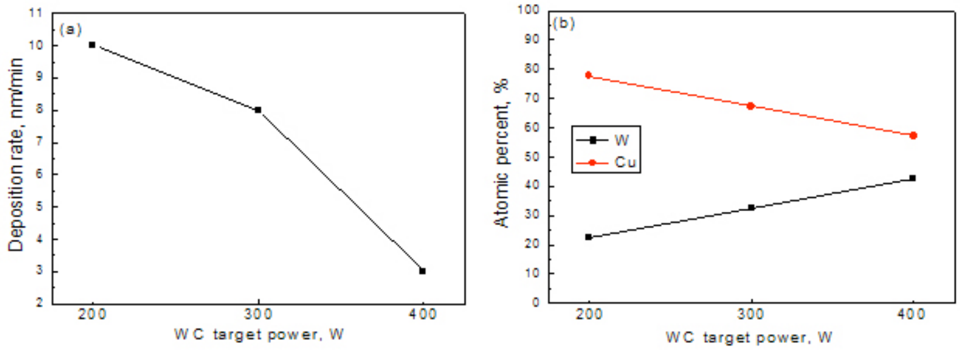

Figure 3: Deposition rate (**a**) and relative atomic percent of Cu and W (**b**) of CuN-WC films at various WC powers.

increasing, intensity of WC (100) and (002) planes becomes larger. And WC (111) plane appears in the film under 400 W.

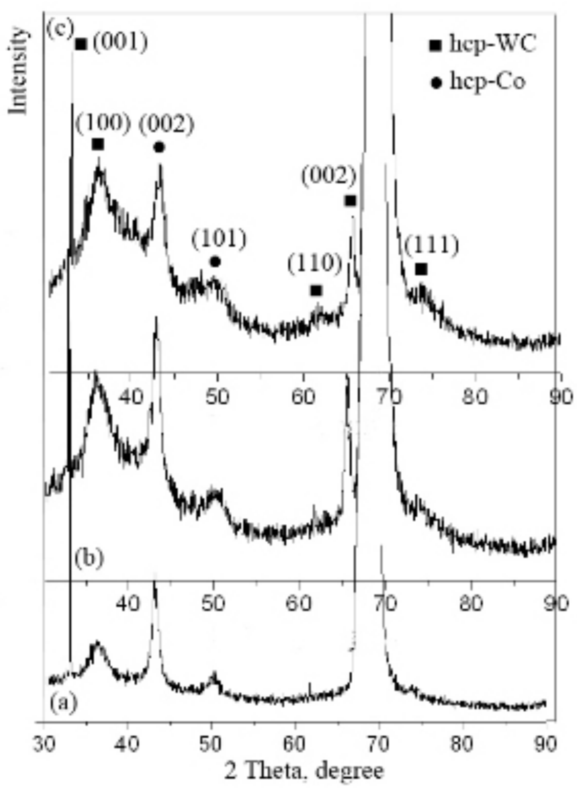

Figure 4: XRD results of CuN-WC films deposited at various WC powers (**a**) 200 W (**b**) 300 W (**c**) 400 W.

To further confirm the structure of CuN and investigate the microstructural evolution of CuN-WC films, TEM investigations were conducted on typical specimens and the results are shown in Figure **5**. As shown in Figure **5a**, a few small WC rods, around 10~30 nm in size, completely embedded in the amorphous CuN matrix (CuN phase was also confirmed by XPS refered [2]). With the increase of WC target power to 300 W, net-structure WC grains could be found as shown in Figure **5b**. Amounts of WC columnar crystals appeared with further increasing the WC target power to 400 W as shown in Figure **5c**. The selective area diffraction pattern (SADP) in Figure **5a** shows a bright spot, which corresponds to the main amorphous CuN phase in CuN-22at.%WC film. The SADP in Figure **5b** exhibited discontinuous diffraction rings, which indicates the increase of nanocrystal WC content. As seen in Figure **5c**, the diffraction rings of WC grains become clear with further increasing WC target power. Lattice fringes corresponding to crystalline WC structure with d-spacing of 2.15 and 2.50 Å can be measured. In this case, the ratio of crystalline phase to amorphous phase is clearly increased in respect to the previous film. In this study, the equilibrium structure of WC is the hexagonal A/B_2 structure with lattice constants a= 2.905 Å and c = 2.836 Å and $\gamma = c / a$ = 0.976 [10].

Figure **6** displays representative HRTEM images obtained from nc-WC/a-CuN_2 films prepared under various WC target powers. The sample prepared at 200 W power (Figure **6a**) is comprised of amorphous CuN and a little of WC crystals. The sample prepared at 300 W power (Figure **6b**) is formed by amorphous CuN and a part of WC crystals of 5–10 nm of random orientation. With increasing WC target power to 400 W, many WC dendrite crystals of 5~10 nm oriented along [001] orientation appeared (Figure **6c**). The diffraction pattern shown as inset in the figure is obtained by performing fast Fourier transformation on the grain located in the center of the micrograph, and the obtained results correspond to a WC crystal oriented along [001] direction.

Figure **7** shows the hardness of nc-WC/a-CuN films deposited under various WC target powers. It could be found that the hardness of all the nc-WC/a-CuN films is more than 40 GPa. As the volume fraction of nc-WC increases to 42 at.%, the hardness goes up to 55 GPa. This value even exceeds the reported hardness of superhard nc-WC/DLC and nc-TiN/a-Si_3N_4 films [4, 11]. It could be concluded that with the increase of the nc-WC phase, the hardness of nc-WC/a-CuN films increases rapidly. Since Koehler [12] proposed the concept of designing strong solid by multilayer structure, several papers appeared in which the material is consists of, e.g., amorphous CNx layer and a transition metal nitride such as TiN or ZrN [13, 14]. Thus, in this case, we can conclude that the maximum value of the critical shear stress $\sigma_c(\lambda)$ which can cause the movement of a dislocation from weaker layer 1 (a-CuN) into stronger layer 2 (nc-WC) is larger than

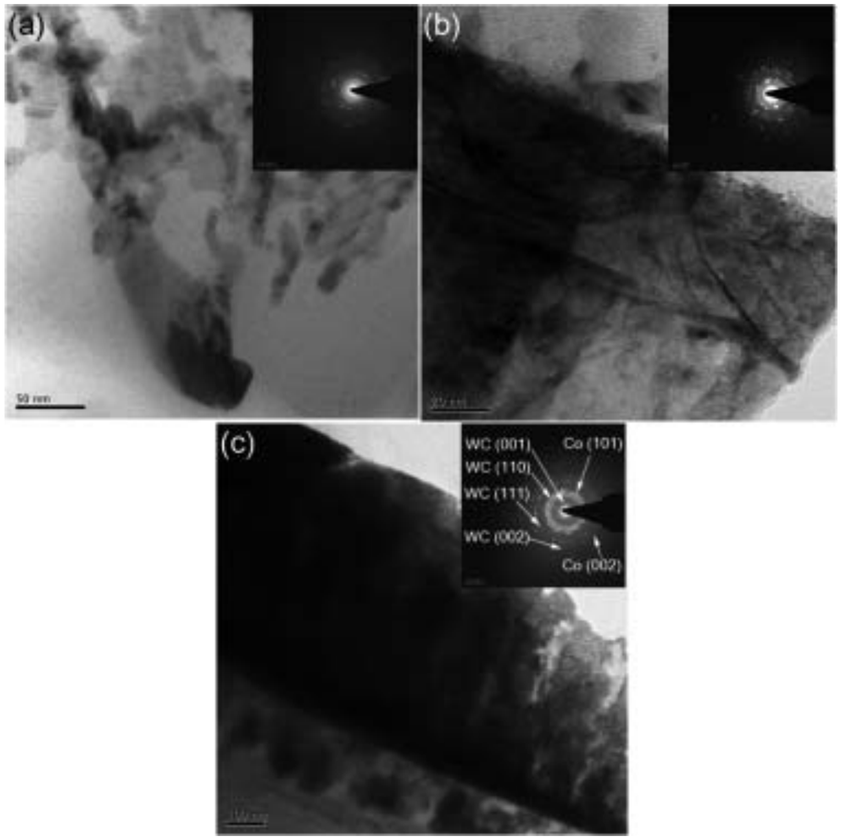

Figure 5: Typical cross-sectional TEM images and corresponding SADP of MS CuN-WC films deposited at various WC powers (**a**) 200 W (**b**) 300 W (**c**) 400 W.

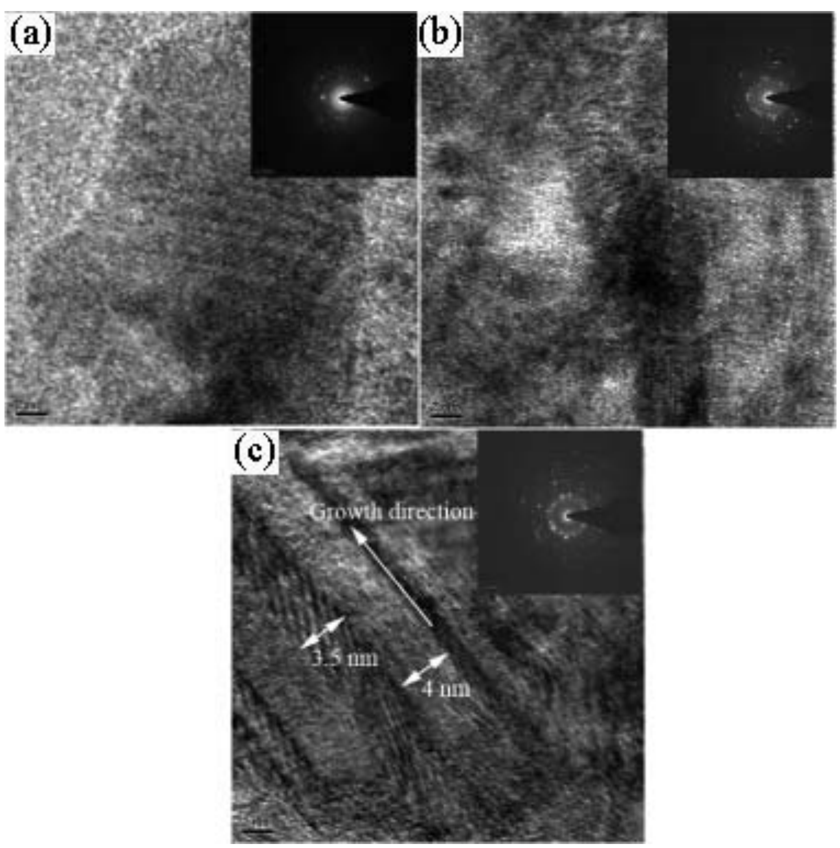

Figure 6: Bright field image and TED pattern of HRTEM of MS CuN-WC films deposited at various WC powers (**a**) 200 W (**b**) 300 W (**c**) 400 W.

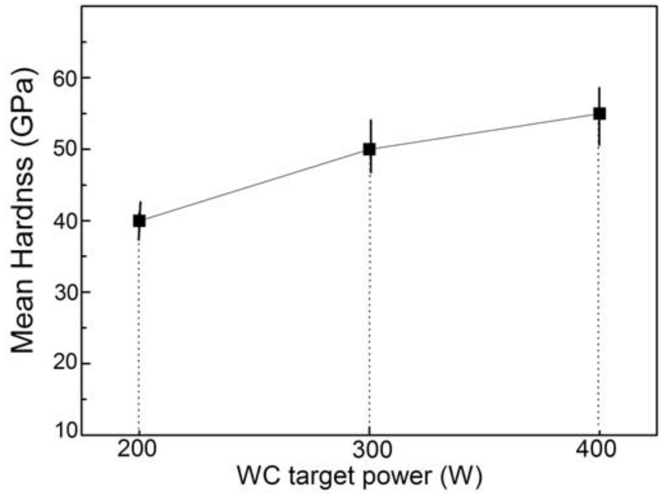

Figure 7: Hardness of CuN-WC films by various WC powers (a) 200 W (b) 300 W (c) 400 W.

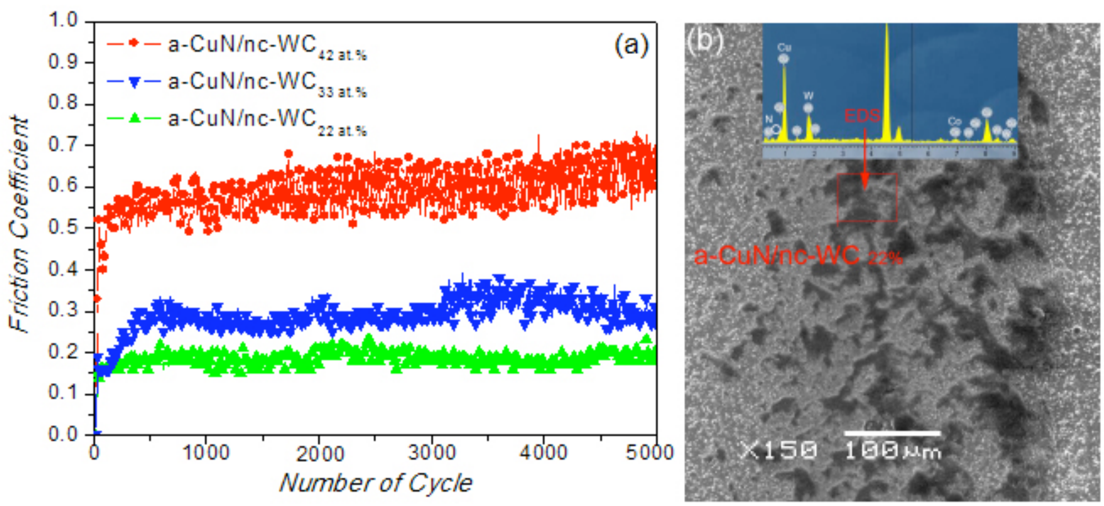

Figure 8: Friction coefficient (**a**) and wear trace (**b**) of nc-WC/a-CuN 22, 33, 42 at.% films vs ruby counter-ball at 600 °C.

that of the reported multilayer systems such as nc-WC/DLC and nc-TiN/a-Si_3N_4 films.

Up to now, although a few superhard films (>40 GPa hardness) have been developed to satisfy the practical application, the wear and friction performance of hard films still needs to be improved further, especially at elevated temperature. In this paper, at the sliding condition of 600 °C, nc-WC/a-$CuN_{22\ at.\%}$ film could achieve a low friction coefficient (less than 0.2) against high chemical stability ruby counter-material of 25 GPa hardness (Figure **8a**). The SEM morphology and EDS pattern of the wear trace (Figure **8b**) show that reactive process of $4CuN+O_2=2Cu_2O+2N_2$ happened at 600 °C. In the meantime, successive oxides thin film formed on sliding surface at elevated temperature. It is concluded that this novel film possesses comparable excellent friction performance which is attributed to the self-lubricant function of a-CuN introduction. Therefore, both super-low friction coefficient and super-high hardness could be obtained. In summary, nc-WC/a-CuN films are very promising for high speed dry sliding machine and other high-temperature applications.

4. CONCLUSION

In summary, nc-WC/a-CuN film consisting of amorphous CuN films embedded nanocrystalline WC phase deposited by reactive dc magnetron sputtering is described in this paper. The deposition efficiency, microstructure, hardness, high-temperature friction and wear behavior of nc-WC/a-CuN films have been investigated by FESEM, XRD, HRTEM, Nano-indentation and ball-on-disc wear apparatus. When the WC target power is increased to 400 W, the deposition rate is only 3 nm/min, which is because the movement of Cu atoms to substrate is blocked by large numbers of WC molecules. The nc-WC/a-$CuN_{42\ at.\%}$ film which is composed of many WC dendrite crystals of 5~10 nm with (001) orientation embedded to amorphous CuN possesses ~55 GPa hardness. The high-temperature wear analysis shows that this novel film possesses the excellent friction performance because of the self-lubricant function of a-CuN; simultaneously the film still maintains large enough hardness.

ACKNOWLEDGEMENT

This work was supported by the National Science Foundation of China (Grant no. 51305002), the International Science & Technology Cooperation Programme of China (Grant no. 2014DFG72720) and the Science Foundation of Anhui Province (Grant no. 1408085QE92).

REFERENCES

[1] Zhang SH, Cho TY, Yoon JH, Li MX, Shum PW, Kwon SC. Investigation on microstructure, surface properties and anti-wear performance of HVOF sprayed WC–CrC–Ni coatings modified by laser heat treatment. Mater Sci Eng: B 2009; 162: 127. http://dx.doi.org/10.1016/j.mseb.2009.03.017

[2] Zhang SH, He YS, Li MX, He YZ, Kwon SC, Yoon JH, Cho TY. Synthesis and characterization of Cu3N-WC nanocomposite films prepared by direct current magnetron sputtering. Thin Solid Films 2010; 518: 5227-5232.

[3] Pujada BR, Tichelaar FD, Janssen GCAM. Stress in tungsten carbide-diamond like carbon multilayer coatings. Appl Phys Lett 2007; 90: 021913. http://dx.doi.org/10.1063/1.2430905

[4] Liu Y, Gubisch M, Haensel T, Spiess L, Schaefer JA. Evaluation of the friction of WC/DLC solid lubricating films in vacuum. Tribol Int 2006; 39: 1584. http://dx.doi.org/10.1016/j.triboint.2006.02.061

[5] Shi J, Lu YF, Cherukuri RS, Mendu KK, Doerr DW, Alexander DR, Li LP, Chen XY. Laser-assisted nanoscale deposition of diamond-like carbon films on tungsten tips. Appl Phys Lett 2004; 85: 1009. http://dx.doi.org/10.1063/1.1777816

[6] Chen LY, C Franklin- H Nan. Diamond-like carbon nanocomposite films. Appl Phys Lett 2003; 82: 3526. http://dx.doi.org/10.1063/1.1576909

[7] Mayrhofer PH, Mitterer C, Hultman L, Clemens H. Microstructural design of hard coatings. Prog Mater Sci 2006; 51: 1032. http://dx.doi.org/10.1016/j.pmatsci.2006.02.002

[8] Musil J, Daniel R. Structure and mechanical properties of magnetron sputtered Zr–Ti–Cu–N films. Surf Coat Tech 2003; 166: 243. http://dx.doi.org/10.1016/S0257-8972(02)00819-8

[9] Lao JJ, Shao N, Mei FH, Li GY, Gu MY. Mutual promotion effect of crystal growth in TiN⁄SiC TiN⁄SiC Nanomultilayers. Appl Phys Lett 2005; 86: 011902. http://dx.doi.org/10.1063/1.1844045

[10] Zhu LN, Li GL, Wang HD, Xu BS, Zhuang DM, Liu JJ. Microstructures and nano mechanical properties of the metal tungsten film. Curr Appl Phys 2009; 9: 510. http://dx.doi.org/10.1016/j.cap.2008.05.003

[11] Ma DY, Ma SL, Xu KW, Veprek S. Effecting of oxygen and chlorine on nano-structured TiN/Si_3N_4 films hardness. Mater Lett 2005; 59: 838. http://dx.doi.org/10.1016/j.matlet.2004.10.062

[12] Tritremmel C, Daniel R, Rudigier H, Polcik P, Mitterer C, Surf Coat Tech 2014; 57-64: 246.

[13] Liu ZJ, Vyas A, Lu YH, Shen YG. Structural properties of sputter-deposited CN*x*/TiN multilayer films. Thin Solid Films 2005; 479: 31. http://dx.doi.org/10.1016/j.tsf.2004.11.106

[14] Yu DL, Tian YJ, He JL, Xiao FR, Wang TS, Li DC, Li L, Zheng G, Yanagisawa O. Preparation of CN*x*/TiN*y* multilayers by ion beam sputtering. J Cryst Growth 2001; 233: 303. http://dx.doi.org/10.1016/S0022-0248(01)01492-0