Effect of C content on structure and the hardness of MoAlCN films

Zhigang Yuan, Yangjie Tian, Li Sun*, Wenbang Gong, Xiao Wu and Xiangyang Zhou
Hubei Key Laboratory of Digital Textile Equipment, Wuhan textile university, Wuhan 430073, People’s Republic of China

*Corresponding author e-mail: sunli@wtu.edu.cn

Abstract. In this paper, Mo-Al-C-N films with different C content were deposited by magnetron sputtering. To investigate the effect of C content on the microstructure and hardness of Mo-Al-C-N films, surface morphology, composition, phase constituent and hardness of these films were characterized by field emission scan electron microscope, Energy Dispersive Spectroscopy, X-ray diffraction, Nanoindentor, respectively. Experiment results illustrate the diffraction peaks of Mo-Al-C-N films shift gradually toward lower angles due to the element C was dissolved into the Mo2N lattice by substituting N. The grain size decreases gradually from 35.8 to 16.7nm with the increase of C content in the range of 0−16 at.% may be due to the amorphous CNx exited in the grain boundary. With increasing C content, the hardness of Mo-Al-C-N films increases firstly and reaches the maximum of 26 GPa at C content of 9 at.%, and then decreases to 21 GPa at C content 16 at.%

Keywords: Nitrides; Magnetron sputtering; Films; X-ray diffraction; Hardness

1. Introduction

Transition metal nitrides were used as protective layers on the cutting tools, such as CrN and TiN, is widespread today. Typical requirements for these coatings include high hardness, low friction coefficient and corrosion resistance. In recent years, because of high hardness, low coefficient and good adhesion with steel, Molybdenum nitrides (Mo-N) film has received widespread attention [1-3]. In these performances, the hardness is the critical properties effecting the useful time. However the hardness of Molybdenum nitrides is not very high to substitute TiN and CrN. The hardness often depend strongly on the microstructure of coatings, including residual stress, grain size and the prefer orientation. Therefore, many methods to change the structure was used to enhance the hardness of Mo-N films, such as C, Si, Al et al. element was added in the structure, varying the deposition conditions et al.[4-6]. Previous researches have illustrated that addition of C element has a great influence on the microstructure of films [7, 8]. The purpose of this work is to develop quaternary Mo−Al−C−N films by varying C composition using direct current (DC) magnetron sputtering. The effect of C composition on the microstructure and the hardness of these films were investigated, including the grain size, phase constituent, composition, surface morphology and hardness of these films.
2. Experimental details
Quaternary MoAlCN films with different C content were deposited by magnetron sputtering using composite target technical. Si wafer and stainless steel substrates were used to characterizing the microstructure and the hardness, respectively. In this case, the composite target consisted with Mo (99.5%), Al(99.999%) and C(99.999%). C content in the films was changed by changing the area ratio of Mo and C, and the Si area was fixed at a constant. The substrates were ultrasonically cleaned in ethanol, de-ionized water for 20 min in proper order, and then installed on the substrate holder. The distance is about 65 mm between substrate and target. Before deposition, the vacuum chamber was pumped to 2.3×10-3 Pa, and then the mixture of Nitrogen and Argon gas was injected into the chamber. During the deposition, the partial pressure ratio between N2 and Ar was 30 and 40 sccm, respectively. The total pressure is fixed at 0.8Pa. The deposition temperature, current and voltage were about 450 oC, 0.4 A and 250 V, respectively.

The phases constituent of the films were determined by X-ray diffraction (XRD, Philips X’pert PRO MPD) using monochromatized Cu Kα radiation (λ=1.5406Å) operating at 40 kV and 40 mA in the scanning range from 30o to 90o with a step of 0.06o. The surface morphology of films were characterized by field emission scan electron microscope (FESEM, Sirion 200, FEI). And the composition of films were determined by energy dispersive spectroscopy (EDS) equipped in the FESEM.

The hardness of films were measure by nanoindnetor XP system(MTS nano indenter G200) with a Berkovich diamond tip at approximate 25 oC under a load of 40 mN. The data of hardness were averaged from 8 indentation tests for each sample to improve measurement accuracy.

3. Results and discussion
The XRD patterns of MoAlCN films with different C/(Mo+Al+C+N) atoms ratio were shown in the Fig. 1. Five diffraction peaks for all samples was found at about 37o, 43o, 63o, 75o, 78o, respectively. This diffraction results is consistent with the phase constituent of face-centered cubic (fcc) \(\gamma\)-Mo2N structure corresponding to the (111), (200), (220), (311), (222) planes. This result illustrates that the main phase constituent of films were fcc \(\gamma\)-Mo2N. Other XRD peaks corresponding to crystalline phases such as MoCx, AlN, CNx were not observed. This result illustrated that C existed as the dissolved atoms in the Mo2N crystal lattice or as amorphous phase. As the C content increases, the diffraction peaks of Mo-Al-C-N films shift gradually toward lower angles, which indicates that the lattice parameter of films increases with the increase of C content. This phenomena may be due to the element C was dissolved into the Mo2N lattice by substituting N, resulting in the expansion of the lattice, since the radius of C is bigger than that of N [9-11].

The average grain size was deduced from the XRD patterns by scherrer equation. The results of deduce was shown in the Fig.2, the grain size decreases gradually from 35.8 to 16.7nm with the increase of C content in the range of 0−16at.%. This results be due to the amorphous CNx exited in the grain boundary, which inhibited the growth of thin film.

The surface morphologies of film with four different C content of 0, 5, 9 and 16 at.% were shown in Fig.3. Fig.3a shows the surface morphology of Mo-Al-N film. It is clearly observed that the similar-circular colloid nono-particles of different size were distributed on the surface of the films. With the increase of C content, the distribution of films’ particle gradually becomes uniform, and shape of the particles changed to polygon. These phenomena illustrates that the addition of C content has a strongly influence on the surface morphology of the films.

The hardness of MoAlCN films with different C content were shown in Fig.4. The hardness of MoAIN films are about 19 GPa. With increasing C content, the hardness of MoAlCN films increases firstly and reaches the maximum of 26 GPa at C content of 9 at.%, and then decreases to 21 GPa at C content 16 at.%. The increase of hardness mainly due to grain-size refinement, when grain-size is smaller than 100 nm, the hardness will comply with hall-petch relation. The reduction of hardness may be due to the increase of volume fraction of amorphous CNx phase. Similar effects were also observed in the systems of Mo-Si-C-N [11].
**Fig 1.** The XRD patterns of Mo-Al-C-N films with different C/(Mo+Al+C+N) atoms ratio: (a) 0 at.% , (b) 5 at.% , (c) 9 at.% , (d) 16 at.%.

**Fig 2.** Grain size of Mo-Al-C-N films as a function of C content

**Fig 3.** FESEM morphologies of Mo-Al-C-N films with different C content: (a) 0 at.%, (b) 5 at.% , (c) 9 at.% , (d) 16 at.%. 
4. Conclusion
In this paper, Mo-Al-C-N films with different C content were deposited by magnetron sputtering. The main conclusions can be summarized as follows: 1) XRD result illustrates that the main phase constituent of films were fcc $\gamma$-Mo2N. 2) As the C content increases, the diffraction peaks of Mo-Al-C-N films shift gradually toward lower angles due to the element C was dissolved into the Mo2N lattice by substituting N atoms. 3) The grain size decreases gradually from 35.8 to 16.7nm with the increase of C content in the range of 0–16at.% due to the amorphous CNx exited in the grain boundary. 4) With increasing C content, the hardness of Mo-Al-C-N films increases firstly and reaches the maximum of 26 GPa at C content of 9 at.%, and then decreases to 21 GPa at C content 16 at.%.

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References
[1] J. Valli, U. Mäkelä, H.T.G. Hentzell, Tribological properties of MoN x coatings in contact with copper, J. Vac. Sci. Technol. A 4(6) (1986) 2850-2854.
[2] M.K. Kazmanli, M. Ürügen, A.F. Cakir, Effect of nitrogen pressure, bias voltage and substrate temperature on the phase structure of Mo–N coatings produced by cathodic arc PVD, Surf. Coat. Technol. 167 (2003) 77-82.
[3] Y. Wang, R.Y. Lin, Amorphous molybdenum nitride thin films prepared by reactive sputter deposition, Mater. Sci. Eng. B 112 (2004) 42-49.
[4] Q. Liu, Q.F. Fang, F.J. Liang, J.X. Wang, J.F. Yang, C. Li, Synthesis and properties of nanocomposite MoSiN hard films, Surf. Coat. Technol. 201 (2006) 1894-1898.
[5] J. Musil, P. Dohnal, P. Zeman, Physical properties and high-temperature oxidation resistance of sputtered Si3N4/MoNx nanocomposite coatings, J. Vac. Sci. Technol. B 23 (2005) 1568–1575
[6] A. Singh, P. Kuppusami, Shabana Khan, C. Sudha, R. Thirumurugesan, R. Ramaseshan, R. Divakar, E. Mohandas, S. Dash, Influence of nitrogen flow rate on microstructural and Nanomechanical properties of Zr–N thin films prepared by pulsed DC magnetron sputtering, Appl. Surf. Sci. 280 (2013) 117–123.
[7] Z.L. Wu, J. Lin, J.J. Moore, M.K. Lei, Microstructure, mechanical and tribological properties of Cr–C–N coatings deposited by pulsed closed field unbalanced magnetron sputtering Surf.Cot. Technol. 204 (2009) 931-935
[8] M. Stueber, U. Albers, H. Leiste, S. Ulrich, H. Holleck, P.B. Barna, A. Kovacs, P. Hovsepian, I. Gee, Multifunctional nanolaminated PVD coatings in the system Ti–Al–N–C by combination of metastable fcc phases and nanocomposite microstructures, Surf. Coat. Technol. 200 (2006) 6162-6171.

[9] E.Y. Choi, M.C. Kang, D.H. Kwon, D.W. Shin, K.H. Kim, Comparative studies on microstructure and mechanical properties of CrN, Cr–C–N and Cr–Mo–N coatings, J. Mater. Process. Technol. 187–188 (2007) 566-570.

[10] Y.Z. Huang, M. Stueber, P. Hovsepian, The significance of carbon on the microstructure of TiAlN–C coatings deposited by reactive magnetron sputtering, Appl. Surf. Sci. 253 (2006) 2470-2473.

[11] Z.G. Yuan, J.F. Yang, X.P. Wang, Z.J. Cheng, Q.F. Fang, Characterization and properties of quaternary Mo–Si–C–N coatings synthesized by magnetron sputtering technique, Surf. Coat. Technol. 205 (2011) 3307–3312.