Rare Metal Materials and Engineering
Volume 46, Issue 10, October 2017
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com
ScienceDirect

Cite this article as: Rare Metal Materials and Engineering, 2017, 46(10): 2857-2862.

ARTICLE

Microstructures and Mechanical Properties of TiN/CrN Multilayer Films

Jin Qiaoling[1,2], **Wang Haidou**[2], **Li Guolu**[1], **Zhang Jianjun**[1], **Liu Jinna**[2,3]

[1] Hebei University of Technology, Tianjin 300130, China; [2] National Key Laboratory for Remanufacturing, Academy of Armored Forces Engineering, Beijing 100072, China; [3] Harbin Engineering University, Harbin 150001, China

Abstract: In order to study the relationship between mechanical properties and microstructure of TiN/CrN multilayer coatings, the TiN, CrN film and three TiN/CrN multilayer films with different periodicities were prepared on monocrystalline silicon by magnetron sputtering. Atomic force microscope and X-ray diffraction were adopted to analyze the surface morphology and phase constitution of the films, respectively. The hardness and indentation plasticity were studied using nanoindenter. Residual stress was measured by a curvature method. The results show that TiN/CrN multilayer films exhibit a mixture of TiN and Cr_2N phases, the interface zone between TiN layer and CrN layer becomes small and sharp with the increasing of periodicity. Hardness and indentation plasticity of multilayer films are better than those of monolayer films, and increase as the bilayer period decreases. For multilayer films, the residual stress increases gradually with the increasing of periodicity. From the above observation, it can be concluded that the improvement in mechanical property depends on minor periodicity. The results agree well with Hall-Petch theory.

Key words: TiN/CrN multilayer films; microstructure; mechanical properties; periodicity; residual stress

With the development of industry, protective coating deposition has been employed on the high speed steel and metal tool to increase the tool life[1-3]. Attributed to the high hardness, high wear resistance and good chemical stability, TiN film has been widely used in improving the surface mechanical properties of machine component. However, the TiN film shows low toughness, and tends to peel off from the substrate in the process of production or working. In recent years, some researchers have improved the performance of TiN thin films by multilayer nano thin film mechanism[4-12], which can reduce the residual stress, alleviate the impact force in process of service, and improve the fracture toughness, such as TiN/CrN multilayer film. Nowadays, TiN/CrN multilayer coatings were widely used as protective coatings to improve the performance and lifetime of components in complex environments because of their great mechanical properties and wear resistance in comparison with traditional TiN coatings[13,14]. For example[15-17], Ph. Steyer has studied the tribological behavior of TiN/CrN multilayer films deposited on M2 tool steel by ball on disc wear tester, and found that the fatigue resistance of multilayer membrane was far higher than that of single layer film and abrasion resistance was enhanced greatly. J. J. Roa and cooperators made TiN/CrN multilayer coatings and TiN, CrN monolayer coatings using multisource cathodic reaction arc evaporation. Indentation and scratch test were used to study the failure mechanism of TiN/CrN coating. Results showed that the critical load was lower than multilayer films when the fault occurred in a single layer coating. In this paper, we studied the mechanical properties of TiN/CrN multilayer coatings associated with the microstructure such as surface grain size, periodicity, and interface structure. Then we discussed the relationship between the mechanical properties and the microstructure, such as residual stress and plasticity which is rarely seen in other literatures.

Because of complex service environment and distinct heterogeneous constraint effect in membrane material[18,19], classical theory of material performance characterization is difficult to fully describe the mechanical properties of films.

Received date: October 27, 2016
Foundation item: National Nature Science Foundation of China (51535011, 51275151); National Key Basic Research Development Program of China (“973” Project) (61328304)

Corresponding author: Wang Haidou, Ph. D., Professor, National Key Laboratory for Remanufacturing, Academy of Armored Forces Engineering, Beijing 100072, P. R. China, Tel: 0086-10-66718475, E-mail: wanghaidou@aliyun.com

Nanoindenter, with high load and displacement resolution, has become a multi-functional micro/nano mechanics measuring probe. In order to study film mechanical properties accurately, the author measured hardness (*H*) and elastic modulus (*E*) of film using nanoindenter. And the plasticity and residual stress of thin films were measured by nanoindentation technology and the curvature method, respectively.

1 Experiment

Five different coatings (TiN/CrN with three different periodicities (λ): 20, 50 and 90 nm; as well as TiN, CrN monolayer films) were deposited in single crystal silicon substrate system using radio frequency dc-sputtering with different powers. Cathodes of TiN and CrN, located in each side of the reactor, were used to produce TiN and CrN films with different bilayer periods. Before loading into the chamber, substrates were cleaned with alkaline detergent as well as in an acetone ultrasonic bath. First, TiN and CrN monolayer films were prepared by magnetron sputtering technology. In the process of sputtering, the Ar gas flow rate was 80 cm^3/min, the indoor sputtering temperature was 400 ℃, the bottom vacuum was 8×10^{-4} Pa, and the sputtering pressure was 0.1 Pa. The power of TiN and CrN was 50 and 150 W, respectively. The time of sputtering was 4 h. Then we prepared the multilayer films with the same technological parameter of monolayer films. Periodicity of the multilayer was controlled by the target alternation, resulting in bilayer periods λ=20, 50, 90 nm. The thickness of specimens was 200, 960, 916, 707, 880 nm.

The prepared samples monolayer TiN, CrN and TiN/CrN multilayer were characterized in various ways. N-500LS atomic-profiler was used to measure the thickness. Surface morphology and average surface roughness were measured by atomic force microscope (AFM). Construction was analyzed by D8 X-ray diffraction. The mechanical characterization of the coated systems included the evaluation of their effective *H* and *E* through instrumented indentation with a Berkovich tip. It was performed using a nanoindenter XP equipped with a continuous stiffness measurement module, the latter allowing a dynamic determination of *H* and *E* during the indentation. Indentations were organized in a regularly spaced array of 3 indentations at 1000 nm penetration depth with a constant distance between each imprint of 40 μm in order to avoid any overlapping effect, and the results were averaged. The values of hardness and elastic modulus were calculated by the Oliver and Pharr method, assuming a constant Poisson ratio for the specimens of study equals to 0.25.

In classical mechanics, fracture toughness is measured as the maximum stress intensity factor under plane strain condition[20-22]. Classical measurement of toughness for bulk materials are the Charpy test, three-point and four-point bending[23-26]. However, the thickness of the thin film is too thin to be measured. Then researchers make use of nanoindentation on coatings to generate different types of hard coating cracking[26-28]. In addition, toughness of coatings can be also evaluated by crack density[29]. Due to the operational simplicity, indentation plasticity is one of the most widely used qualitative methods for determining the toughness of coatings[26], which is defined as the ratio of the plastic displacement divided by the total displacement in the load-displacement curve of a nanoindentation measurement.

$$\text{Plasticity} = \frac{\varepsilon_{\mathrm{p}}}{\varepsilon} \qquad (1)$$

where ε_{p} is the plastic deformation and ε is the total deformation. In this paper, we evaluated the toughness of the film qualitatively by this method because it is convent and swift. However, it should be pointed out that plasticity is not fracture toughness[26]. Plasticity means the ability of a material to resist plastic deformation, while toughness is the capacity to resist crack propagation.

2 Results and Discussion

2.1 Surface morphology of coatings

Fig.1 shows the three-dimension AFM images of the TiN/CrN coatings with different bilayer periods. When the bilayer period is 90 nm, the grain size on the surface of multilayer films is not uniform. According to the thin film growth diffusion principle, we can know that with the increasing of the modulation period atoms are easier to migrate on the surface of the substrate, and the islands are connected gradually. As a result, the grain size of each sublayer increases with thickness. Therefore, when the modulation period is up to 90 nm, a large grain size region appears on the surface of the film.

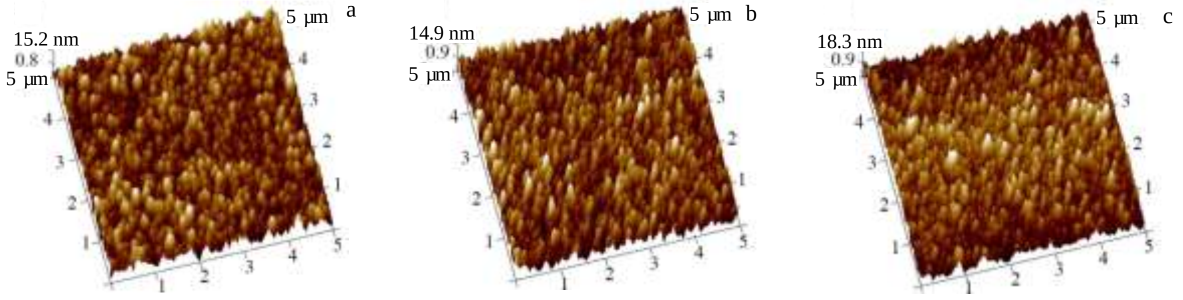

Fig.1 AFM images of the surface of TiN/CrN multilayer film with different bilayer periods: (a) λ=20 nm, (b) λ=50 nm, and (c) λ=90 nm

Surface roughness and grain size of five kinds of thin film systems are shown in Table 1. From the Table we can find the surface grain size and roughness of multilayer thin films are between two single layer films. As is known to all, the greater the sputtering power, the more easily Ar ions and substrate atoms can migrate on the surface of the substrate. What's more, because of combination and growth of island structure, the grain size of each sublayer increases with the thickness of film. Therefore, when the modulation period is up to 50 nm, the large grain size region appears on the surface of the film.

2.2 Phase constitution and grain size analysis

The phase constitution of film was characterized by X-ray diffraction technology. Fig.2 shows the XRD patterns of the TiN/CrN multilayer films with 20, 50, 90 nm bilayer period. It can be seen that the TiN/CrN films exhibit a mixture of TiN and Cr_2N phases. All the microstructures of TiN and CrN in the TiN/CrN system, whatever the period, are found to be fcc NaCl and SC single phase, respectively. The intensity of the (200) peak is strong for TiN, and intensity of the (111) peak is strong for CrN (Fig. 3). In order to study the intensity of preferred orientation, the concept of "Lotgering factor F" is introduced[30], which is determined from the intensity of X-ray diffraction pattern, as follows:

$$F_{(00l)} = \frac{P_{(00l)} - P_0}{1 - P_0} \qquad (2)$$

where $P_{(00l)} = \Sigma I(00l)/I(hkl)$, and $P_0=\Sigma I_0(00l)/I_0(hkl)$. $\Sigma I(00l)$ and $\Sigma I_0(00l)$ are the sum of diffraction intensities of oriented and randomly oriented specimens, respectively. $I(hkl)$ and $I_0(hkl)$ are the sum of peak intensities in the diffraction pattern range of $0^\circ<2\theta<80^\circ$. The result shows that the intensity of preferred orientation slightly increases with the increasing of periodicity.

Table 1 Surface roughness and grain size of films

Sample	TiN film	CrN film	TiN/CrN multilayer films		
Bilayer periods, λ/nm	–	–	20	50	90
Thickness/nm	200	960	916	707	880
R_a/nm	1.63	6.09	3.06	2.97	3.33
Grain size/nm	76	140	126	114	137

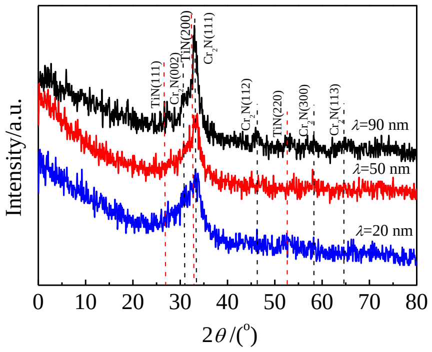

Fig.2 X-ray diffraction patterns of TiN/CrN coatings deposited on Si substrates with various periods

The cross-sectional TEM bright field image and the corresponding SAED pattern of the TiN/CrN multilayer coating are shown in Fig.3. The TiN and CrN layers are alternately along the growth direction, as shown by the dark and bright layers, respectively. Dark region is rich in Cr and bright region is rich in Ti, which indicates the existence of 20, 50 and 90 nm modulation period in multilayer coating. The dark layers with an average thickness of 12, 35 and 60 nm are CrN and the bright layers with an average thickness of 8, 15 and 30 nm are TiN in Fig.3a, 3c and 3f, respectively.

The detailed layer morphology and crystal phase of TiN/CrN films are analyzed in Fig.3b, 3d and 3f. The interface zone has great differences in three coatings. It is clearly found that the interface zone gradually decreases with the increasing of bilayer period. As shown in Fig.3b, the multilayer film with 20 nm periodicity, the interface becomes very rough and mixed, and a disordered region with thickness of about 3.2 nm is observed at the interface zone between TiN layer and CrN layer. From the magnifying micrographs at bright white strip area (the lower right corner of Fig.3d), we can see that some of the CrN amorphous locally grow into TiN layers, so the bright white strip area is not porous. The small white strip regions in the transmission electron microscopic specimen may be caused by ion milling. While in Fig.3f, there seems no interface zone between TiN layer and CrN layer. The selective area electron diffraction (SAED) pattern reveals a pattern of both spotty and continuous rings that correspond to the superposition of individual diffraction patterns of TiN (111) and (200) and CrN (100), (110), (111), (210) and (112)[31,32], which further confirms the orientation index tested by XRD. In TiN layer, there are more amorphous, and CrN layer is rich in polycrystal which has a 0.23 nm lattice distance. With the periodicity increasing, the layer structure of the multilayer is more similar to that of single layer films.

In the early growth stage of each layer, the atoms are easier to migrate on the surface of the substrate which gives possibility to mixed TiN and CrN layers. While in large periodicity, the last layer structure of the multilayer has grown to dense structure, and then the next layer is more likely to grow with a sharp interface. From the above observation, it can be concluded that the microstructure of TiN/CrN multilayers greatly depends on the periodicity, but the microscopic mechanisms which contribute to interface growth for multilayer films, however, remain uncertain.

2.3 Mechanical properties

Variation in indentation H and E as a function of penetration depth is shown in Fig.4. Generally, in the continuous stiffness method, the hardness of the film refers to the hardness of the indentation depth which equals to 1/10 of the film thickness. From Table 1, it can be seen that the thickness of TiN film, CrN film and multilayer films with periodicity of 20, 50, 90, are 200, 960, 916, 707 and 880 nm, respectively. So the hardness of these films can be read at 20, 96, 91.6, 70.7 and 88 nm in the load-displacement curve, respectively. And

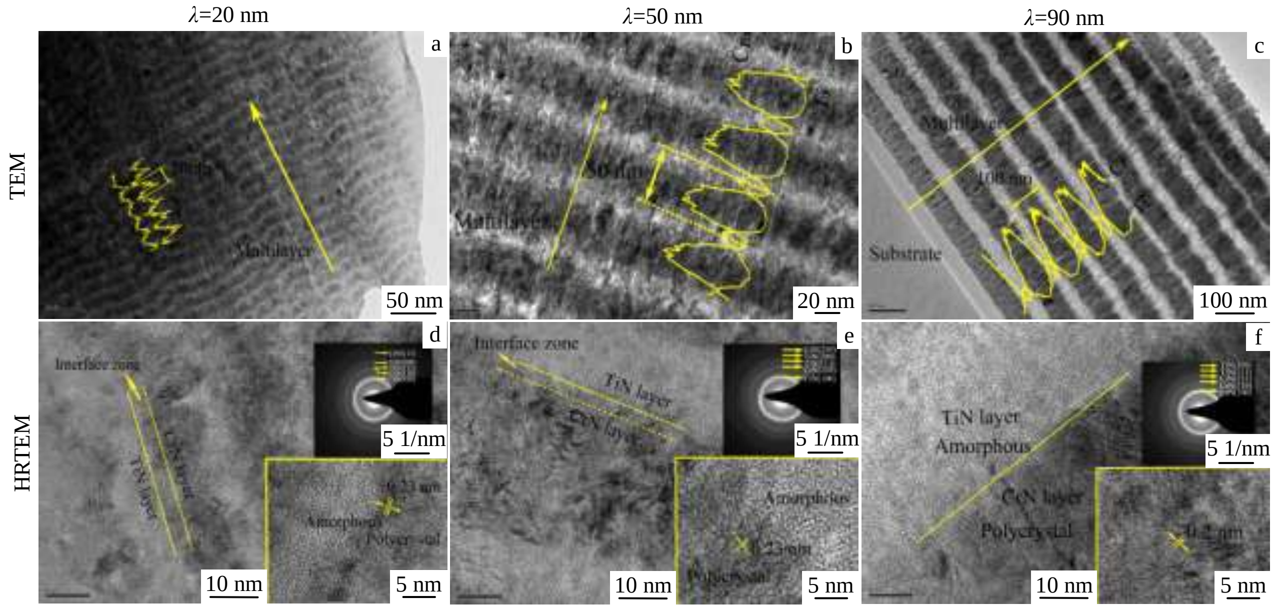

Fig.3 TEM micrographs and HAADF images of the cross-section of the TiN/CrN multilayer films (a, b, c) and HRTEM image and SAED patterns of the interface for the TiN/CrN multilayer film (d, e, f)

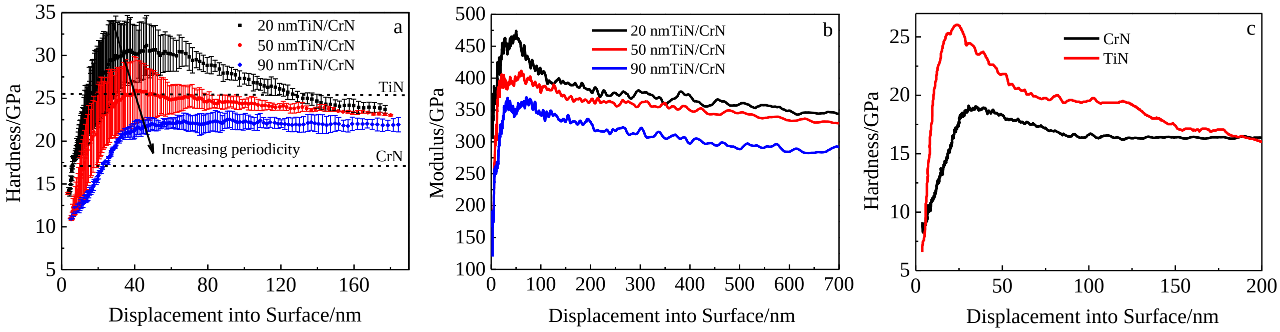

Fig.4 Hardness (a) and elastic modulus (b) vs penetration depth for TiN/CrN multilayer coatings, and hardness vs penetration for TiN and CrN monolayer coatings (c)

the hardness of TiN film, CrN film and multilayer films with periodicity of 20, 50, 90 nm are 26, 17, 28, 25, 22 GPa, respectively. At larger penetration depths, hardness values tend to be the hardness of substrate 14 GPa. From Fig.4a and 4c, it can be seen that the multilayered coatings with minor periodicity present higher values than monolayer. Hardness shows a slight increasing trend with the decreasing of bilayer period, which is in good agreement with the results reported by other workers[33,34]. In addition, for multilayer films, the elastic modulus exhibits the same trend as hardness (Fig 4b).

Generally, grain boundaries will prevent cracks from propagating[35-37], so multilayered coatings have a better hardness than monolayered coatings because of more interface. For the as-deposited multilayers, hardness increases with decreasing layer thickness. According to the result of TEM, we can conclude that the hardness is dependent on the interface zone based Hall–Petch scaling law. It should be mentioned that the hardness of thin films is dependent on the periodicity similar to that given in Eq:

$$H=H_0+KD^{1/2} \tag{3}$$

where H is the hardness of polycrystalline materials with the grain size D. H_0 is the hardness of the same materials with large grains. K is a constant determined by the correlation of hardness and grain boundary. The Hall-Petch model considered that dislocation cannot across the grain boundary, but can be gathered at a grain boundary and create new dislocation source in its neighboring grain boundary at the same time. Dislocation blocking occurs in a rough and mixed interface more easily than a clear interface. Moreover the particular composite structure that amorphous and polycrystal phases arrange alternately will generate an alternating strain field due to the lattice mismatch between the layers, a fluctuating stress field will reduce the growth of cracks, but this effect is believed to be small compared to dislocation line energy effects.

As shown in Fig.5a, multilayers exhibit lower residual stress than monolayer coatings. The residual stress of TiN/CrN multilayers with 20 nm periodicity is compressive stress, while the other is tensile stress, and tensile stress of TiN/CrN increases gradually with the periodicity. Fig.5b, 5c and 5d show the distribution of residual stress measured by electronic film stress distribution tester. When the periodicity is 20 nm, the integral residual stress of film is the minimum, and the distribution the residual stress range is the most homogeneous. However, the overall trend is that the larger the periodicity of the multilayers, the more heterogeneous the distribution of the residual stress. Considering the microstructure observed in TEM, we can see that appropriate interface can reduce the generation of stress. This result is similar to the report in Ref.[38].

The calculated values of the indentation plasticity of the coatings are shown in Fig.5a. It shows that multilayer coatings have higher plasticity than single layer coatings. TiN monolayer is harder than CrN monolayer, but its plasticity is lower than that of CrN. As known to all, K_{IC} increases with the increasing resistance to plastic deformation. So the aggrandizement of fracture toughness would reduce the hardness in film. For the TiN/CrN multilayers, the higher compressive stress value is, the higher the plasticity is, and the higher the fracture toughness is. And the H and E of multilayer increase gradually with the residual stress decreasing. This result is in good agreement with the results reported by Suresh[39]. It indicates that compressive stress effectively improves fracture toughness. However, the toughness decreases rapidly with increasing tensile stress. As a result, tensile stress can significantly degrade film fracture toughness. Tensile stress would drive the crack initiation and growth[40], while the residual compressive stress at the crack tip can close the crack. When crack propagates, the tensile stress driving the crack initiation and growth must overcome the compressive stress in the film, consuming additional energy. Meanwhile, the decreasing of periodicity does well to both hardness and toughness. It provides possibility to prepare hard coatings with good comprehensive properties.

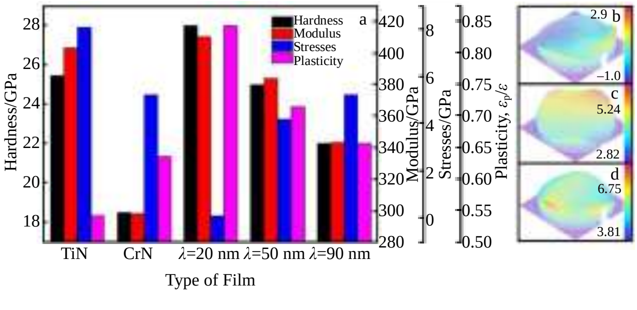

Fig.5 Mechanical properties of as-deposited films (a) and three-dimensional distribution of residual stress for TiN/CrN multilayer films with periodicity of 20 nm (b), 50 nm (c), and 90 nm (d)

3 Conclusions

1) TiN/CrN multilayer coatings have better comprehensive mechanical properties than single layer coatings with high hardness (28 GPa) and lower residual stress.

2) The mechanical properties of multilayer thin film slightly increase as the bilayer period decreases, which well agrees with Hall-Petch theory.

3) According to the indentation plasticity, compressive stress effectively improves fracture toughness, while the tensile stress decreases fracture toughness.

References

1 Huang Bensheng, Liu Ge, Jiang Zhongying *et al*. *Rare Metal Materials and Engineering*[J], 2015, 44(6): 1357
2 Komarov F F, Konstantinov V M, Kovalchuk A V *et al*. *Wear*[J], 2016, 352-353: 92
3 Zhou Guanghong, Wang Xiangming, Yin Feng *et al*. *Rare Metal Materials and Engineering*[J], 2016, 45(2): 498 (in Chinese)
4 Luo Junming, Zhang Liuxi, HuangJun. *Rare Metal Materials and Engineering*, 2017, 46(2): 491 (in Chinese)
5 Wang Yuwei, Liu Ping, Li Wei *et al*. *Rare Metal Materails and Engineering*[J], 2014, 43(9): 2203 (in Chinese)
6 Kovalev A I, Wainstein D L, Rashkovskiy A Y *et al*. *Vacuum*[J], 2010, 84: 184
7 Tang P H, Song R G, Chai G Z *et al*. *Surface Engineering*[J], 2012, 28: 165
8 Hovsepian P E, Lewis D B, Münz W D. *Surface and Coatings Technology*[J], 2000, 133-134: 166
9 Sun Pei-Ling, Su Cherng-Yuh, Liou Tai-Pin *et al*. *Journal of Alloys and Compounds*[J], 2011, 509: 3197
10 Major L. *Archives of Civil and Mechanical Engineering*[J], 2014, 14: 615
11 Upadhyay R K, Kumaraswamidhas L A. *Surface Enginee*ring[J], 2015, 31: 123
12 Yin Deqiang. *Investigation to Micro-Structure and Interfacial Mechanical Properties of Metallic Nitride Superhard Nano-Multi-Layer Coatings*[D]. Chongqing: Chongqing University, 2012 (in Chinese)
13 Ou Y X, Lin J, Che H L *et al*. *Surface & Coatings Technology*[J], 2015, 276: 152
14 Ou Y X, Lin J, Ton S *et al*. *Applied Surface Science*[J], 2015, 351: 332
15 Mendibide C, Steyer P, Fontaine J *et al*. *Surface & Coatings Technology*[J], 2006, 201: 4119
16 Steyer P, Mege A, Pech D *et al*. *Surface & Coatings Technology*[J], 2008, 202: 2268
17 Roa J J, Jiménez-Piqué E, Martínez R *et al*. *Thin Solid Films*[J], 2014, 571(2): 308
18 Dong meiling, Cui Xiufang, Wang Haidou *et al*. *Rare Metal Materails and Engineering*[J], 2016, 45(4): 843
19 Mueller M G, Pejchal V, Žagar G *et al*. *Acta Materialia*[J], 2015, 86: 385

20 Peng Yibo, Wang Gang, Zhu Tianxing *et al*. *Journal of Mechanical Engineering*[J], 2014, 50: 32

21 Hosokawa H, Desai A V, Haque M A. *Thin Solid Films*[J], 2008, 516: 6444

22 Zhang Yujuan, Zhai Yuhao, Li Fengji *et al*. *Surface & Coatings Technology*[J], 2013, 232: 575

23 Kumar S, Zhuo D, Wolfe D E *et al*. *Scripta Materialia*[J], 2010, 63: 196

24 Azadi M, Sabour Rouhaghdam A, Ahangarani S *et al*. *Surface and Coatings Technology*[J], 2014, 245: 156

25 Zhang Xiaomin, Zhang Sam. *Thin Solid Films*[J], 2012, 520: 3423

26 Zhang S, Zhang X M. *Thin Solid Films*[J], 2012, 520: 2375

27 Zhang Taihua. *The Nano Test Technology and Application*[M]. Beijing: China Machine Press, 2004: 72 (in Chinese)

28 Li Xiaodong, Bharat Bhushan. *Thin Solid Films*[J], 2001, 398-399: 313

29 Zheng Liyun, Wang Yuguo, Zhao Lixin *et al*. *Rare Metal Materials and Engineering*[J], 2008, 37(S1): 752 (in Chinese)

30 Makiya A, Kusumi Y, Tanaka S *et al*. *Journal of the European Ceramic Society*[J], 2007, 27: 797

31 Wang Mei, Toihara Takaomi, Sakurai Masatoshi *et al*. *Tribology International* [J], 2014, 73(5): 36

32 Liu D G, Gu C D, Chen R *et al*. *Surface and Coatings Technology* [J], 2010, 205: 2386

33 Su Cherng-Yuh, Pan Cheng-Tang, Liou Tai-Pin *et al*. *Surface and Coatings Technology*[J], 2008, 203(5): 657

34 Li Yuge, Li Guanqun, Yang Duo *et al*. *Materials Letters*[J], 2012, 80: 155

35 Mendibide C, Steyer P, Fontaine J *et al*. *Surface and Coatings Technology*[J], 2006, 201: 4119

36 Yashar Philip C, Sproul William D. *Vacuum*[J], 1999, 55(3): 179

37 Wei M, Li N, Mara N *et al*. *Acta Materialia*[J], 2011, 59: 6331

38 Kotn M. *Archives of Civil and Mechanical Engineering*[J], 2012, 12: 464

39 Suresh S, Giannakopoulos A E. *Acta Mater*[J], 1998, 40: 5755

40 Zhang Liqiang, Yang Huisheng, Pang Xiaolu *et al*. *Surface & Coatings Technology*[J], 2013, 224: 120

TiN/CrN 多层薄膜的微观结构与力学性能

靳巧玲[1,2]，王海斗[2]，李国禄[1]，张建军[1]，刘金娜[2,3]

(1. 河北工业大学，天津 300130)

(2. 装甲兵工程学院 装备再制造技术国防科技重点实验室，北京 100072)

(3. 哈尔滨工程大学，黑龙江 哈尔滨 150001)

摘　要：为了研究 TiN/CrN 多层薄膜微观结构与力学性能的关系，采用磁控溅射技术制备了 TiN、CrN 单层薄膜和 3 种不同调制周期的 TiN/CrN 多层薄膜。通过原子力显微镜和 X 射线衍射仪分析了膜的表面形貌和相结构。使用纳米压痕仪测试薄膜的硬度和压入塑性，用曲率法测定薄膜的残余应力。结果表明，TiN/CrN 的多层薄膜是由 TiN 和 Cr_2N 两相组成，随着调制周期的增大，TiN 层与 CrN 层之间的界面区域变小，界面平滑且明显。力学性能方面，多层薄膜的硬度和压入塑性比单层膜好，并且多层薄膜随调制周期的减小，硬度和压入塑性增大，残余应力随周期的增加而逐渐增大。综上可见，TiN/CrN 多层薄膜的力学性能的改善取决于界面区域的大小和形貌，即调制周期。该结论与 Hall-Petch 理论相吻合。

关键词：TiN/CrN多层薄膜；显微结构；力学性能；调制周期；残余应力

作者简介：靳巧玲，女，1992 年生，硕士生，装甲兵工程学院装备再制造技术国防科技重点实验室，北京 100072，电话：010-66718475，E-mail: 15222778206@163.com