Microstructure and indentation toughness of Cr/CrN multilayer coatings by arc ion plating

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Abstract: Cr/CrN multilayer coatings with bilayer periods in the range from 1351 to 260 nm were prepared on 304 stainless steel substrates by arc ion plating to study the microstructure and properties of multilayer coatings and stimulate their application. SEM results confirm the clear periodicity of the Cr/CrN multilayer coatings and the clear interface between individual layers. XRD patterns reveal that these multilayer coatings contain Cr, CrN and Cr_2N phases. Because Cr layer is softer than its nitride layer, the hardness decreases with the shortening of the bilayer period (or increasing volume fraction of Cr layer). The Cr/CrN multilayer coating with 862 nm period possesses the highest indentation toughness due to a proper individual Cr and nitride layer thickness. However, for the Cr/CrN multilayer with the bilayer period of 1351 nm, it possesses the lowest toughness due to more nitride phase. The indentation toughness of Cr/CrN multilayer coatings is related with their bilayer period. A coating with a proper individual Cr and nitride layer thickness possesses the highest indentation toughness.
Key words: Cr/CrN multilayer coating; bilayer period; hardness; indentation toughness

1 Introduction

In recent years, the growth and characterization of transition metal nitride-based multilayered structures have attracted a large amount of attentions from both the scientific and the industrial communities because they exhibit more promising properties compared with their monolayer metal nitride coatings [1−5]. Many efforts on the influence of bilayer period on the hardness, adhesion strength and wear resistance of coatings have been made [6−8]. The Cr/CrN multilayer coatings have been extensively studied due to their high hardness, excellent wear and corrosion and oxidation resistance. WIECINSKI et al [9] showed that the decrease of Cr/CrN thickness ratio from 0.81 to 0.15 resulted in the increase of hardness from HV 1275 to HV 1710 and elastic modulus from 260 to 271 GPa. Research works showed a complex relation of the mechanical properties of multilayer coating to its bilayer period. By studying the Cr/CrN multilayer coatings with bilayer period of 1000, 270 and 110 nm, BAYON et al [10] showed that

the highest hardness of 29 GPa was obtained in the multilayer with bilayer period of 270 nm, not in the smallest bilayer period coating. The wear resistance was the highest for the 1000 nm coating followed by the 110 nm coating. PAULITSCH et al [11] found that the wear resistance of CrN/TiN multilayer coating was enhanced by shortening the bilayer period thickness. CABRERA et al [12] showed that the plastic deformation resistance (H^3/E^2) of the CrN/AlN multilayer coating was improved when the bilayer period was increased and it exerted higher wear resistance. MARTINEZ et al [13] revealed that the main sliding wear mechanisms of multilayer coatings were abrasion, tribochemical wear and finally coating detachment. The further wear analysis of the hard coatings showed that the deterioration of the parts protected by these hard coatings was often promoted by the protective coatings splitting and breaking off substrate due to their higher brittleness. During wear, the fatigue cracks can easily develop due to their relatively lower fracture toughness, following the debris broken off the coating and the abrasives formation [14]. This accelerated the wear process. Therefore, the

toughness of coatings is also an important factor affecting their wear resistance, as well as the hardness and adhesion strength. The multilayer structures generated by depositing two alternative materials with different characteristics often exhibit a better toughness compared with their monolayer metal nitride coatings. For metal/metal nitride multilayer coatings, toughening of lamellae structure of the multilayer coatings can be a result of several mechanisms, e.g., energy dissipation by easy deformation and ductile fracture of the metal layers, delamination of interfaces and sliding or shearing at interfaces. This modification increases the deformation ability and rupture work by metal layers, which is expected to improve the fracture toughness of multilayer coatings. WOLFE et al [15] showed that the fracture toughness of TiC/CrC multilayer coatings decreased from 4.179 to 1.411 MPa·m$^{1/2}$ with shortening bilayer periods from 1.2 to 0.1 μm. The results were quite surprising as the fracture toughness decreased instead of increased as expected with increasing interfacial volume (shortening bilayer periods). They thought that the anticipated increase in fracture toughness was overshadowed by the dramatic increase in hardness due to more interfacial volume. HUANG et al [16] measured the indentation toughness of CrN/ZrN multilayer coatings and revealed that the toughness of multilayer coatings was between those of the CrN and ZrN coatings. A minimum toughness value occurred at 6 nm with variation of the bilayer period from 5 nm to 30 nm. The 30 nm coating with higher hardness, plastic deformation resistance (H^3/E^2) and indentation toughness exhibits the best wear resistance.

Despite a significant number of works about the hardness and wear resistance of multilayer coatings, there is still a lack of information about their relations between microstructure and toughness. In general, the coatings used as protective aim are often deposited by arc ion plating due to a proper thickness. In this work, the Cr/CrN multilayer coatings were prepared by arc ion plating, followed by a systematically study on the microstructure and mechanical properties (hardness, wear resistance and toughness) related to bilayer period.

2 Experimental

304 stainless steel substrates were mechanically ground, polished with a final surface roughness of the order of 5−6 nm, followed by ultrasonic cleaning in alcohol and acetone solution and then rinsing in deionized water before being located into the reactor chamber. For conveniently study properties of the Cr/CrN multilayer coatings, the stainless steel was used as substrate due to the easily obtained clean surface of sample. Target was high purity chromium (99.9%, molar
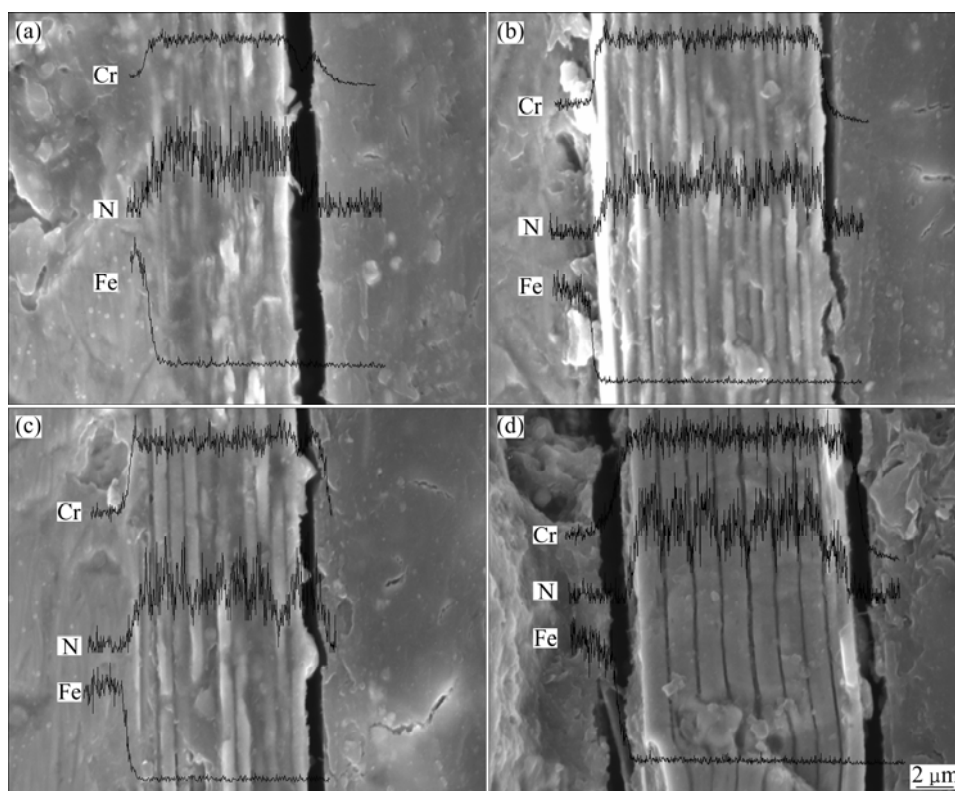
fraction) with diameter of 60 mm. The distance between target and substrate was approximately kept at 240 mm. Prior to deposition, the chamber was evacuated to a pressure of 6.7×10^{-3} Pa, and then sputtering-cleaned with Ar for 5 min at pulse bias voltage of −800 V, duty cycle of 30% and frequency of 52 kHz to remove the oxide and contaminant layer on the substrate. All coatings were prepared at 0.6 Pa pressure in deposition chamber with a −150 V bias voltage, duty cycle at 20% and 60 A arc current by arc ion plating. The mass flow rate of Ar and N_2 gas is 30 and 35 mL/min, respectively. The Cr/CrN multilayer coatings were prepared at time ratio of 2:2, 2:4, 2:7 and 2:10 min for the Ar and N_2 gas being alternately fed into the chamber during deposition, corresponding to 23, 16, 11 and 8 layers in multilayer coatings, respectively. The first individual layer on substrate was Cr with the last being CrN.

The cross-section images of the multilayer coatings were observed by scanning electron microscopy (SEM). In order to get a clear interface of the Cr/CrN multilayer coatings and to get a sharp photographic image, the Cr/CrN multilayer coatings were immersed in a HF and HNO_3 mixed solution (1:9 in volume) for 30 min, which preferentially etches Cr over CrN. Secondary electron images and backscattered electron images were used to characterize the overall coating thickness and multilayer structure. Microstructure of the multilayer coatings was analyzed by X-ray diffraction with a Cu K_α source. Nanoindentation test was performed on the coatings to investigate their mechanical properties. A micro-hardness tester was applied using a load of 500 g to obtain the indentation by which the toughness of deposited coatings was studied by observing the crack numbers (or length). The scratch tests were also performed by MFT-4000 multi functional tester.

3 Results and discussion

3.1 Morphology

Figure 1 shows the SEM image and the elemental scanning curves of Cr, N and Fe elements of the cross-section of Cr/CrN multilayer coatings with different time ratios for Ar and/or N_2 gas being alternately fed into deposition chamber. The images demonstrate that the Cr/CrN multilayer coatings are produced at an excellent periodicity. The relative dark layers represent the Cr layers while the grey-white ones are the CrN layers, which is agreed with the result of elemental scanning curves of the Cr, N and Fe elements (see Fig. 1). The bilayer periods (the total thickness of an individual CrN layer and Cr layer) are approximately 1351, 862, 603, 260 nm as the time ratios for Ar and/or N_2 gas being alternately fed into the deposition chamber are 2:10, 2:7, 2:4, 2:2, respectively, as shown in Fig. 1.

Fig. 1 SEM images and elemental scanning curves of Cr, N and Fe elements of cross-section of Cr/CrN multilayer coatings with different time ratios for Ar and/or N_2 gas being alternately fed into chamber: (a) 2:2; (b) 2:4; (c) 2:7; (d) 2:10

The thickness of multilayer coatings is about 10 μm. The coatings adhere well and no defects such as pores and holes are produced at the interface between the coating and substrate. The multilayer coating with 1351 nm period (Fig. 1(d)) is broke off the substrate, which may be produced in inlaying sample process. Figure 2 shows their magnified images. A clear interface between individual layers can be found from Fig. 2. Often, some droplets, which were produced by metal melt drops from target surface sputtering on samples, occur on the surface of coatings by arc ion plating. However, it is found by experimental observation that CrN coating has smaller and less droplets compared with TiN coating. Thus, the droplets on the cross-section of the Cr/CrN multilayer coatings are not obviously observed.

3.2 Structure

The XRD patterns of the deposited Cr/CrN multilayer coatings with different bilayer periods are shown in Fig. 3. From the XRD patterns, it can be seen that all multilayer coatings distinctly present reflection peaks of body-centered cubic (BCC) metal Cr, face-centered cubic (FCC) CrN and hexagonal close packed (HCP) Cr_2N. All Cr/CrN multilayer coatings contain BCC structure Cr phase, FCC structure CrN phase and HCP structure Cr_2N phase. But for 260 nm multilayer, the reflection peak of Cr phase becomes more obvious, while the peak strength ratio of CrN (220) to

Cr_2N (300) decreases. This implies that the volume fraction of Cr, CrN and Cr_2N phases varies with the thickness of individual nitride layers (bilayer periods). The volume fraction of Cr phase is higher than that of CrN and Cr_2N phases as bilayer periods is shorter. The volume fractions of CrN and Cr_2N phases increase with increasing the bilayer periods. The volume fraction of Cr_2N phase increases with further increasing the bilayer periods.

3.3 Hardness and elastic modulus

The hardness and elastic modulus of the Cr/CrN multilayer coatings as a function of their bilayer periods are shown in Fig. 4. It is observed that the hardness slightly increases with increasing bilayer periods but the hardness of whole multilayer coating is lower than that of monolayer CrN coating. Because the Cr layer is softer than its nitride layer, the hardness decreases with shortening the bilayer period (or increasing volume fraction of Cr layer). Due to relatively longer bilayer period, the layer interface effect of multilayer coatings is not observed in this work. A moderate enhancement of the hardness with increasing the bilayer period (or increasing the nitride layer thickness) is attributed to the nitride effect, which is based on the blocking of dislocation motion by hard phase. Elastic modulus of the Cr/CrN multilayer coatings also increases with increasing the bilayer period.
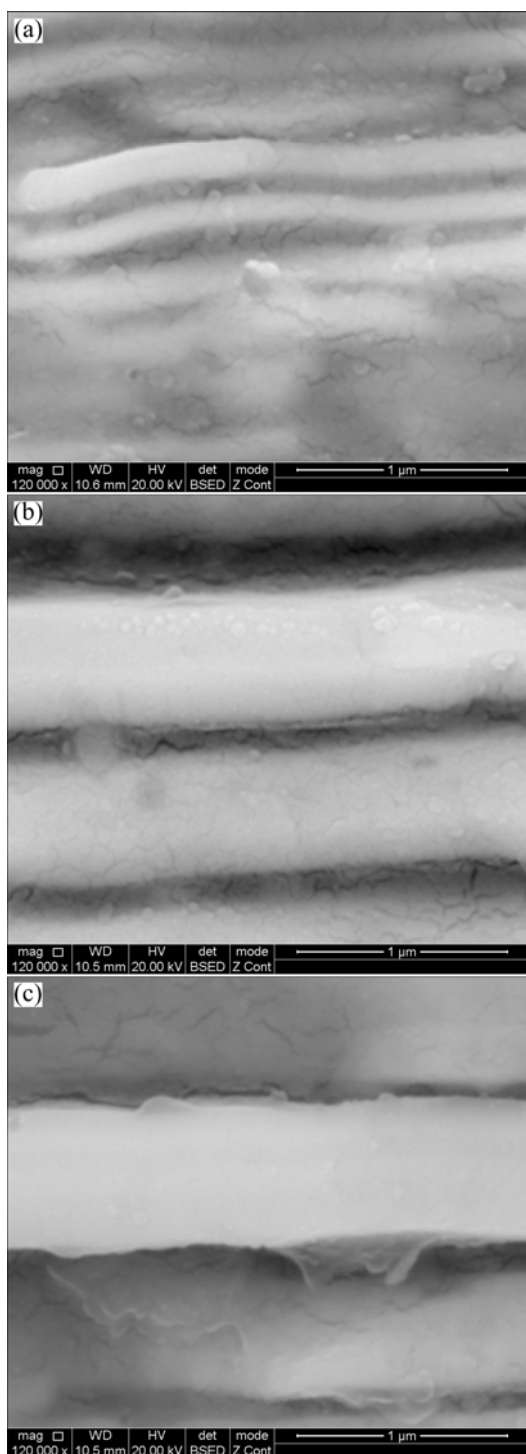
Fig. 2 Magnified SEM images of Fig. 1: (a) 2:2; (b) 2:4; (c) 2:7

Fig. 3 XRD patterns of deposited Cr/CrN multilayer coatings with different bilayer periods

Fig. 4 Hardness and elastic modulus of deposited Cr/CrN multilayer coatings with different bilayer periods

Fig. 5 Critical load of deposited Cr/CrN multilayer coatings

3.4 Adhesion strength

Figure 5 shows the curve of critical load of deposited Cr/CrN coatings versus their bilayer period by scratch test. The adhesion strength (critical load) increases with shortening the bilayer period. The results are in agreement with that in Ref. [13]. However, it makes a little difference to their critical load for 260, 603, 862 and 1351 nm multilayer coatings because the interlayer of the four multilayer coatings is Cr.
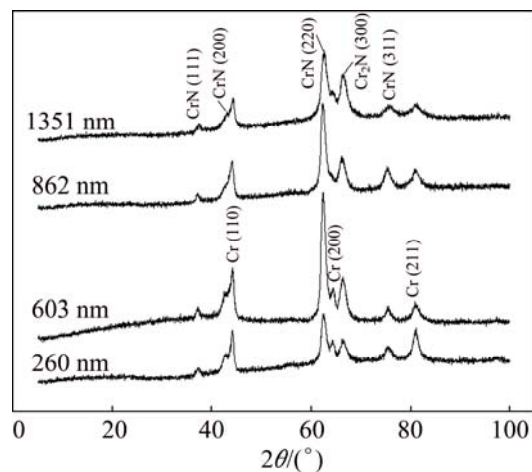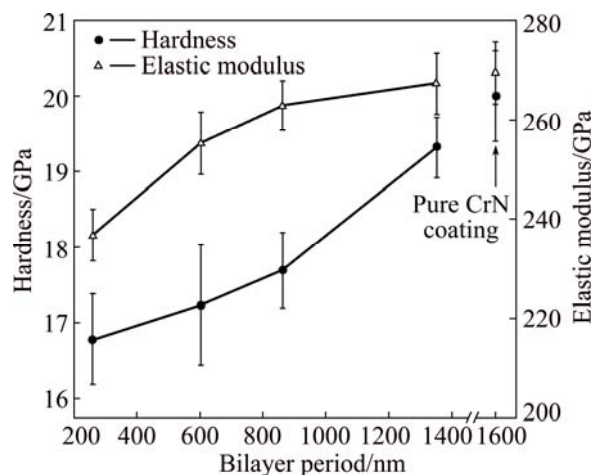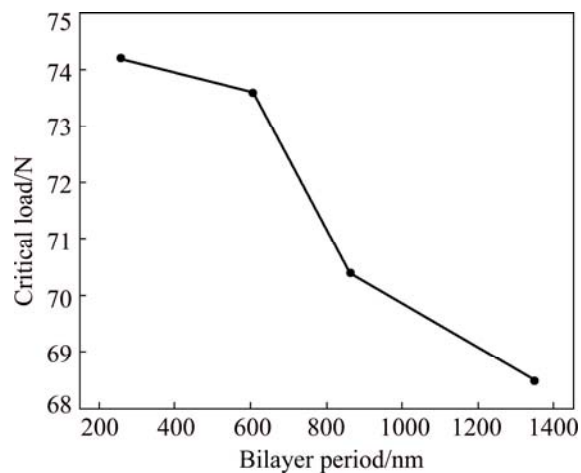
3.5 Indentation toughness

In essence, toughness is the ability of a material to absorb energy during deformation up to fracture.
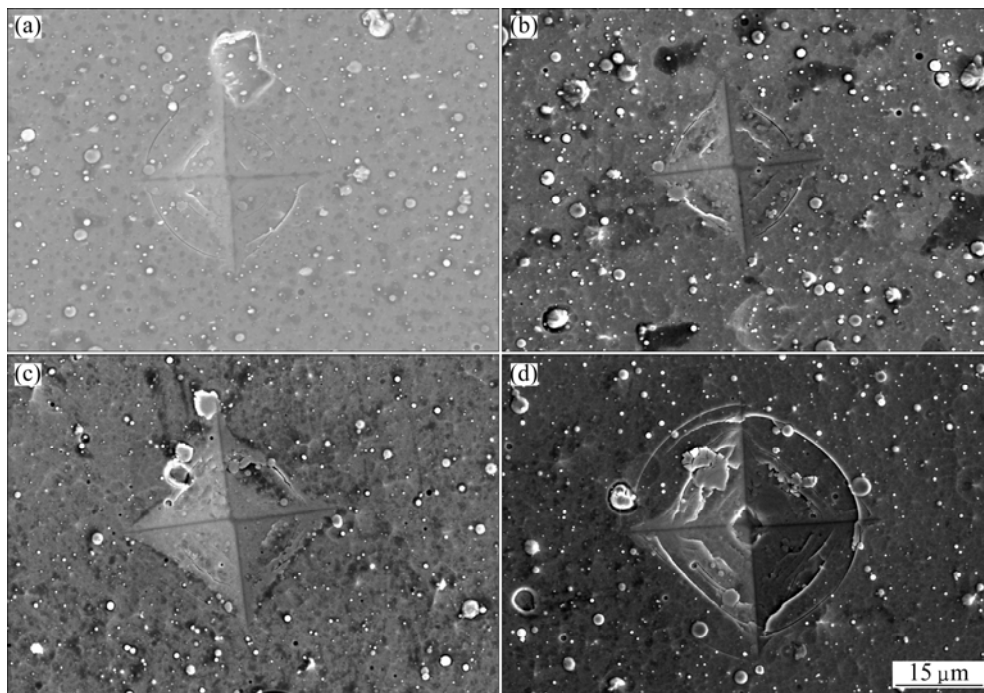
According to this definition, toughness encompasses the energies required both to create the cracks and to enable them to propagate until fracture. Toughness measurement of the coating is different. The indentation method is widely used because of its simplicity [17]. The cracks formed during indentation under a fixed load can be partly considered as an index for coating toughness. The longer the crack is, the lower the toughness is. WIECINSKI et al [18] studied the failure and deformation mechanisms during indentation in nanostructured Cr/CrN multilayer coatings. It was revealed that the small radial cracks observed only in the CrN layers initiated at the interface and propagated across a given layer. They were arrested at the next interface. The result suggested that the thicker CrN layer is easy to form cracks. The interface of multilayer coating is a barrier to crack growth. The indentation toughness is greatly influenced by the bilayer period in multilayer coatings. Figure 6 shows the indentation images for different Cr/CrN multilayer coatings at a load of 500 g. The 1351 nm coating possesses longer crack length, while the cracks hardly occur in the indentation for 862 nm coating. The 260 nm coating possesses slightly longer crack length than 603 nm coating. The 1351 nm coating possesses lower toughness due to thicker nitride layer and less interface numbers. But the 260 nm coating possesses lower toughness due to lower hardness of coatings which is sensitive to plastic deformation and crack initiation. A coating with a good combination of hardness and ductility will have a high toughness. The Cr/CrN multilayer coating with 862 nm period possesses the highest toughness due to a proper individual Cr and nitride layer thickness. In general, the metal Cr individual layer can easily plastically deforms and has a high ductility. The CrN or Cr_2N individual layer has high hardness to prevent from plastic deformation. Thus, the crack does not easily initiate in this coating compared with a monolayer coating. If crack initiates under a high load, due to the deflection of cracking at every layer interface, more energy is required for the crack to propagate again at the interface, which leads to an improvement of coating toughness. It is confirmed that the multilayer coating should be prepared in a moderate bilayer period to achieve high level of toughness with an adequate hardness.

4 Conclusions

1) The hardness of Cr/CrN multilayer coatings decreases with bilayer period variation from 1351 nm to 260 nm. The hardness of the whole Cr/CrN multilayer coatings is lower than that of monolayer CrN coating. A moderate increase of the hardness with increasing nitride layer volume fraction is attributed to the nitride effect, which is based on the blocking of dislocation motion by hard phase.

2) The indentation toughness of Cr/CrN multilayer coatings is related with their bilayer period. A coating with a proper individual Cr and nitride layer thickness possesses the highest indentation toughness.

Fig. 6 Indentation images for Cr/CrN multilayer coatings deposited with different bilayer periods under 500 g load: (a) 260 nm; (b) 603 nm; (c) 862 nm; (d) 1351 nm

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电弧离子镀 Cr/CrN 多层膜的微结构与压痕韧性

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摘　要：采用电弧离子镀在 304 不锈钢衬底上制备双层周期为 1351~260 nm 的 Cr/CrN 多层膜。扫描电镜清晰地显示 Cr/CrN 沉积膜的多层结构和层界。X 射线衍射谱显示沉积的多层膜含有 Cr、CrN 和 Cr$_2$N 相。随着沉积膜双层周期的增加，制备的多层膜的硬度和弹性模量略有增加，但是所有多层膜的硬度和弹性模量都低于单层 CrN 膜的硬度和弹性模量。因为 Cr 层比其氮化物层软，所以多层膜的硬度随双层周期的缩短或 Cr 层体积分数的增加而减小。由于具有适当厚度的 Cr 层和氮化物层，双层周期为 862 nm 的 Cr/CrN 多层膜的压痕韧性最高。然而，由于拥有更多的氮化物相，双层周期为 1351 nm 的 Cr/CrN 多层膜的压痕韧性最低。Cr/CrN 多层膜的压痕韧性与双层周期有关，具有适当厚度 Cr 层和氮化物层的 Cr/CrN 多层膜具有最高的压痕韧性。

关键词：Cr/CrN 多层膜；双层周期；硬度；压痕韧性

(Edited by Yun-bin HE)