CrN films deposited by ion source-assisted magnetron sputtering

LIU Chuansheng[1] TIAN Canxin[1] LI Ming[1] HE Jun[1] YANG HuiJuan[1]
YANG Bing[2] WANG Hong Jun[1] FU Dejun [1, *]

[1] *Key Laboratory of Artificial micro- and nano-Materials of Ministry of Education and School of Physics and Technology,*
Wuhan University, 430072 Wuhan, China

[2] *School of Power and Mechanical Engineering, Wuhan University, 430072 Wuhan, China*

Abstract CrN coatings were deposited on Si(100) and piston rings by ion source assisted 40 kHz magnetron sputtering. Structure and composition of the coatings were characterized by X-ray diffraction, atomic force microscopy, scanning electron microscopy and transmission electron microscopy. Mechanical and tribological properties were assessed by microhardness and pin-on-disc testing. The ion source-assisted system has a deposition rate of 3.88 μm/h, against 2.2 μm/h without ion-source assistance. The CrN coatings prepared with ion source assistance exhibited an increase in microhardness (up to 16.3 GPa) and decrease in friction coefficient (down to 0.48) at the optimized cathode source-to-substrate distance. Under optimized conditions, CrN coatings were deposited on piston rings, with a thickness of 25 μm and hardness of 17.85 GPa.

Key words CrN, Cathode source-substrate distance, Ion source, Deposition rate, Microhardness, Friction coefficient

1 Introduction

Nitrides of transition metals, especially chromium nitride (CrN), have been studied extensively due to their unique properties of hardness and resistance to wear, corrosion and high temperature oxidation [1–4], and are widely used as protective coatings[5–7]. Also, CrN was found to have magnetic properties[8–9], suggesting its applications in the electronic industries. CrN films can be deposited with several methods, among which unbalanced magnetron sputtering produces good quality samples at high deposition rates[2]. It is known that low ionization efficiency in the plasma is a hurdle of magnetron sputtering, hence the development of plasma- or ion sources-assisted magnetron sputtering[10,11]. In particular, Wei *et al*.[12,13] prepared dense and thick films of ZrN and TiN by plasma-enhanced magnetron sputtering, with a key technique of using an electron source of thermal-filament type. For preparing thick protective coatings with improved properties in microhardness and surface chemistry, it is necessary to introduce high density plasma in magnetron sputtering systems.

In this work, we prepared CrN coatings at various source-substrate distances by 40 kHz magnetron sputtering with or without a thermal-filament ion source. The samples were characterized to compare the properties and optimize the process parameters. Thick CrN coatings were successfully deposited on piston rings of automobile engines.

2 Experiment

The CrN coatings were deposited by using a modified closed-field twin unbalanced magnetron sputtering system. Prior to deposition, the vacuum was better than 5×10^{-3} Pa. The substrates were p-type Si (100) and mirror polished WC-Co plates, which had been ultrasonically cleaned in acetone and methanol, rinsed in de-ionized water, and dried in N_2. They were ion etched for 30 min in Ar atmosphere at 2.0 Pa, and a

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* Corresponding Author, *E-mail adderss*: djfu@whu.edu.cn

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–800 V bias was applied to the substrate holder. N_2 (99.99%) and Ar (99.99%) were used as working gases. A layer of pure Cr was deposited onto the substrate for 5 min in Ar ambient at 0.25 Pa and –100 V to improve the adhesion. For forming CrN, N_2 and Ar were let in at a flow rate of Ar : N_2=1:1, with a total pressure of 0.25 Pa and the substrate bias of −100V. The medium-frequency power was 7.0 kW. The cathode source-substrate distance changed from 50 mm to 140 mm. The substrates temperature was kept at 150°C. The ion source was a tungsten filament. It emits electrons to ionize the Ar gas fed to outlet of the ion source, which was installed at upper part of the chamber. The details can be found in Ref.[14].

The CrN film samples were characterized by X-ray diffraction (XRD, Bruker-axs D8 advanced) with Cu K_α ray and transmission electron microscopy (TEM, JEOL JEM 2010). The deposition rate was evaluated from the film thickness measured with an FTSS2-S4L-3D step profiler. The films' cross-section was imaged by scanning electron microscopy (SEM, Sirion FEG). The film composition was determined by energy dispersive spectroscopy (EDS, EDAX genesis 7000) at 12 kV. The surface topography was analyzed by atomic force microscope (AFM, (Shimadzu SPM-9500J3) in tapping mode. The hardness was measured using an HX-1000 micro-hardness tester at 25-g load (dwell time 15 s), averaged from five measurements. Wear resistance of the CrN coatings was checked by an MS-T3000 ball-on-disk tester, at 30°C, in air and relative humidity of 70%, with a Φ3 mm Si_3N_4 ball as the mating materials, on which a 4-N load was applied. The average sliding speed was 0.02 m/s for a fixed sliding time of 30 min and the friction coefficients were recorded during the test.

3 Results and discussion

Fig.1 shows XRD patterns of the CrN coatings deposited under various source-substrate distances, d_{ss}. The CrN (200) peak of the coating deposited at just d_{ss} = 90 mm could be observed for both the samples, whearas the film structure changed from CrN to a mixture of Cr_2N + CrN for the films deposited at d_{ss}=50 mm and 140 mm. At d_{ss}=50 mm, the planes of Cr_2N (002), together with CrN (200) and (111), can be seen, whereas at d_{ss}=140 mm, the films exhibit inconspicuous overlap of Cr_2N (002) and CrN (200) orientations.

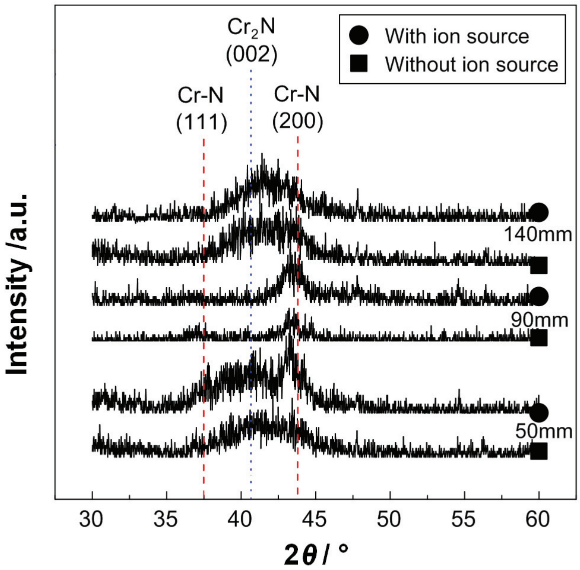

Fig. 1 XRD patterns of CrN coatings deposited at various d_{ss}.

With short source-substrate spacing, the N ions may not react sufficiently with the sputtered Cr, and the ion bombardment causes deficient of N in the film, hence poor crystallization, whereas with a large spacing, the Cr and N atoms lose much energy via collisions with the plasma in their paths to the substrate, hence poor crystallization, too. The CrN films prepared at d_{ss}=90 mm are of the best crystallization. This shows that the plasma could be accumulated at an optimized position.

Fig.1 also shows effect of the hot filament ion source. The CrN films from ion source assisted deposition have stronger diffraction peaks, particularly at d_{ss}= 90 mm, where the intensity of (200) peak is the strongest. With the ion-source, a high ion-to-atom ratio could be achieved [13], hence more N ions to react with the sputtered Cr atoms, leading to improved crystallization.

The bright field TEM images of CrN films prepared at d_{ss}= 90 mm are shown in Fig.2. With the use of ion source (Fig.2a), CrN grains distribute uniformly, and the selected area diffraction (the insertion) shows obvious diffraction rings of CrN and Cr_2N, revealing the polycrystalline nature of the film, with diffraction points attributed to the Si(100) substrate. The uniform CrN grains with distinct grain boundaries suggest lower strain in the film. On the contrary, without ion-source assistance (Fig.2b), the image is featured with non-uniform CrN grains embedded in amorphous matrix, and the selected area diffraction reveals the CrN and blurry Cr_2N phases.

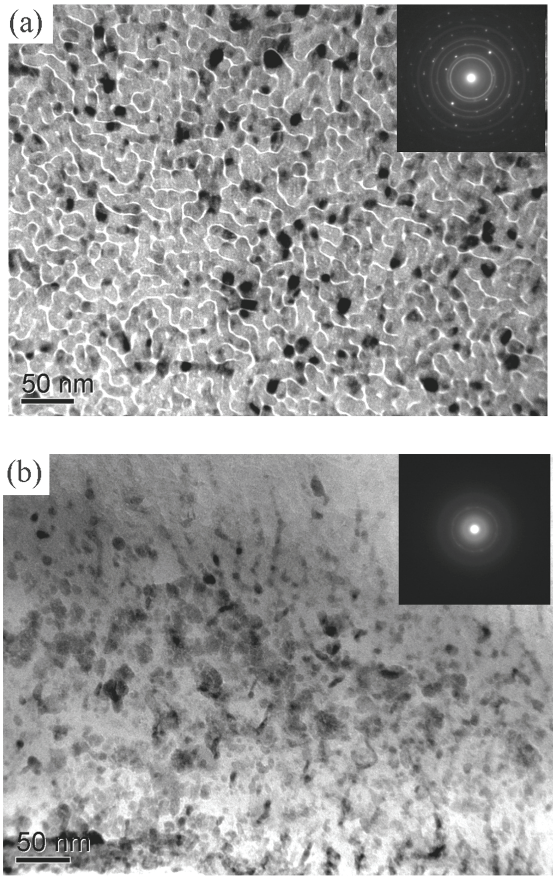

Fig.2 Bright field TEM images and selected area diffraction of CrN coatings deposited at d_{ss} = 90 mm. The view directions are normal to the coating surface. (a) Samples prepared with ion source assistance; (b) without ion source assistance.

Fig.3 shows deposition rate of the CrN films as a function of d_{ss}. The deposition rate decreases with increasing d_{ss}. At d_{ss} = 90 and 140 mm, the deposition rate with ion source is greater than without ion-source assistance, but the ion source-assisted deposition rate at d_{ss}=50 mm is smaller than without ion-source assistance.

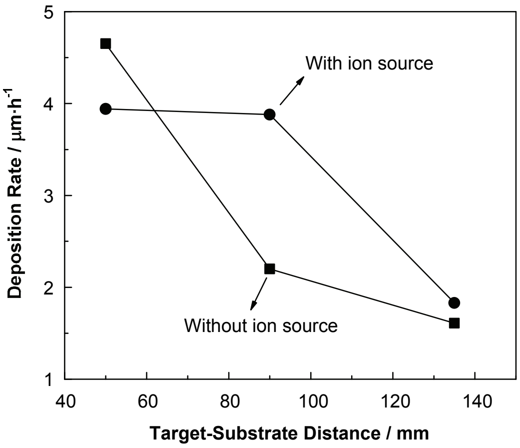

Fig. 3. Deposition rate as a function of d_{ss} for preparing the CrN films.

At a large d_{ss}, the sputtered Cr and N atoms arrive at the substrate in decreased numbers due to collisions with the N_2 and Ar plasma. However, using the thermal filament ion-source generates more ions, especially Ar ions, to bombard the Cr target and produce more Cr particles. As a result, the deposition rate is higher than without ion-source assistance. However, in ion source assisted deposition at a short d_{ss}, the increased number of Ar and other ions would cause more re-sputtering of the film surface, and this decreased the deposition rate.

Fig.4 shows typical three-dimensional AFM morphologies taken from the CrN coatings deposited at d_{ss} of 50, 90 and 140 mm with and without ion-source assistance. The topographies in Fig.4(a) reveal that the CrN films deposited at 50 mm are composed of columns with irregular tops. At d_{ss}=90 mm (Fig.4b), sizes of the extrusive tops were significantly reduced. At d_{ss}=140 mm (Fig. 4c), the extrusive tops became more regular, with an smooth surface. The root-mean- square (RMS) roughness values calculated from the AFM images were sequenced as d_{ss}(50 mm) > d_{ss}(90 mm) > d_{ss}(140 mm). At d_{ss}= 50 mm, the ion-source assistance reduced the RMS roughness by 8.6–10.3 nm, while the change became negligible at d_{ss}= 140 mm.

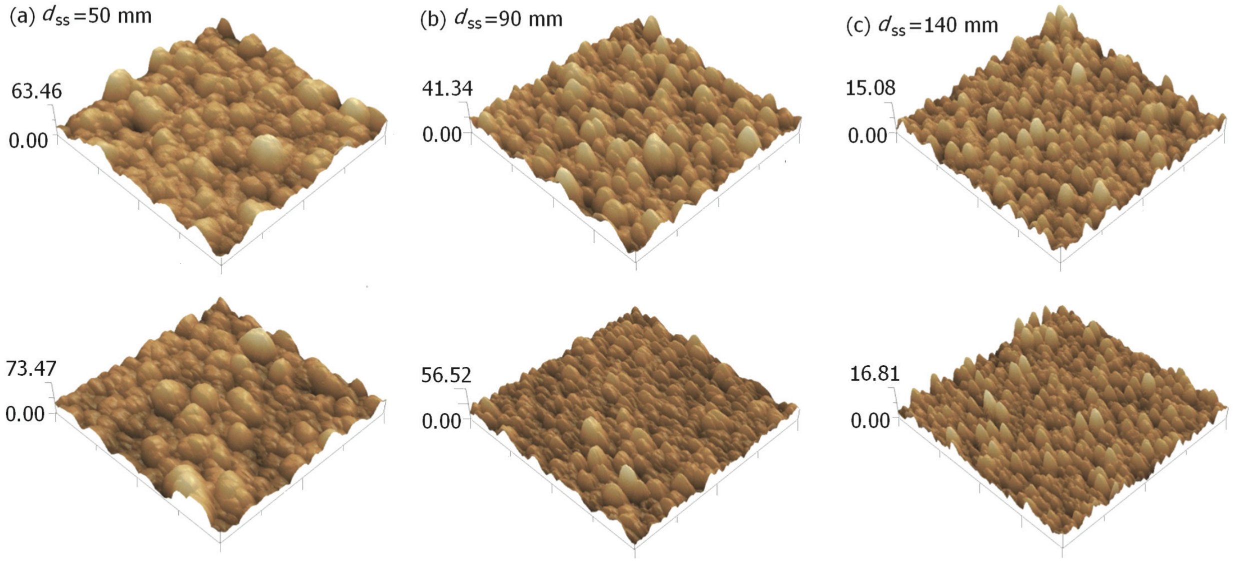

Fig.4 AFM images (2 μm× 2 μm) of CrN coatings deposited at different source-substrate distances (d_{ss}) with (upper) or without (lower) ion source assistance.

From Fig.5(a), the cross-section SEM image of the CrN films deposited at d_{ss}=90 mm without ion-source assistance, one sees a columnar growth throughout the film thickness. With the ion-source assistance (Fig.5b), the columnar growth is not obvious, and the coating becomes denser, due to bombardment by ions produced with the ion-source assistance.

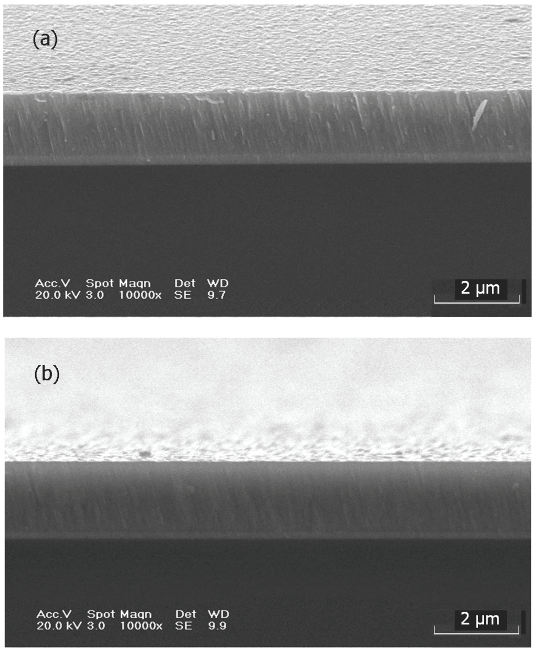

Fig.5 Cross-section SEM images of CrN films deposited at d_{ss} = 90 mm with (a) and without (b) ion source assistance.

Measurement results in Fig.6 indicated that the CrN coating microhardness are higher with the samples prepared by ion source assisted deposition. At d_{ss}=90 mm, the hardness is the highest. This is accounted for by better crystallization (Fig.1), and higher N concentration as revealed by EDS analysis of the samples (data not shown here).

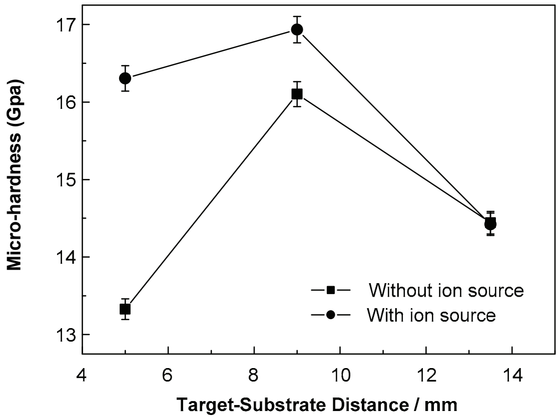

Fig.6 Variation of microhardness of CrN coatings as a function of d_{ss}.

The average friction coefficient of the CrN films prepared without ion source was 0.53 and the value decreased to 0.48 when ion-source assistance was used. This is consistent with enhanced microhardness and the reduction in the surface roughness of the CrN coatings.

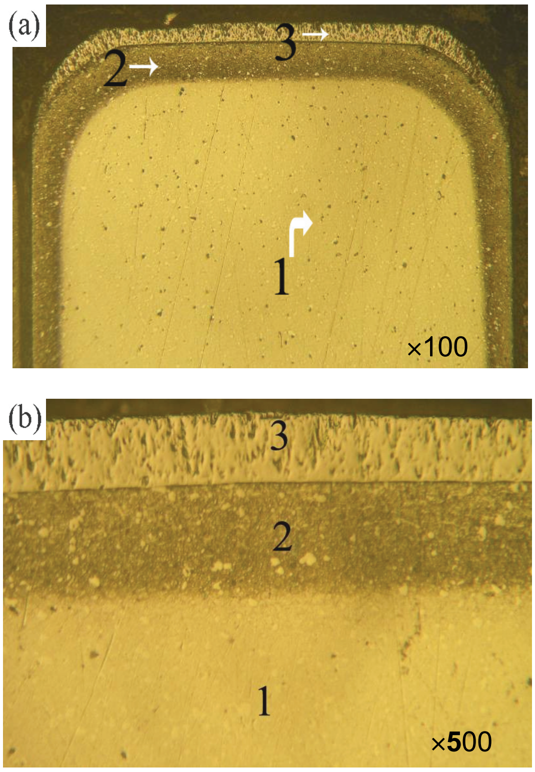

Fig. 7 Cross-section microscope images of 25-μm CrN coatings on a stainless piston ring of automobile engine.

The high hardness and low friction coefficient means the thick CrN coatings are applicable to mechanical parts, such as piston rings of automobile engines. Fig.7 shows microscopic cross-sections of CrN coatings on nitrogen-diffused steel piston rings, deposited under optimized conditions. Labels 1–3 denote the steel matrix of the piston ring, nitrided layer, and CrN coating, respectively. The piston ring itself has a hardness of 4.1 GPa measured under 1.0 g load. The hardness of the nitrided layer and CrN overcoating is 11.85 GPa (under 0.2 g) and 17.85 GPa (under 0.05 g). The thicknesses of the CrN coatings are in the range 15–25 μm and the hardness in 13–18 GPa, without affecting the mechanical properties of the piston ring body.

4 Conclusion

We have prepared CrN coatings by medium frequency magnetron sputtering and demonstrated improvement of the structure and mechanical properties of coatings by using a filament ion source during deposition. The CrN coatings deposited with ion source assistance exhibited an increase in microhardness from 13.25–16.3 GPa at a source-substrate distance 50 mm and from 16.0–17.0 GPa at the optimized $d_{ss} = 90$ mm. A deposition rate of 3.88 μm/h was achieved and CrN coatings of 25 μm thick were deposited on nitrided piston rings of automobile engines. The hardness of the coatings reached 17.85 GPa and significantly changed the properties of the mechanical part.

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