DEPOSITION OF CrN HARD FILMS BY CATHODIC ARC	LẮNG TỤ MÀNG CỨNG CrN

PLASMA EVAPORATION

ABSTRACT

The CrN films were deposited on AISI H13 tool steel substrate using chromium cathode by typical cathodic arc plasma evaporation equipment. The influence of the nitrogen pressure, deposition temperature and bias voltage on the mechanical and the structural properties of the films were investigated. The hardness of the films increased with the increase of the pressure from 0.7 Pa to 2.0 Pa and then decreased when pressure exceeded 2.0 Pa. The hardness of the films increased with the increase of temperature in the range of 250 oC and 350 oC while the adhesion was decreased. The hardness of the films decreased with the increase of bias voltage. The highest hardness was obtained at the bias voltage of -50 V. The morphology changed depending on the deposition conditions. All XRD peaks exhibited the CrN crystalline phases.

INTRODUCTION

The CrN coatings are commonly used as the material which exhibits oxidation and corrosion

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TÓM TẮT

Công trình này tiến hành chế tạo các màng CrN trên đế thép công cụ AISI H13 bằng cách sử dụng cathode crom và thiết bị bốc bay plasma hồ quang điển hình. Sau đó chúng tôi tiến hành nghiên cứu ảnh hưởng của áp suất khí nitơ, nhiệt độ lắng đọng và điện áp phân cực đến các tính chất cơ học và cấu trúc của màng. Độ cứng của các màng tăng khi áp suất tăng từ 0.7 Pa đến 2.0 Pa và sau đó giảm khi áp suất vượt quá 2.0 Pa. Độ cứng của màng cũng tăng theo nhiệt độ trong khoảng từ 250 oC đến 350 oC, trong khi đó độ bám dính giảm. Độ cứng của màng giảm khi tăng điện áp phân cực. Độ cứng đạt giá trị cao nhất khi điện áp phân cực bằng -50 V. Hình thái học thay đổi tùy thuộc vào các điều kiện lắng đọng. Tất cả các peak XRD đều thể hiện các pha tinh thể CrN.

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resistance and wear properties superior to those of TiN. The hardness of CrN coatings has been found recently in the range of 18 GPa to 25GPa [1-5, 6-9]. However, the hardness of CrN coatings reported by M. Brizuela et al. reached 35 GPa [10]. Like TiN, CrN has been compounded with other elements such as Zr, Al, Si, Ti etc to enhance its physical properties. For examples, CrN/AlN multi-layers had higher hardness and better thermal ability than CrN [5]. TiAlN/CrN and CrN-Ni exhibited superhard properties [13, 14].	[redacted]
CrN films have been deposited using many methods. The deposition method and deposition condition influences strongly on the structure and physical properties of the films. In this work, the effects of deposition conditions on the structure and mechanical properties of the CrN films deposited by cathodic arc plasma evaporation equipment were investigated.	[redacted]
EXPERIMENTAL	

PROCEDURES	[redacted]
CrN films were deposited on AISI H13 tool steel (1.5%C, 11.5%Cr. 0.8%Mo, 0.9%V, Fe bal.) substrate by a typical cathodic arc plasma deposition equipment. The substrate was placed in front of chromium target with the distance of 280 mm. The substrates were manually ground with SiC papers and polished with Al2O3 powder using a low speed polishing machine. Finally, they were cleaned by ultrasonic in pure alcohol. Before deposited, the substrates were etched in argon gas with current of 0.6A for 10 min in order to improve adhesion.	[redacted]
The effects of pressure, temperature, bias and arc current were determined by varying one parameter while keeping the others parameters in constants.	[redacted]
The phases of the films were determined by an X-ray diffractometer (Rigaku, RAD-3C). The morphology was observed by an optical microscope and a field emission scanning microscope (JEOL, JSM-820). Vickers hardness tester was used to measure the hardness of the films.	[redacted]

RESULT AND DISCUSSION

The CrN films were deposited for 60 minute with arc current of 50 A. The SEM cross-section image in Fig. 1 indicated that the thickness of the film was about 4.5 |im. This deposition conditions were used to carry out all experiments.

Fig. 1 SEM cross-section image of CrN film

The films deposited at bias voltage of -50V were used to determine the effect of pressure. Fig. 2 shows the hardness of these films with various pressures. The hardness of the films increased with the increase of pressure from 0.7 Pa to 2.0 Pa and then decreased with a further increase of the pressure. Therefore, the pressure of 2.0 Pa was chosen for subsequent experiments.

Fig. 2 Effect of pressure on the hardness of CrN films (temperature: 300oC, bias voltage: -50V).

The films deposited at temperature of 300 oC were used to determine the effect of the bias voltages. Fig. 3 shows the effect of bias voltage on the

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hardness of CrN films. The highest hardness was observed at the bias voltage of -50V. The hardness of the films deposited without bias voltage could not measure because of rough surface. The hardness decreased rapidly when bias voltage exceeded -50 V.	[redacted]
Fig. 3 Effect of bias voltage on the hardness of CrN films at pressure 2.0 Pa and temperature of300 oC.	[redacted]
The XRD diffractograms of films deposited with various bias voltages (Fig. 4), shows the presence of CrN peaks. The diffraction peaks corresponding to the (111) and (200) planes are the most intense. When the bias voltage increased, the intensity of peaks (111) and (200) decreased while the intensity of peak (220) increased. Applied bias voltages mean strong ion bombardment resulting in a change in microstructure and morphology.	[redacted]
Fig. 4 XRD diffractograms of CrN films deposited with various bias voltages.	[redacted]
O. Piot et al. have proved by experiments that the sputtering effect is significant to contribute	[redacted]

to change of microstructure. Under bias voltages, the grains of which the densest plane (200) is parallel to the film surface are preferentially sputtered. At the same time the (220) planes of which density is lower, begin to grow [15]. Further more, the XRD peaks were narrowed at high bias voltage. The peak narrowing relates with the reduction of grain size. The increase of grain size at high bias voltage was believed to be re-crystallization because of the increase of energy that caused by bias potential. At bias voltage of -50 V, the broadening of diffraction line was strongest, resulting in high hardness of the films.	[redacted]
The surface morphology of CrN films deposited with various bias voltages is shown in Fig. 5. The films without bias voltage were rougher and had more droplets than those with the bias voltage. However, no significant change of morphology was observed in the range of bias voltage from -50 V to -150 V. In this deposition process, there are two kinds of ions: chromium and molecular nitrogen ions occur simultaneously in which chromium ions are approximate	[redacted]

60% and nitrogen ions are approximate 40%. About 90% of chromium species impinging on the growing film are ionized [16]. Consequently, the bias voltage is a significant factor which influences on the properties of films. When the bias voltage is applied, both chromium and nitrogen ions were driven to the substrate, activated reaction, sputtered and transfered energy to the substrate. Without bias voltage, the density of plasma is low and the number of ions arriving at the substrate is less, causing for the formation of CrN particles in the space instead of the substrate. This could explain the poor properties of films deposited without bias voltages. The explanations agree with the opinions of Mingsheng Li et al. who believe that the nitridation reaction occurring in the space instead on the film surface decreased the density of plasma and led to weakened ion bombarding effect and poor property of the films [17].	[redacted]
The sputtering effect depends on collision between the growing film and the arriving particles.	[redacted]

However, the collision effect is controlled by momentum rather than energy. Since:	[redacted]
where U is bias voltage, m is the mass of ion. From (2), it is easy to deduce that the intensity of peaks corresponding to orientation of (111) and (200) planes reduces rapidly when bias voltage increases from 0 V to -50 V while the change of orientations occurs negligibly with higher bias voltage. By the same explanation, the surface morphology of the films was not changed significantly at the high bias voltage. The optimum condition was chosen to determine effect of deposition temperature.	[redacted]
was observed on the films deposited at temperature of 350oC. The adhesion decreases with the increase of temperature (Fig. 7). The critical load decreased from 10N down to 5N corresponding to the increase of temperature from 250 oC to 350 oC. The low adhesion is found on the films with high hardness in general, resulting in this event.	[redacted]
Fig. 6 Hardness of CrN films deposited with various	[redacted]

temperatures (bias voltage: -50 V, pressure: 0.2 Pa).	[redacted]
Fig. 5 Optical microscope images of CrN films deposited with various bias voltages.	[redacted]
Fig. 6 shows the influence of the deposition temperature on the hardness. The maximum hardness	[redacted]
Fig. 7 Optical micrographs of scratch tracks of CrN films deposited with various temperature (a: 250 oC, b: 300 oC, c: 350 oC).	[redacted]
Fig. 8 XRD diffractograms of CrN films deposited with various temperatures.	[redacted]
Fig. 8 shows the XRD diffractograms of the films. The results indicated that the present peaks are CrN with mixed orientation of (111), (200), (220), (311) and (322) planes. At low temperature, the diffraction peak corresponding to the (220) plane dominates.	[redacted]
At higher temperature, the peak intensity corresponding to the (111) plane increased while the others decreased. At the temperature of 400 oC, only the	[redacted]

peak with orientation of (111) was observed and the other peaks were hidden. The broadening of diffraction line calculated from the preferred peaks show that the XRD line was broadened at the film deposited at 350 oC. The broadened peak resulted in increasing hardness.

CONCLUSION

The CrN coatings with thickness of 4.5^m were deposited on the AISI H13 tool steel substrate. The optimum pressure to film deposition is 2 Pa. The hardness of the films decreased with the increase of bias voltage. The highest hardness was obtained at the bias voltage of -50 V. The hardness of the films increased with the increase of temperature in the range of 250 oC and 350 oC while the adhesion was decreased. The highest hardness of 29 GPa was observed on the samples deposited at pressure of 2Pa, bias voltage of -50 V and temperature of 350oC.

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