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High rate magnetron sputtering of thick Cr-based tribological coatings

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Abstract

In this study, high rate deposition of thick CrNx films was carried out by crossed field unbalanced magnetron sputtering for the special application such as piston ring employed in automobile engine. For the high rate deposition and thick CrNx films formation with thickness of 30㎛, high power density of 35 W/cm^2 in each target was induced and the multi-layer films of Cr/CrN and α-Cr/CrN were synthesized by control of N_2 flow rate. The dynamic deposition rate of Cr and α-CrN film was reached to 0.17㎛/min and 0.12㎛/min and the thick CrN_x film of 30㎛ could be obtained less than 5 hours.

The maximum hardness was obtained above 2200 kg/mm^2 and adhesion strength was measured in about 70N, in case of multi-layers films. And the friction coefficient was measured by 0.4, which was similar to the value of CrN single-layer film.

1. Introduction

CrNx films deposited by physical vapor deposition (PVD) have been developed for the replacement of electroplated Cr coatings due to environmental problems[1-3]. In resent, CrNx films with a thickness of 1-3㎛ were widely used in many industrial applications such as cutting tools, die and molds owing to superior mechanical properties compared with electroplated Cr coatings. However these thin CrN_x coatings have some limitation in special mechanical components as piston ring is used in severe operation conditions in combustion engines because it demands duration of mechanical properties for long times.

From a few years ago, CrN_x films with a thickness of 30㎛ is adapted for piston ring in Germany and Japan. However, there have some circumscription to low deposition rate and high residual stress in films[1, 4]. In case of some industrial information, it have been reported that it takes 8 hours to deposit CrN_x film with thickness of 30㎛, and annealing process was carried out after coating. In this study, we investigated thick CrN_x multilayer coatings by crossed-field unbalanced magnetron[5] with two high power magnetron to realize high rate deposition[6] and low residual stress in films without post-annealing process. Deposition processes for such purpose were varied with N_2 flow rate simultaneously. The film deposition rate and microstructure were analyzed by α-step and X-ray diffraction (XRD), and mechanical properties were evaluated by microhardness, adhesion and ball-on-disk type wear test.

2. Experimental

2. 1 Film deposition

CrN_x films were deposited on stainless steel (STS430) by closed-field unbalanced magnetron sputtering with 2 Cr targets, designed for high rate deposition, in our laboratory. The distance between substrate and target was 110mm and the jig was rotated by 14 rpm for uniform films. The detailed schematic diagram of coating system was illustrated in Fig. 1.

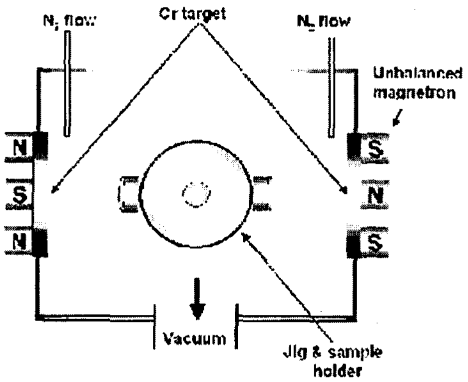

Fig. 1 The schematic of cross field unbalanced magnetron sputtering systems for CrN_x coating

Prior to deposition, STS430 steel specimens were polished mechanically to a surface roughness of below Ra=0.05㎛ and cleaned ultrasonically by a standard alkaline cleaning method. Then, CrN_x films were deposited with target power density of 35W/cm^2 and various N_2 flow rate of 0~30sccm. The detailed deposition conditions are listed in Table.1

For the deposition of thick CrN_x films (30㎛), CrN_x coatings were deposited by single α-Cr and CrN films and multi-layer films of it's combinations. The period of layer was 4㎛ and the ratio of thickness is 1:3, such as Cr/CrN and α-Cr/CrN.

Table.1 Conditions for CrN_x coating process

Deposition steps and parameters
(1) Pump down and radiation heating Base pressure : 4.0×10^{-5} Torr Temperature : 250℃ Heating time : 10 minute
(2) Ar plasma cleaning Ar pressure : 2.0×10^{-2} Torr DC bias voltage : -800 V Time : 20 minute
(3) CrN films deposition Ar pressure : 3.0×10^{-3} Torr Distance between target and substrate : 110 mm Substrate bias voltage : -100 V Target power density : 35 W/cm^2 N_2 flow rate : 0-30 sccm Cr interlayer : 1㎛

2. 2 Coating evaluation

To examine the phases and structures of the coatings, X-ray diffraction (XRD) was used. The X-ray was generated by a Cu K radiation at 30KV and 400mA. The scanning rate was 8°/min. The specimens were investigated using the glancing-incidence X-ray diffraction mode with incidence angles fixed at 3°. The analysis was performed in the 2 range 30° ~90° The measurements of thickness of films were carried out by profilometer, Tencor co., α-step. The mechanical properties were evaluated by micro-hardness, adhesion and friction coefficient as be compared with electroplated Cr. Micro-Knoop hardness was measured at a normal load of 0.05N. The adhesion strength was compared by scratch test, CSEM RAVETEST was used to produce the frictional force versus load curve to obtain the critical load (Lc2). The applied Load is changed continuously from 0 N to 100 N in 10 mm distance. Wear tests were performed using a ball-on-disk test under rotating, the rotating velocity was 0.094m/s and the sliding distance was 1Km. The applied normal load was 10N and used steel balls were 10mm in diameter.

Wear volume of steel ball was measured after ball-on-disk test. All the mechanical properties of each film were compared with electroplated Cr.

3. Results and discussion

3. 1 Deposition rate and microstructure

X-ray diffraction analyses of the various CrN coatings produced can be seen Fig. 2. According to the CrN binary phase diagram[7], as N_2 gas flow is increased, phase change is appeared : bcc Cr, bcc α-Cr, hexagonal α-Cr_2N and fcc CrN phase[2].

The diffraction pattern of N_2 flow of 0 sccm corresponds to that of chromium with a strong (110) reflection and weak (211) and (200) reflection. At N_2 flow of 10sccm, (211) peak was disappeared and the (110) and (200) peak positions are shifted about 0.5° 2Θ towards lower angular positions. This is due to the insertion of nitrogen atoms in the chromium cubic lattice[8] As increase N_2 gas flow, the diffraction pattern of N_2 flow of 20sccm, 30sccm corresponds to Cr_2N and CrN phases respectively. The preferred orientation of CrN is along (200) peak.

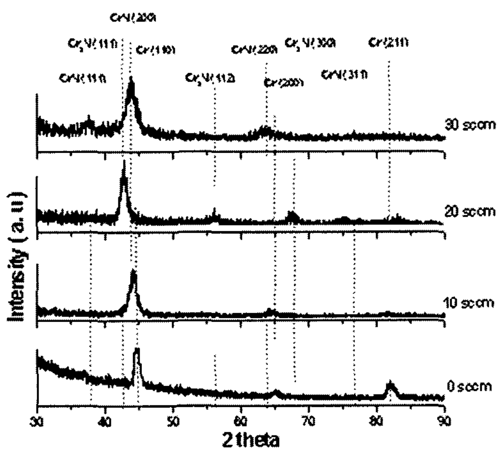

Fig. 2 X-ray diffraction patterns of CrN_x films deposited on Si wafer with various N_2 flows.

Fig. 3 illustrates the deposition rate of CrN_x films with various N_2 flow rate and the distance from target to substrates. The deposition rate was decreased as nitrogen flows was increased. This reduction of deposition rate is due to the formation of chromium nitride at the target surface, so called 'poisoning effect'[2, 9]. The dynamic deposition rate of Cr and CrN film was reached to 0.17㎛/min and 0.12㎛/min and the thick CrN_x film of 30㎛ could be obtained less than 5 hours. This can be estimated for high rate deposition and if we reduce distance to 60mm, we will deposit for more short times.

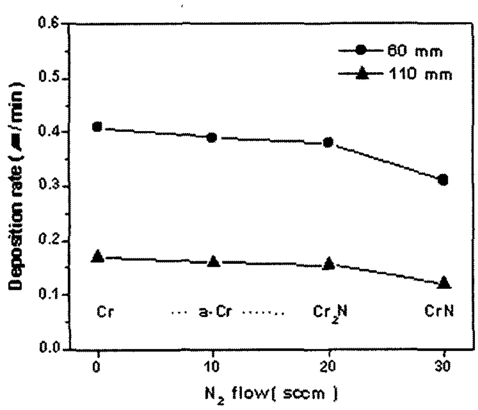

Fig. 3 Deposition rate of CrN_x films by nitrogen flows and distance between target and substrate

3. 2 Mechanical property

Fig. 4 illustrates the microhardness of electroplated Cr and CrN_x films deposited with various N_2 flow rates. The maximum hardness value of 2400 Kg/mm^2 was obtained for CrN single-layer, is compared with low hardness value of electroplated Cr and α-Cr film. And then multi-layer films of Cr/CrN and α-Cr/CrN tend to reduce the hardness in the range of 2000-2200 Kg/mm^2. In general, multi-layer coatings show the high values of

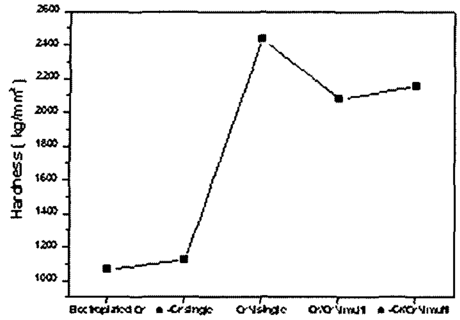

Fig. 4 Microhardness changes measured at normal load of 0.05 N for CrN_x films with various forms of single-layers and multi-layers

hardness, compared with single-layers by hall-patch effect[10, 11]. However in our case improvement of hardness was not observed. It is estimated that thick layer period is not influenced to increase of hardness. The adhesion strength was measured to be 80 and 55 N (Fig. 5).

The adhesion strength of multi-layer films was increased above 70N compared with lower that of CrN single-layer (55N) and residual stress of multi-layer was decreased by ductile interlayer (Cr, α-Cr) and interfaces[12]. Ball-on-disk type wear was carried out and coefficients of friction were measured. The coefficients of friction of each coating were shown in Fig. 6.

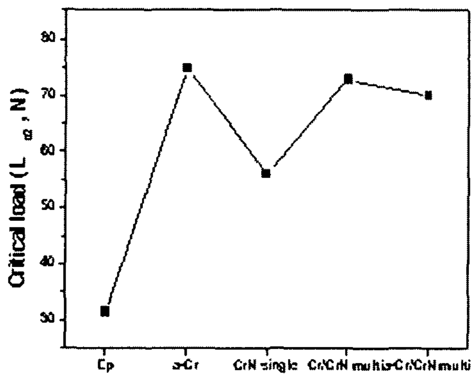

Fig. 5 The value of critical load (Lc_2) was measured by acoustic emission of scratch test.

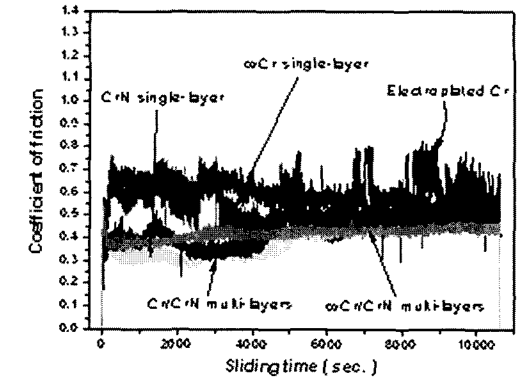

Fig. 6 Wear test of ball-on-disk was carried out and coefficients of friction were measured. Applied load was 10 N and sliding distance was 1 Km.

The friction coefficients of α-Cr and CrN single-layer were displayed 0.6 and 0.4 individually and it is a lower value in comparison with electroplated Cr. The multi-layers were acquired small values of friction coefficient of 0.4. It is due to high hardness and adhesion.

Fig .7 illustrates wear volume of steel ball. CrN single-layer and two multi-layers show a similar value of about 0.27mm³. It means that ball wear was progressed owing to hardness of films. On the contrary, the electroplated Cr showed a small wear volume (0.064mm³) of steel ball for lower hardness.

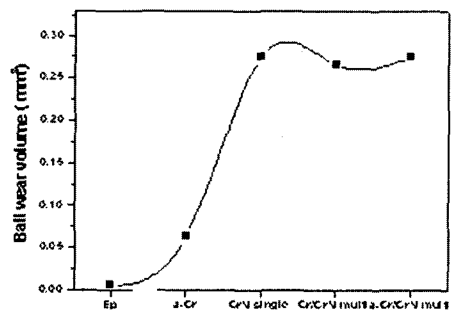

Fig. 7 The wear volume of steel ball was measured after ball-on-disk test.

4. Summary

The high rate deposition of CrN_x films was carried out by high power crossed-field unbalanced magnetron sputtering. In this study, the following results have been obtained :

1) The dynamic deposition rate of Cr and CrN film was reached to 0.17㎛/min and 0.12㎛/min and the thick CrN_x film of 30㎛ could be obtained less than 5 hours.

2) Single-layer films of α-Cr and CrN were deposited and show hardness of 2400 Kg/mm^2, critical load (Lc2) of 75, 55N respectively. It appears good properties as compared with electroplate Cr.

3) Multi-layer films of Cr/CrN and α-Cr/CrN were deposited by 1㎛ : 3㎛ ratio. They were obtained hardness value of 2200 Kg/mm^2 and the best critical load (Lc2) of about 70 N due to relaxation of residual stress by ductile interlayer (Cr, α-Cr) and interfaces.

4) As a result of wear test, Cr, Cr/CrN, α-Cr/CrN films showed a good wear property, respectively. And the coefficient of friction of these compound to electroplated Cr, α-Cr single-layer films was measured to be 0.4

Acknowledgements

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