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Effect of nitrogen flow rate on properties of CrN films Prepared by HCD-gun

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Properties

ABSTRACT

Purpose: The effect of reactant nitrogen gas flow rate on the tribological properties of CrN thin films was studied.
Design/methodology/approach: Hollow Cathode Discharge gun (HCD-gun) was employed for the coating of CrN films on the glass and SS-316 sub strum. The reactant nitrogen with different flow was fed in to the vacuum chamber of $3x10^{-3}$ Pa pressure to form Cr N composite under experimental condition.
Findings: The crystalline phase and micro structural studies of the specimens were carried out by XRD and SEM respectively. It was found that the preferred orientation for CrN films was (200) and that for Cr_2N was (111). The micro hardness measurement fulfilled by Vickers test, and the hardness value obtained was $2100kgm^{-2}$. The glow discharge optical emission spectroscopy (GDOES) was used for compositional analysis of the content elements. The wear resistance test was performed under specific condition.
Research limitations/implications: We have completed our discussion by commenting the results on small deposition area, and therefore, we endeavor further attempt on large area coating.
Practical implications: The Cr - N composite due to higher hardness, wear resistance and anticorrosion characteristics is widely used in cutting tools, aerospace and industrial fields.
Originality/value: It may be remarked that the hardness and wear resistance values obtained in this work is very encouraging and therefore makes thin composite suitable in various technical applications.
Keywords: Chromium-nitride; Thin layer coating; Hollow cathode discharge-gun; Micro hardness; Wear resistance

1. Introduction

One of the main takes in manufacturing of tools is to enhance the hardness of industrial components. This is obviously requires chemical stability, long life time, condensed structures and so on. As, the PVD, and CVD technologies for the coating of tools are very well established, the scientists and industrialists have keen interest on its applications. In particular, at last decade enormous results have been reported from these studies. Among the materials with an important consideration CrN has shown to be a promising coating for higher hardness, good adhesion and wear protection. In literature survey there are variety of techniques for preparation and characterization for this composite. Hollow cathode discharge gun is widely used for coating CrN composition on different sub strums.

Komiya et al [1, 2], first deposited refractory compound films by introducing reactant gases in to the chamber during HCD coating process. There have been successive several reports on CrN films [3-5]. There are two kinds of crystal structure for chromium nitride, that is: CrN and Cr_2N which their component ratio must be controlled by apparatus geometry and deposition techniques. This paper has undertaken to investigate the correlation between the deposition parameters, nitrogen flow rate, substrate bias voltage, wear test and micro hardness measurement.

2. Experimental details

Deposition of chromium nitride films on stain less steed 316 were carried out in active N_2 ambient using hollow cathode discharge gun (HCD-gun). The experimental set up was the same as described in our previous work [6].

Granules of chromium with 99.98% purity supplied by the Merck company were put in to the graphite boat which is mounted on a copper plate acts as an anode electrode. Substrates are washed thoroughly in a usual manner using ultrasonic bath, detergent, acid, alcohol and acetone and then, fixed in the fixtures. Prior to deposition substrates were bombarded by argon ions produced in electric discharged chamber to end-process of surface cleaning. The steered plasma with chromium arc target was operating with focused electron beam on boat to evaporate and ionize material. The current between the ionization filament and evaporator was controlled by the ionization current. The source to substrate distance was 15 cm and deposition rate was about 0.15 µ min^{-1}. The system was initially evacuated to a pressure about 3×10^{-3} Pa. One KV bias voltage was supplied between boat and substrate.

Finally, the chromium metal was evaporated and N_2 gas was introduced in to the chamber. To study crystalline structure and phases present in the coating, X-ray diffraction analysis were carried out by PW1849 model Philips with mono chromatic copper radiation (Cu Ka). To investigate micro structural composition, scanning electron microscopy (SEM XL-30) Philips was employed. By performing micro hardness tests by Vickers lits Wetzelar MM6 model, information about the hardness of samples was gained. Finally, glow discharge optical emission spectroscopy (GD-OES) was utilized for qualitative analysis of coating elements.

3. Results and discussion

Fig.1 (a, b) represent the glow discharge optical emission spectroscopy (GD-OES) analysis of nitrogen and chromium distribution in SS- 316 substrate.

On the basis of this operation CrN film was sputtered from the sample and spread in to the glow torque and then constituent particles were analyzed from top to bottom of the surface as a function of sputtering time by optical emission spectroscopy process, which was measured with respect to standard values.

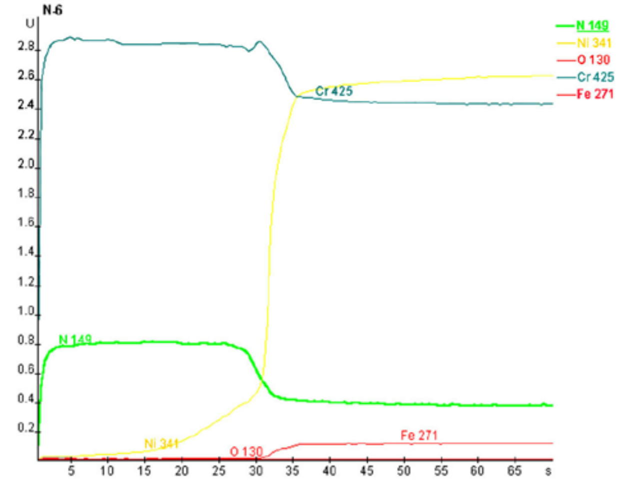

Fig. 1a. GD-OES analysis of CrN on stainless steel 316

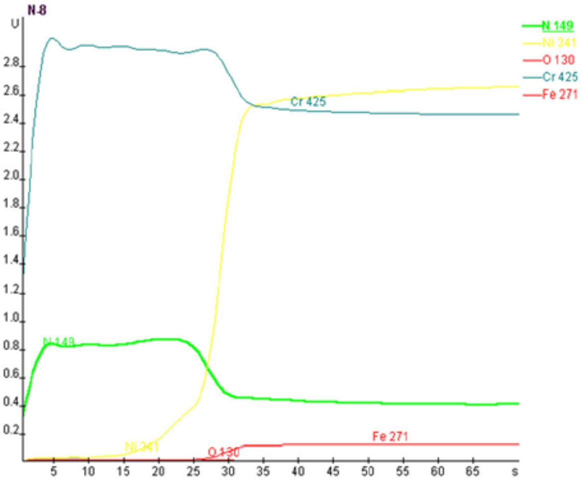

Fig. 1b. GD-OES analysis of CrN on stainless steel 316

In fig. 1(a) the existence of Cr (with code 425) and N (with code 149) was shown in the sample with thickness of 1.5 µm. Comparing both figures, gives that, thickness of deposited layers does not affect the Cr and N distribution. In this work Cr and N are essential elements, while the others appeared in fig. 1(a, b) are belong to the substrate matrix, which are not dominant from the view point of present article. To investigate the effect of nitrogen gas flow rate on the crystal phase and structure, the X-ray diffraction pattern on glass and stainless steel substrates were analyzed on verity of CrN samples prepared with same history , but in different gas flow rate of $7\text{cm}^3\text{min}^{-1}$, $9\text{cm}^3\text{min}^{-1}$ and $12\text{cm}^3\text{min}^{-1}$ is show in fig. 2 (a, b, c) respectively. These samples were all fcc cubic structure with dominant (200) plane of reflection.

The discrepancy was explained in terms of diffraction intensity. It is clear that, the sharp peak with higher intensity i-e fig. 2(c) corresponds to high flow rate. The similar observation was reporter by Louse et al [7] and Wang and Oki [8]. As it is seen from the fig. 2 (a, b, c), by increasing nitrogen flow rate, the peaks width are decreased. There fore, it is convenient to regard this as an increasing of grain size corresponding to fig. 2 (c). It may be remarked that the effect can be accounted for by inclusion of relation:

$$G.S = \frac{\lambda}{D\cos\theta} \qquad (1)$$

Where λ is the wave length of X-ray beam G.S is the grain size, θ is the Bragg angle and D is half width maximum intercity line [9].

Furthermore the XRD spectrum for the CrN films coated on SS-316 is given in fig. 3.

The sharp peak near 45° belongs to (200) plane, while the other phases are mainly due to substrum.

Fig.4 exhibits the scanning electron microscopy (SEM) pictures of CrN compound layers. The columnar growth layers as well as general view of chromium nitride at $12\text{cm}^3\ \text{min}^{-1}$ N_2 gas flow (optimized condition) are shown in fig. 4. It must be remarked that, the films are not free of Crystal defects.

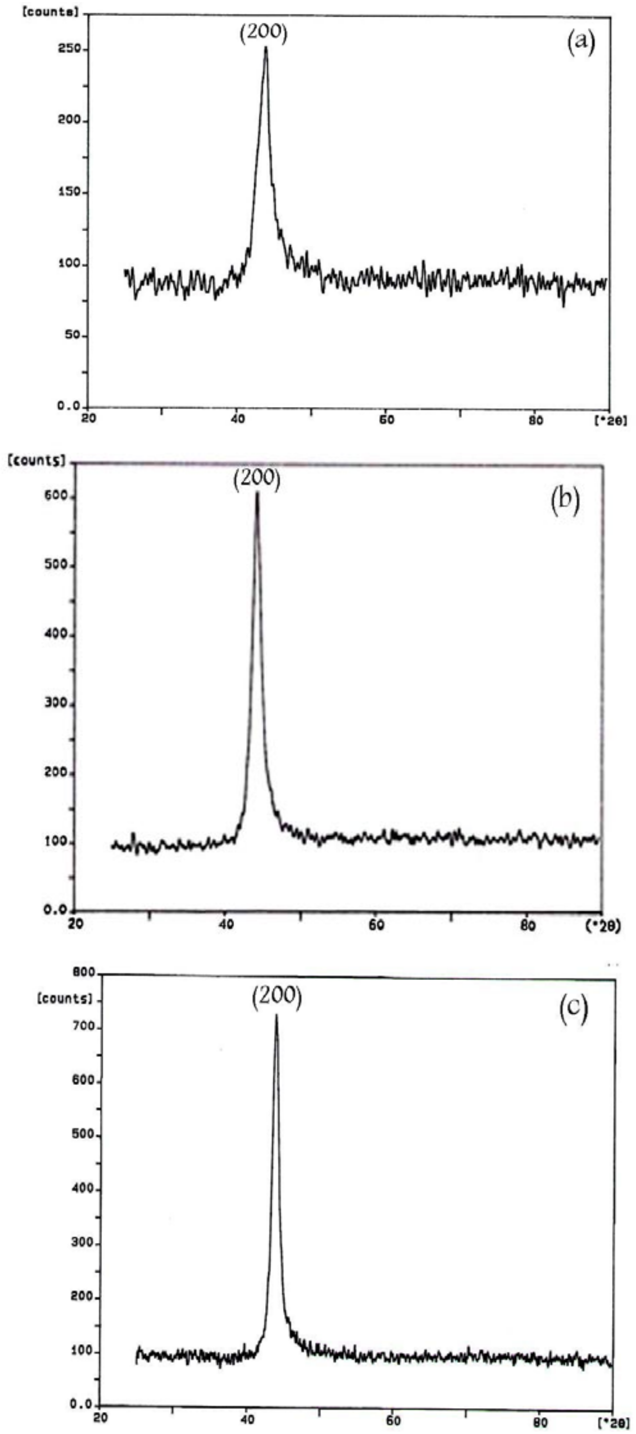

Fig. 2. X-Ray diffraction patterns of CrN coatings on glass; (a): at $7cm^3min^{-1}$, (b): at $9cm^3min^{-1}$, (c): at $12cm^3min^{-1}$

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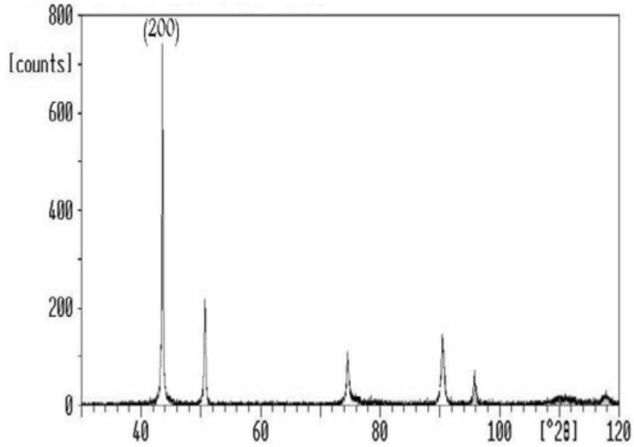

Fig. 3. X-ray diffraction pattern of CrN deposited on SS-316

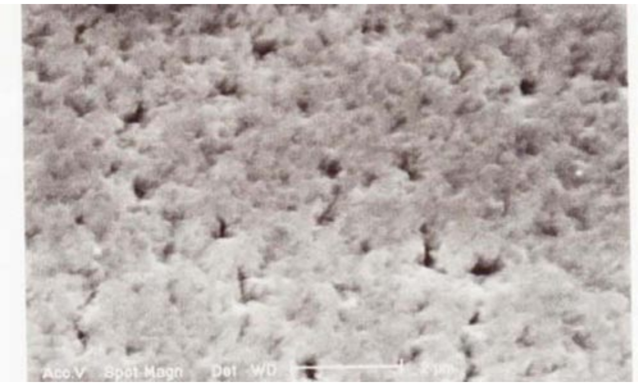

Fig. 4. SEM micrographs of CrN deposited films at 12 cm^3 min^{-1} N_2 gas flow

Fig. 5 is the plot of micro hardness values as a function of nitrogen gas flow rate. As the plot reveals, by in creasing N_2 flow rate, the hardness is also shows increment and becomes maximum at 12 cm^3 min^{-1}. A reason for this event, as discussed before, is that the metallic bond is changed to covalent bond during the injection of nitrogen elements to the Cr matrix. As a result, the tight covalent binding is formed [10]. Our observations on many samples indicate that, the more flux of nitrogen creates many pin holes in the surface and therefore, hardness was decreased. References [11, 12] have reported the similar phenomena on TiN compound.

The wear test can be carried out by measurement of volume removed from the deposited surface by to and fro motion of a roller which is pressed on the sample surface and which acts as a grinding wheel . The Cr-N coated on SS– 316 base with different N_2 flow rates was studied to compare the wear resistance. The result, obtained from this investigation which is illustrated in fig.6 indicate that, wear protection of the samples increased as the rate of flow of nitrogen was increased, where, the maximum value corresponding to flow rate of 12 cm^3 min^{-1} was obtained .

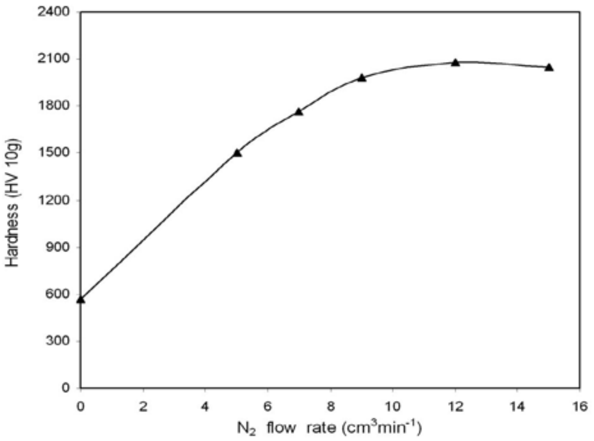

Fig. 5. Micro hardness of CrN film with different N_2 flow rate

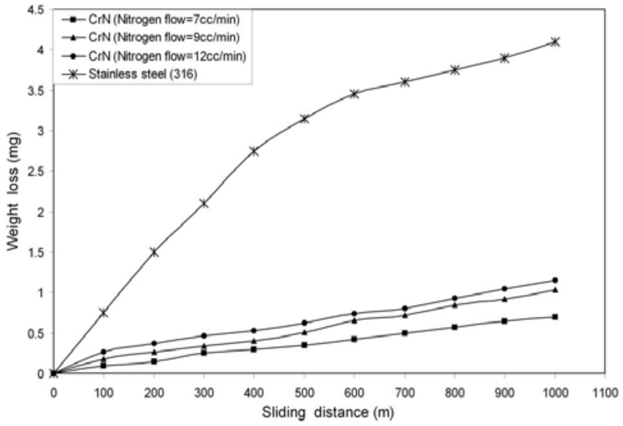

Fig. 6. Variation of wear resistance as a function of N_2 flow rate of CrN coated on SS-316

Mucha and Braun [13] have given the similar comment on wear resistance of Ti-A 6Al- 4V specimens which was affected by nitrogen doses. A significant change of wear resistance can be noticed in fig. 6 between uncoated substratum (SS-316) and that of coated with CrN compound.

4. Conclusions

Thick hard coating of chromium nitride films with very good uniformity and adhesion are obtained by HCD–gun process on the glass and SS-316 Substrates. In his work, we have shown that the main properties of CrN composite like crystalline structure and tribological are strongly depend upon to the arrival rate of N_2 element in to the chromium matrix. The qualitative analysis of specimens was carried out by GDOES, detected the existence of Cr and N elements from top of the surface. Samples prepared with different flow of nitrogen rate, all have cubic fcc. Crystal structure with prepared reflection plane (200). Where as, at 42 angle, the intensity of peak corresponding to 12 cm^3 min^{-1} flow rate was remarkably higher.

The micro hardness behavior of CrN compound was affected by nitrogen gas flow rate and the maximum amount was 2100 HV. The change in the hardness of the specimens can be attributed to change in metallic bond to covalent bond in CrN composite. The wear resistance test was accomplished by allowing the grinding wheel scratch and removes the surface. It was found the high flow rate of nitrogen, leads to higher value of wear resistance.

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