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Microstructures & Properties Changes Induced by Nitrogen Ion Implantation on Chromium Films

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Abstract: The chromium thin films were prepared using ion beam deposition on stainless steel 304. Chromium film implanted by nitrogen ions at doses in the range of 4.5×10^{17} to 2.7×10^{18} N+/cm² and energy of 30kev. The formation of nitride phases and corrosion behavior after nitrogen implantation were characterized by XRD and corrosion test respectively. The results show that corrosion resistance rise, reach to a maximum at dose of 1.8×10^{18} , and then fall at higher doses. In addition, the effect of corrosion tests was analyzed using scanning electron microscopy (SEM). Keywords: Nitrogen, Implantation, Stainless steel, Corrosion, Cr N, Thin film.

1. Introduction

In many tri biological applications coatings of metal nitrides are now commonly used $^{1-2}$. The properties required for such coatings are not only focused on wear and hardness resistance but, because of severe operating conditions, an increasing number of work pieces need to combine these mechanical features with corrosion resistant properties. These coating are generally deposited by physical vapor deposition techniques (ion plating, sputtering, arc evaporation) allowing the formation of dense Adhesive films at low deposition temperatures. Titanium nitride (Ti N) is the coating most extensively used in industry, but to withstand aggressive environments, either a third element (commonly Al) or an inter layer (sputtered Ti or electrochemical Ni) can be added³. For some years, chromium nitride coatings are gaining popularity and becoming important technological materials in the fields of cutting and forming tools, bearing and machine parts, dies and moulds⁴. The physical and mechanical properties of CrN have been

studied; it has a low coefficient of friction, high surface hardness and high taughness compared with TiN⁵⁻⁶⁻⁷. So CrN thin films have proven their capability of enhancing the wear protection of a coated piece. In addition to its superior wear resistant property, Cr N is thought to be chemically inert in various environments.

Some studies have been performed in acidic solutions H_2SO_4 deposits often made of mixtures of chromium nitrides . However, knowledge of the anticorrosion properties of identified and selected chromium nitride films is still limited. In order to estimate the corrosion behavior of various and selected chromium nitride nitrogen – doped chromium, Cr_2N and Cr N, electrochemical tests were performed in solutions 1 M H_2SO_4 . The aim of the present paper is the study the dose effects on the formation of chromium nitride phases and corrosion resistance of Crthin films.

2. Materials and Experimental Techniques

The AISI 304 steel substrates of $20 \times 18 \times 1$ mm size ultrasonically cleaned using alcohol and acetone. Thin chromium layer prepared using ion beam deposition by hallow cathode ion beam system. The sample temperature during deposition was 280°C to 300°C, which increased the adhesion of the deposited chromium layer at substrate. The PVD process at pressure of 4.2×10^{-4} torr carried out using argon gas. During the process voltage of 52V applied to Bias. After 40 minutes deposition, thickness of samples (1µm) measured with a quartz microbalance.

Nitrogen ion implantation of samples performed using implanter of Plasma Physics Research Center of I.A. University. The ion implanter system can generate gas ions and accelerate to maximum 30keV with an elliptic beam size 110×250 mm. In this study different nitrogen ion doses in the range of 4.5×10^{17} to 2.7×10^{18} N⁺/cm² have been carried out. During implantation, the background pressure of 4.8×10^{-6} torr decreased to 1.6×10^{-5} torr. The implantation parameters summarized in table 1.

X-ray diffraction analysis carried out to study micro structural changes and new phases formation induced by the ion implantation in the Cr layers. X-ray diffraction patterns were recorded at room temperature by the X-ray (SISERTE Model 3003PTS) diffract meter using Ni filtered Cu kal radiation with a step size of 0.05° 20.

The electrochemical behavior studied by potentiodynamic methods. The samples polarized in $1MH_2SO_4$ solution made of analytical grade reagent and double distilled water. The samples were prepared at $1cm^2$ area exposed on only one face. The tests

performed by EG & G model 273A potential state coupled to PC. A saturated calomel reference electrode (SCE) and platinum counter electrode used in three – electrode set up. The samples were polarized from – 250mv.vs open circuit potential at a scan rate of 1mvs⁻¹. The ends of scanning selected after considering trans-passive behavior in polarization curves. All of the potential that presented in this paper are versus SCE.

In order to study the samples' surface morphology after corrosion testes we used scanning electron microscopy (LEO4401).

3. Results and Discussion

XRD patterns of implanted and un-implanted samples were shown in fig.1. From this figure, it is clear that the un-implanted sample presents Cr and substrate phases. The formation of nitride phases as Cr N and Cr₂N confirmed in figures (1) 4.5×10^{17} through 2.7×10^{18} .

Figure 2 presents the polarization curves of unimplanted and implanted samples. For all samples active – passive behavior observed in the same passivation range. It is generally accepted that chromium oxide is responsible for the passivity behavior. This indicates that after nitrogen ion implantation the role of initial surface composition dose not change. In corrosion test the potential of passivation and trans- passive of chromium nitride layers were the same after ion implantation process. The only parameter which changes by nitrogen implantation was passivation current.

Sample	1	2	3	4	5
Energy (k e v) Ion	-	30	30	30	30
Ion Current	-	20	20	20	20
$(\mu A/cm^2)$	_				
Dose (ions/cm ²)		4.5×10 ¹⁷	1.8×10^{18}	2.2×10^{8}	30×10 ¹⁸
Time (s)	-	3600	14400	18×10 ³	21.6×10 ⁶
Temperature (°C)	-	330	330	330	330

Table 1. The process parameter during implantation.



Fig.1 X-ray diffraction pattern.



Fig.2 Potential dynamic polarization curves.



Fig.3The variation in passive current with implantated dosage of nitrogen.



Fig.4The corrosion potential as a function of nitrogen.



Fig.5 The variation of corrosion current.

Figure 3 shows the variation of passivation current versus ion doses. By increasing of nitrogen ion doses to 4.5×10^{17} , passivation current decreased. In the other word, the corrosion rate decreased.

Figure 4 shows the corrosion potential variation in terms of nitrogen implanted doses. The variation of corrosion current with enhancement of nitrogen dose is shown in figure 5 nitrogen implantation on chromium surface reduces the corrosion current up to ten times. In contrast to this, by increasing the dose from 2.25×10^{18} to 2.7×10^{18} the corrosion current is increased. The same behavior observed in Ti alloys⁸⁻⁹.

Polarization curve in passivation are a have a horizontal peak as shown in figure 2. At low dose this peak is small but at higher doses (2.25×10^{18}) and 2.7×10^{18} it is noticeable. Existence of this peak is related to formation of secondary phase or grain boundary which their corrosion current is very higher than matrix phase¹⁰. The measured current in the total polarization curve is summation of secondary phase

and matrix corrosion current. As shown in XRD patterns formation of Cr_2N secondary phases increase by doses and this phase is result in this peak.

Conclusions

The study of the corrosion resistance properties of implanted and un-implanted chromium layers on the stainless steel 304 substrata in $1M H_2SO_4$ allowed the following conclusion to be drawn:

- I. The improved corrosion resistant of nitrogen ion implanted chromium layers in $1M H_2SO_4$ is due to the change in nature and composition of the passive film formed after implantation. This improvement arises from the formation of precipitates of CrN and Cr₂N, which screen underlying chromium atoms.
- II. The data indicates that the best protection against corrosion can be obtained at a dose of 1.8×10^{18} ions cm⁻² after that the corrosion current was increased.

III. The corrosion potential was increased by enhancement of nitrogen implanted doses.

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