Reactive DC Magnetron Sputtered Zirconium Nitride (ZrN) Thin Film and its Characterization

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ABSTRACT: Zirconium nitride (ZrN) thin films were prepared by using reactive direct current (DC) magnetron sputtering onto different substrates. A good polycrystalline nature with face centered cubic structure was observed from X-ray Diffraction for ZrN thin films. The observed ‘d’ values from the X-ray Diffraction pattern were found to be in good agreement with the standard ‘d’ values (JCPDS-89-5269). An emission peak is observed at 587nm from Photoluminescence studies for the excitation at 430nm. The resistivity value (£\rho$ cm) was observed. ZrN has high wear resistance and low coefficient of friction. A less negative value of \text{E} \text{corr} and lower value of \text{I} \text{corr} observed for ZrN / Mild Steel (MS) clearly confirm the better corrosion resistance than the bare substrate. Also the higher \text{R} \text{ct} value and lower \text{C}_{dl} value was observed for ZrN / MS from Nyquist – plot.

1. Introduction

Zirconium nitride is an attractive material due to its good chemical and physical properties. Due to their superior mechanical properties, ZrN films have been long applied in hard coatings [1,2]. ZrN thin films have been attracting much attention for various applications such as wear resistant coating on steel drill bits, as diffusion barrier in IC technology, as cryogenic thermometer, as hard coatings, as a protective coating on steel vessels handling molten metal, and as solar energy collector surface film, Josephson junctions [3-6]. These coatings appear to have substantial potential in aeroengine, Industrial and biological application [7-9]. ZrN thin films have been synthesized by chemical vapor deposition, pulsed laser deposition [10], ion-beam assisted deposition [11,12], reactive sputtering [13,14], plasma nitridation [15], vacuum arc deposition [16], ion plating [17], cathodic arc evaporation [18,19], and ultra high vacuum sputtering [20,21]. The physical properties of thin films are often anisotropic and controlled by their detailed microstructure, including atomic ratio (stoichiometry), crystallinity and preferred-orientation, which are complex functions of the growth parameters for a given growth method. For a protective coating material, the corrosion resistance of the film is one of the most important properties in addition to mechanical properties. Corrosion properties of hard PVD nitride coatings have been recently reviewed [22]. Studies regarding the electrochemical [23] and thermal [24] oxidation of ZrN coatings are relatively scare compared to those of TiN.
Here, in this paper, we have investigated the materials properties of the reactive dc magnetron sputtered ZrN thin films and its corrosion resistance in 3.5 % NaCl solution.

2. Experimental

ZrN thin films were deposited on Mild steel (MS), Silicon wafer and glass using a 12” HINDHIVAC DC magnetron sputter deposition unit. The base vacuum of the chamber was below 1x10^-6 Torr at different substrate temperatures. High purity argon was fed into the vacuum chamber for the plasma generation. The deposition parameters for ZrN sputtering are summarized in Table. 1. X-ray diffraction (XRD) was used to examine the changes in preferred grain orientation. XRD patterns were recorded using an X’pert pro diffractometer using Cu Kα (1.541 Å) radiation from 40kV X-ray source running at 30 mA. The surface of the coating was characterized by molecular imaging Atomic Force Microscope. Micro hardness of the films on steel was evaluated by using a DM-400 micro hardness tester from LECO with Vickers indenters. A dwelling time of 15 s and a load of 25 g and 5 g were used for the measurement.

(i) Table.1: Deposition parameters of ZrN thin film

| Objects                          | Specification          |
|----------------------------------|------------------------|
| Target                           | Zr (99.9 %)            |
| Substrate                        | Mild steel, Glass, Si  |
| Target to substrate distance     | 60 mm                  |
| Ultimate vacuum                  | 1 x 10^-6 m bar        |
| Operating vacuum                 | 2 x 10^-3 m bar        |
| Sputtering gas (Ar: N2)           | 60:40                  |
| Power                            | 180 Watt               |
| Substrate temperature            | 200 °C                 |

Porosity of the coatings was measured using Ferroxyl test. The test solution was prepared by dissolving 10 g of potassium ferri cyanide (K₃[Fe(CN)₆]), 60 g of sodium chloride (NaCl), and 30 g of NH₄Cl in 1 litre of warm deionized water. The surface of the coatings were cleaned and degreased with acetone. A piece of filter paper was dipped into the solution (the excess solution was allowed to drain off) and then the wet paper was applied to the test area and allowed to remain undisturbed for 10 minutes. At the end of the test period the filter paper was removed and tested for pinholes if any. Wear tests were carried out in a Block-on- Ring system. All tests were carried out at room temperature, ambient humidity and without lubrication. Steel ball bearing was used as a counter body. The ring material having the diameter of 60 mm was made of High Chromium High Carbon Tool Steel with Vickers hardness 850 HV. The load applied on a specimen was 400 g (3.924 N) with the sliding speed of 100 rpm. The wear rate was calculated by measuring the weight change of a specimen before and after the test.

Electrochemical polarization studies were carried out using a BAS IM6 Electrochemical analyzer. Experiments were conducted using a standard three-electrode configuration, with a platinum foil as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode and the sample as the working electrode. The specimen (1.0 cm² exposed area) was immersed in the test solution of 3.5% NaCl. Experiments were carried out at room temperature (28 °C). In order to establish the open circuit potential (OCP), prior to measurements the sample was immersed in the solution for about 60 min. Impedance measurements were conducted using a frequency response analyzer. The spectrum was recorded in the frequency range 10mHz-100 kHz. The applied alternating potential had root mean square amplitude of 10 mV on the open circuit potential. After reaching the stable OCP, the upper and lower potential limits of linear sweep
voltametry were set at +/- 200 mV with respect to OCP and the sweep rate was 1 mV s\(^{-1}\). The Tafel plots were obtained after the electrochemical measurements.

3. Results and Discussion

3.1. Structure and Morphology

In order to understand the mechanism of structure evolution with variation of substrate temperature (Ts) X-ray diffraction analysis were carried out. Fig. 1 shows the X-ray diffraction patterns for ZrN films on mild steel prepared at the substrate temperature of 200 °C. Major diffraction peaks (111) & (222) corresponding to FCC structured ZrN are observed in the diffraction pattern, which is in good agreement with the reported literature [1].

![XRD patterns for the ZrN film deposited on Mild Steel.](image)

The comparison of d value obtained from the observed patterns and standard values from the JCPDS file no 00-002-09556, the grain size, strain dislocation density, texture coefficient were calculated and given in Table.2. The value of texture coefficient, (TC), was calculated using the equation:

\[
T_c = \frac{\frac{1}{n} \sum_{1}^{n} \frac{I_m(hkl)}{I_o(hkl)}}{1}
\]

\[\text{………………..(1)}\]
where $I_m$ $(hkl)$ is the reflected intensity from $hkl$ crystallographic planes in the textured specimen, and $I_0$ $(hkl)$ is the standard intensity, and $n$ is the total number of reflections measured. The TC value for a particular set of planes $(hkl)$ is proportional to the number of grains that are oriented with this plane parallel to the surface of the specimen.

Ex-situ atomic force microscope (AFM) has been used independently to access surface quality of the DC magnetron sputtered ZrN thin films. The AFM pictures of the ZrN thin films grown at 200 °C are shown in Fig.2 in 2D views. The top view of the 2D pictures recorded in area of 5 m x 5 m show the presence of spherical granular on the top of homogeneous granular surface. This indicates the roughness of the surface of the films.

Table 2. Structural parameters obtained for the ZrN thin film

| $d$ observed (Å) | $d$ standard (Å) | $(hkl)$ | Grain size nm | Dislocation density $\times 10^{15}$ | Strain $\times 10^{-3}$ | Texture coefficient $T_c$ |
|------------------|------------------|--------|---------------|----------------------------------|----------------------|-------------------------|
| 2.66             | 2.64             | 111    | 9.6           | 0.7                              | 3.7                  | 2.82                    |
| 2.29             | 2.29             | 200    | 21.5          | 2.1                              | 1.6                  | 0.90                    |
| 1.62             | 1.62             | 220    | 9.6           | 10.8                             | 3.7                  | 0.07                    |
| 1.38             | 1.38             | 311    | 8.7           | 13.0                             | 4.1                  | 0.17                    |

3.2 Photoluminescence, Electrical and Thermal properties:

Fig. 3 shows the emission spectra of ZrN films on Si wafer at three different substrate temperatures at 200 °C. For excitation at 390 nm, an emission peak is observed at 533 nm, which is in the visible legion, showing the good optical quality of the film. When the $T_s$ is varied, only a slight
change is observed in the emission spectra. The band value of 2.33 ev is calculated from the plot, which is in good agreement with the reported value of 2.36-2.42 ev calculated from the optical studies [25].

Electrical resistivity measurements on ZrN films deposited on glass substrates were performed using four-probe method at room temperature. A resistivity value of $15.234 \times 10^{-4}$ $\Omega \text{ cm}$ was obtained, which is in good agreement with the reported value for dual ion beam ZrN films [26].

![Emission spectra for ZrN/Si thin films deposited at 200 °C](image)

ZrN[Exc=390nm]

Fig. 3. Emission spectra for ZrN/Si thin films deposited at 200 °C

The TGA, DTA & DSC curves for ZrN hard coatings are shown in Fig.4a and b. In TGA technique, the sample is heated in an environment whose temperature is changing in a predetermined manner. From the TGA curve, we observed that upto 472.5 °C; there is no appreciable change in weight, which indicates stability of the material. Then for the variation in temperature from 479.5 °C to 868.4 °C, there is a slight gain in weight, which may be due to the oxidation of ZrN.
In DTA curve, there are two exothermic peaks observed at 553.8 °C and 718.1 °C, which may be due to the oxidation processes. Due to the evaporation, two endothermic peaks were obtained at 608.5 °C & 724.4 °C in DSC curve. The area of the peak measures the energy transfer to the material.

3.3 Mechanical and Corrosion properties:

The micro hardness values of ZrN/ MS samples were measured with an average of minimum three readings taken at 5 gm load was 1700 Hv, which is in good agreement with the value reported in the literature [27]. No pinholes were observed from the Ferroxyl test.

The wear characteristics of these films were measured using block-on-ring test. The ring material used for this test is high chromium-high carbon tool steel (850 HV). Low and smooth friction behavior typified by a steady trace at an average value of 0.4 friction coefficient was observed for ZrN on MS whereas a higher value of 0.7 was observed for the specimen. The lower friction coefficient for the ZrN on MS indicated that the stack has better wear resistance.

To analyze the surface, the material was subjected to potentiostatic polarizations, one specified potential being impressed on the material at a time. The potentials were either anodic or cathodic with respect to the primary electrochemical process occurring on the surface. The $E_{corr}$ and $I_{corr}$ values have been calculated using the Tafel extrapolation method (Fig.5) and are given in Table 3. There is an appreciable increase in corrosion resistance for the ZrN on MS substrate compared to bare MS substrate. $E_{corr}$ and $I_{corr}$ values improve (a less negative value of $E_{corr}$ and lower value of $I_{corr}$ signifies an improvement in corrosion) for ZrN on MS substrate.
The same three-electrode cell stack, as used for the potentiodynamic polarization experiments, was employed for the AC impedance investigations. Impedance measurements were made at open circuit potential (OCP) applying an AC signal 10 mV in the frequency range of 10 Hz to 1 MHz. The Nyquist plots for the samples used for corrosion tests in 3.5% w/v NaCl solution are shown in Fig. 6. The double layer capacitance $C_{dl}$ value is obtained from the frequency at which $Z$ imaginary is maximum [28].

| Sample  | $E_{corr}$ vs SCE (v) | $b_a$ (v/dec) | $b_c$ (v/dec) | $I_{corr}$ (A/cm$^2$) | $R_{ct}$ (cm$^2$) | $C_{dl}$ (F/cm$^2$) |
|---------|----------------------|--------------|--------------|-----------------------|------------------|---------------------|
| MS      | -0.841               | 0.16         | -0.14        | $1.55 \times 10^{-4}$ | 8.65             | $1.47 \times 10^{-4}$ |
| ZrN/MS  | -0.650               | 0.11         | -0.32        | $1.34 \times 10^{-3}$ | 1245             | $6.56 \times 10^{-5}$ |
At higher frequencies the interception of real axis in the Nyquist plot is ascribed to the solution resistance ($R_s$) and at the lower frequencies, the interception with the real axis is ascribed to the charge transfer resistance ($R_{ct}$). When the sample is immersed in the electrolyte, the defects in the coating provide the direct diffusion path for the corrosive media. In this process, the galvanic corrosion cells are formed and the localized corrosion dominates the corrosion process. The proposed equivalent circuit for such a system is shown in the Fig. 7. The parameters in the equivalent circuit $R_{pore}$ and $C_{coat}$ are related to the properties of the coating and the electrolyte/coating interface reactions. $R_{ct}$ and $C_{dl}$ are related to the charge-transfer reaction at the electrolyte/substrate interface. A higher $R_{ct}$ value was observed (Table 3) for the ZrN/MS substrate than the bare MS substrate which shows that ZrN on steel substrate has higher corrosion resistance.

Fig. 6. Nyquist plot obtained for (a) MS (b) ZrN/MS

Fig. 7. Equivalent circuit used for fitting the electrochemical impedance data
4. Conclusions

Zirconium Nitride films were successfully deposited by reactive DC magnetron sputtering technique on various substrates. The presence of polycrystalline with face centered cubic structure has been predicted from the x-ray diffraction phase analysis. The spherical granular morphology of ZrN hard coatings was observed from atomic force microscopy. The good optical quality of the ZrN hard coatings was confirmed from photo luminescence spectrum. Corrosion test is carried out in 3.5% NaCl solution by using potentiodynamic polarization and electrochemical impedance spectroscopy. There is a positive shift in $E_{\text{corr}}$ and decrease in $I_{\text{corr}}$ values for ZrN/Ms coating signifies that it exhibits higher corrosion resistance.

Acknowledgements:

One of the authors (B.S) thanks the Department of Atomic Energy (DAE), Board of Research in Nuclear Sciences (BRNS), Mumbai, for a research grant (SanctionNo.2006/37/37/BRNS/2068).

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