

## CHAPTER 4

# **EXPERIMENTAL TECHNIQUES**

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#### 4.1 Thin Film Deposition:

The deposition of TiN, ZrN and ZrTiN thin films on 316 stainless steel of 4cm diameter was done at Cathode arc evaporation chamber of Multi Arc (I) Ltd. Umargoan. The cathode materials were Ti(99.99%) and Zr(99.95%) The surface to be coated was finely ground. After pre cleaning as shown in the table 4.1 (a), the samples of 316 Stainless steel (S.S) were placed in 64x 40 cm cylindrical chamber with rotating substrate holder. The chamber was evacuated to a base pressure of  $5 \times 10^{-5}$  torr and the substrates were heated to about  $200^{\circ}\text{C}$  to remove adsorbed gases from the surfaces. Before deposition surface were etched with Argon plasma. High purity nitrogen gas with a maximum limit of all impurities -32 ppm. was later introduced. The target to substrate distance was maintained at 20cm. A thin intermediate layer of Ti for TiN and Zr metal was deposited between substrate and ZrN and ZrTiN. The substrate bias voltage for TiN was 600 V for about 2-3 min initial bombardment and for thin intermediate layer, it was kept at 300V, later kept at 150-450V at evaporation current of 60 amp and nitrogen pressure of 0.005-0.008Mbar. For ZrN and ZrTiN voltage used was 150-600V at evaporation current of 65 amp. and Nitrogen partial pressure of 0.005-0.008Mpa. The deposition parameters and set up is given in Table 4.1.(a) ,4.1.(b) and Fig 4.1

Table 4.1 (a) Individual steps of applied wet cleaning techniques

| Step | Time (min) | Liquid   | Enhancement | Specification |
|------|------------|--|-------------|---------------|
| (A)  | 3 min      | Metaclean(alkaline cleaner) pH 10, Temp 65-70) | Degreaser   | Ultrasonic    |
| (b)  | 3 min      | Tricholor ethylene) ( pH 10, Temp 65-70)       | „           | „             |
| (c)  | 3 min      | Raw water                                      | „           | „             |
| (d)  | 3 min      | STCV (pH 10, Temp 65-70)                       | „           | „             |
| (e)  | 3 min      | NGL galvane (pH 10, Temp 65-70)                | Surfactant  | „             |
| (f)  | 3 min      | Raw water                                      |             |               |
| (g)  | 3 min      | Superclean extra (pH 10, Temp 65-70)           | Surfactant  | „             |
| (h)  | 3 min      | Raw water                                      |             |               |
| (i)  | 3 min      | Optifin(pH 9.5)                                |             | „             |

|     |        |                            |                           |   |
|-----|--------|----------------------------|---------------------------|---|
| (j) | 3 min  | Raw water                  |                           | ” |
| (k) | 3 min  | Orthophosphoric acid(pH 2) | Remove effect of alkaline | ” |
| (l) | 3 min  | Raw water                  |                           |   |
| (m) | 3 min  | Distill water              |                           | ” |
| (n) | 3 min  | Raw water                  |                           |   |
| (o) | 2 min  | Centrifugal drier (100 C)  | Remove adhered water      |   |
| (p) | 30 min | Oven (200-240 C)           | Remove adsorbed gases.    |   |

Table 4.1(b) Process Parameters of TiN/ZrN/ZrTiN coatings by cathodic arc deposition

|                                   |                                   |
|-----------------------------------|-----------------------------------|
| Base pressure (Pa)                | $5.0 \times 10^{-5}$              |
| Target material                   | Ti,Zr (60mm in diameter,99% Pure) |
| Source to substrate distance (cm) | 17                                |
| Substrate bias voltage(-V)        | 150                               |
| Evaporator current (A)            | 60                                |
| Reactive gas                      | N <sub>2</sub>                    |
| Reactive gas pressure (Pa)        | 0.007-0.008Mbar                   |
| Deposition time (min)             | 45 min Depending on thickness     |

Line Diagram of Cathode Arc Evaporation Unit

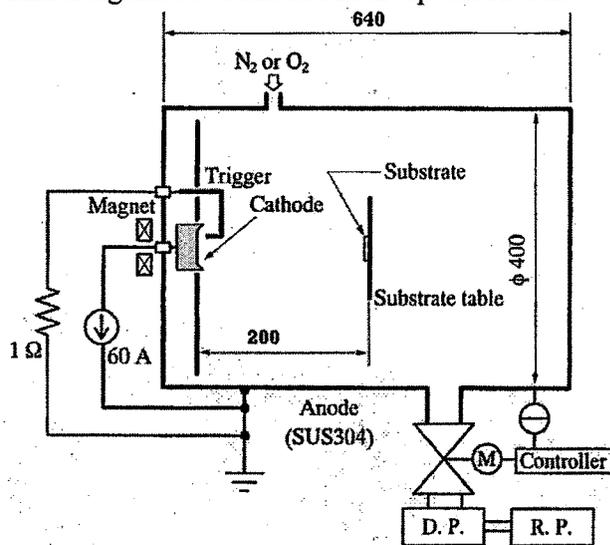


Fig 4.1. Experimental setup of reactive vacuum arc deposition apparatus.

#### 4.2 Scanning Electron Microscopy(SEM) & EDX Analysis

Morphology of deposited coating and chemical composition was determined by SEM & EDX before and after corrosion and wear testing was carried out by JOEL 5610 and Hitachi 3400. Further the composition of macroparticles embedded within the coating was analyzed using EDX analysis at a point and area. Two types of electrons are used for images Secondary electron which gives more information about surface structure and back scattered electrons which gives information about composition, topography and crystallite shape. [Scanning electron microscopy-Basic principles and applications[1]

#### 4.3 X ray Diffraction Analysis:

To effect the best mechanical and tribological properties of a PVD coating an analysis of the produced coating material is always necessary to find the optimized combination of substrate and coating system with the correct deposition parameters for effective wear protection. X-ray diffraction (XRD) is a non-destructive analysis method. Therefore it is also interesting for quality control.

The existing phases in the coatings, evaluated with powder diffraction files (JCPDS) are mainly determined by the value of the nitrogen flow during the deposition process and the thickness of film. [2]

In the present investigation the structural analysis was performed by X ray diffraction (XRD) using a PHILIPS PANalytica Xpert pro diffractometer with Cu K $\alpha$  radiation

The grain sizes of the TiN films were measured from the X-ray diffraction data using the Debye-Scherrer formula:

$$D = \frac{k\lambda}{\beta \cos \theta}$$

where  $D$  is the grain size,

$k = 0.9$  is a correction factor to account for particle shapes,

$\beta$  the full width at half maximum (FWHM) of the most intense diffraction peak,

$\lambda$  the  $k\alpha$  wavelength of Cu target = 1.5406 Å, and  $\theta$  is the Bragg angle. [3]

#### 4.4 Corrosion Testing

##### (a) Potentiodynamic test

Electrochemical corrosion measurements were performed with conventional three electrode cell. A computer assisted potentiostat (EG&G PAR 273A and Gamry potentiostat( reference 600))was employed to apply and scan the potential and display data resulting current density Vs potential curve. Data were analyzed using model M273 and M398 software (fig 4.2). The corrosion coupons of 4cm diameter were masked with lacquer on surface but 10mmx10mm window was left on coated surface. A saturated calomel electrode (SCE) was used as the reference electrode (RE) to measure the potential across the electrochemical interface. A high-purity graphite rod was used as the counter electrode. The sample was placed in such a way that the Luggin capillary of the reference electrode was close to the working electrode and this distance was maintained for all the tests. The polarization curves were measured after 1 hr of stabilization at the corrosion potential so that a quasi-stable potential was reached. The curves were obtained by sweeping the potential from the direction of the cathode to the anode. The sweep-rate setting was 0.2 mV/sec. The electrolyte used was various industrial environment like 1N H<sub>2</sub>SO<sub>4</sub> (commonly used industrial environment), 3.5% NaCl (marine environment), 0.1N HCl(reducing acid and used in chemical conversion reactions) and 11pH Na<sub>2</sub>SO<sub>4</sub> (paper and pulp industry). All tests were carried at surface open to air. The test was in accordance to Potentiodynamic (ASTM G59) practice. The plot of E vs. log I was obtained and was super imposed for various thicknesses in particular environment.



Fig 4.2 Set up for corrosion and impedance test.

**(b)Electrochemical Impedance Spectroscopy(EIS) (ASTM G610)**

Quantitative evaluation of the kinetic parameters of the corrosion mechanism is very difficult using the potentiodynamic polarization technique alone. Electrochemical impedance spectroscopy (EIS) is a well established technique to characterize passive films in situ. [5]EIS is particularly well suited to determine changes in the passive film properties, such as thickness or defect density, that result from changes in an applied voltage or solution composition. [6]

EIS can provide detailed information of the electrochemical reaction that takes place at the electrode/electrolyte interface. This technique is sensitive to the resistive and the capacitive nature of the electrochemical interface and is very useful for studying the localized corrosion behavior through micro-pores. As a small amplitude sinusoidal signal is used throughout the EIS measurements, this technique does not significantly accelerate the corrosion reactions and, therefore, the coating surface is not affected too much and can be considered as a non-destructive method. In the present investigation the EIS data are plotted in terms of Bode Plot (Freq/Impedance/Phase angle)/ (Frequency/Impedance) The testing was in accordance with A.C Impedance (ASTM G106) Test. [4-7]

**(c)Porosity Measurement**

Pinhole defect evaluation was done in terms of the critical passivation current density  $i_{crit}$  determined from the anodic polarization measurement. The defect area ratio %Pi may be expressed as

$$P_i(\%) = \left[ 1 - \left( \frac{i_{corr}}{i_{corr}^0} \right) \right] \times 100$$

Where  $i_{corr}$  refers to current density of coated sample and

$i_{corr}^0$  refers to uncoated substrate

The results obtained are presented in the table which gives idea about % coverage.[8-10]

#### 4.5 Wear Testing

The 'Pin on Disc' configuration was employed as the wear test rig. During testing, the pin specimen was kept stationary while the circular disc was rotated. The specimens were tested under dry (unlubricated) conditions at room temperature on pin-on-disc sliding machine (Model TR-20, DUCOM-Bangalore). The machine had an arrangement of continuous variation of speed and load and provision of measuring the friction force. The apparatus consisted of SAE 52100 steel (Rc 55) disc of diameter 60 mm used as counter face. The test sample was clamped in a holder and held against the rotating steel disc. The surface roughness of the counter face was maintained by polishing with 400 grit polishing paper. A fresh surface of specimen was used each time and before each test. Both the disc and the specimens were cleaned with acetone to remove any possible traces of grease and other surface contaminants. Every time new track radius was used so that the pin was exposed to fresh surface of counter face. Load of 4Kg, rotating speed of 200rpm and time was 20 minutes.

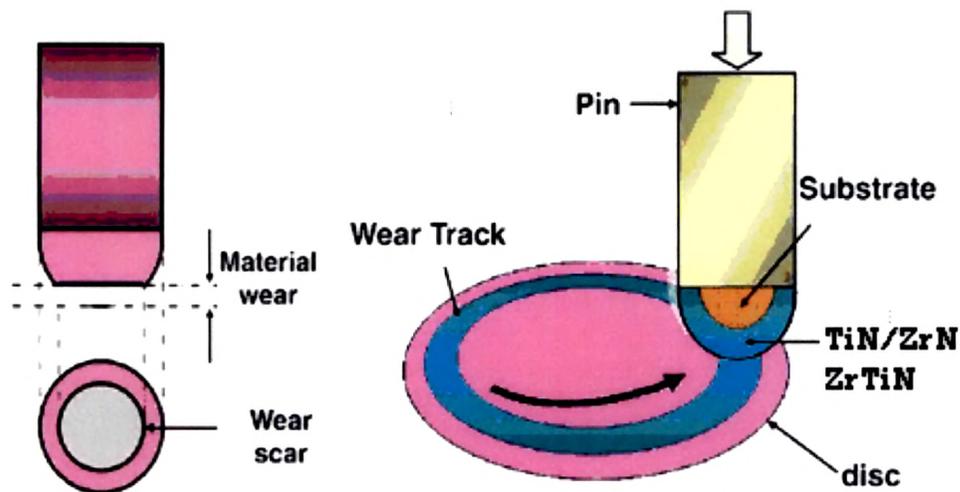


Fig 4.3 Apparatus for wear testing

The following information can be obtained from pin-on-disc experiments:

- Friction coefficient: the last average value and the evolution during one test can be deduced from the value of the tangential force recorded continuously;
- Wear: measurements of the width of the track using scanning electron microscopy (SEM) give valuable information on the wear processes [ 11]

The results are obtained in terms of friction coefficient data as a function of time. All coatings that did not fail showed similar 'pull' and 'push' friction coefficients, whilst coating failure always resulted in an increase in friction coefficient with increasing number of cycles and a marked difference in recorded pull and push friction.[12] Further effect of wear was studied and understood using SEM and EDX analysis at different magnification. The compositional analysis in terms of line analysis, point analysis and area analysis was carried out.

Similar configuration was used by [13-15] as reported in literature.

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