

Corrosion analysis of copper -TiO₂ nanocomposite coatings on steel using sputtering

G.R.Raghav^{1*}, N.Selvakumar², K.Jeyasubramanian³ M.R.Thansekhar⁴

^{1*}Department of Mechanical Engineering, KLN College of Engineering, Madurai, Tamilnadu, India

²Centre for Nano Science and Technology, Department of Mechanical Engineering, Mepco Schlenk Engineering College, Sivakasi.Tamilnadu,India

³Centre for Nano Science and Technology, Department of Mechanical Engineering, Mepco Schlenk Engineering College, Sivakasi, Tamilnadu, India

⁴Department of Mechanical Engineering, KLN College of Engineering, Madurai, Tamilnadu, India

ABSTRACT— The corrosion resistant coatings used conventionally are susceptible to degradation, leading to pitting corrosion. This report summarizes the corrosion resistant nature of thin films of Cu-TiO₂ coated on mild steel, in different corrosion environments. Nano meter thick (100nm, 125nm, 150nm) composite coatings were coated on steel substrate by RF magnetron sputtering technique. The required targets used in sputtering were fabricated indigenously by compacting a mixture of 20% and 25% of TiO₂ nano powder with copper metal powder in a universal testing machine. The thin films of Cu-TiO₂ nano composite coatings obtained by sputtering were characterized using XRD, AFM and SEM. The corrosion resistance of nano composite coatings in different media was analyzed using weight loss and electrochemical methods. Electrochemical polarization results revealed the shifting of corrosion potential of mild steel ($E_{\text{corr}} = -0.413V$ vs. Ag/AgCl) to more positive side when coated with Cu-TiO₂ (-0.377V). Electrochemical impedance spectroscopy analysis results also confirmed 150 nm coated steel has higher resistance values (475Ω) than uncoated steel. The results of the weight loss method also substantiate increase in corrosion resistance of copper based nano composite coatings.

KEYWORDS— Corrosion resistant coating, Sputtering, Tafel plot, Nyquist diagram, Cu-TiO₂

1. INTRODUCTION

Corrosion is one of the inevitable, universally important problems in the worldwide market and growing to an estimated \$900 million by 2015 in the industrial sectors. It is well known that most of the components

undergo corrosion because of the surface initiated defects such as wear, corrosion, fatigue or fracture [1].

There are many techniques that had been already employed to produce protective coatings, such as, plasma spraying, dip coating, electroplating and physical vapour deposition methods [1-4]. Nowadays, nano materials have many applications due to their versatile characteristics. These characteristics are further improved by means of obtaining uniform dispersion of nano coatings using various techniques [5].

Sputtering process is a well-established surface modifying process that involves deposition of a variety of materials either metal or ceramic or combination of both of any in nanometric level over various substrates [6-9]. Although a variety of materials were coated, the coating of Cu-TiO₂ using sputtering process has received wide spread attention as it provides high corrosion resistance and increases the hardness due to homogeneity. The sputter coated Cu- TiO₂ coatings are widely used for corrosion protection in a variety of environments. It is a barrier coating, protecting the substrate by sealing it off from the corrosive environments, rather than by sacrificial action [10-12].

Saeed Reza Allahkaram et al [5] studied the properties of Al₂O₃ nano particle reinforced copper matrix composite coatings using pulse and direct current deposition and found that the use of Al₂O₃ improved the anti-corrosion property. Recent developments involved in the increase of the corrosion resistance includes the use of Cu-composites reinforced with TiO₂, SiO₂, Al₂O₃ and other ceramic materials in nanometric size [13-15]. Copper coated steel shows better corrosion resistance when compared to bare steel. Since the Cu has a lower corrosion potential than steel, the copper coated steel plate

is widely used for a variety of applications [5]. TiO₂ is an excellent anticorrosion material since of its excellent corrosion resistance, thermal stability and less conductivity because of very less free electrons with them. Recently the applications of the TiO₂ coatings for corrosion protection of metals have been studied especially because they can prevent migration of electrolytes such as NaCl to the coated films and high chemical stability [1-3]. They reported that Cu-composite coatings with a low concentration of ceramic reinforcements are able to provide big improvements in corrosion resistance on steel.

This report deals with the preparation of Cu-TiO₂ nano composites coatings using sputtering process on mild steel and evaluating their corrosion resistance using polarization resistance test, electrochemical impedance studies and weight loss method.

II. EXPERIMENTAL PROCEDURE

2.1 Materials

The copper and TiO₂ powders employed were of research grade with a purity level of 99.5% and 99% respectively and were used without further purification.

2.2 Preparation of pellets and substrates

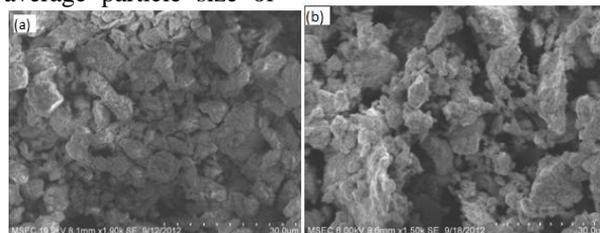
The micron sized TiO₂ powders were reduced to nano size by employing high energy ball milling technique (HEBM). About 40g of TiO₂ powder was fed into the ball mill (Fritsch pulverisette, Germany) comprising of balls and vial made of tungsten carbide (WC). The weight of the balls to that of powder was maintained at a ratio of 20:1. The grinding process was carried out for 5h at a speed of 300rpm to obtain the nano TiO₂ powder. The dwell period was 5 minutes for every 15 minutes of milling to avoid heat / unwanted reactions inside the vial. Then, the micron sized copper and nano TiO₂ powders were intimately mixed by grinding in the ball mill for 30 minutes in the weight based ratios of 80:20 and 75:25 respectively to arrive Cu-20TiO₂ and Cu-25TiO₂ nano composites. The nanocomposites were then compacted into a 2" diameter circular pellet of 3mm thickness by applying a pressure of 8 MPa in a universal testing machine and then sintered to about 850°C and cured at room temperature to obtain a target preform.

The mild steel substrate to be used was cut into proper dimension (75mm x 25mm), so as to properly fit it into the substrate holder of the sputtering machine. The surface of the mild steel was polished and smoothed with emery sheets of various fineness followed by cleaning with acetone. The respective prepared composite pellets were then placed in the sputtering machine (Hind Hivac, Bengaluru) as targets and the mild steel substrates were coated using RF sputtering in argon atmosphere.

2.3 Characterization

The Cu-TiO₂ composite powders used for making preforms (Cu-20TiO₂ and Cu-25TiO₂) were subjected to X-Ray Diffraction analysis. The XRD patterns were obtained at ambient temperature by step scanning on an X-ray powder diffractometer (Xpert-Pro) using a monochromatic CuK α radiation ($\lambda = 1.54056 \text{ \AA}$) in the range of $2\theta = 0^\circ - 90^\circ$ with a step size of 0.05° . The surface topography of the coatings was acquired using

Atomic force microscopy (XE70, Park System, South Korea) operating in non-contact mode, in air at ambient conditions, using a Si₃N₄ tip with a radius of curvature of less than 10 nm and a spring constant of about 40 N/m, at a scan size of $10 \times 10 \mu\text{m}$. The surface morphology of the composites and coatings were characterized using SEM (Hitachi SUI510, Japan operating in secondary electron mode, at an accelerating voltage of 10 kV, emission current of $96 \mu\text{A}$). SEM images of powder mixture used for making the targets after milling process is shown in the Fig.1 (a&b). These images are recorded at an acceleration voltage of 10 kV in secondary electron mode. From the figure, it is clear that the particles are irregular in shape and appeared like an agglomerated state. The average particle size of



the composites is found in the range of 3-5 μm .

Fig.1 SEM image of mixed powder sample (a) Cu-20TiO₂ (b) Cu-25TiO₂

2.4 Potentiometric polarization test

Potentiodynamic polarization measurements were carried out in an electrochemical workstation (CHI 660C, USA) consisting of platinum wire counter electrode, Ag/AgCl reference electrode and the cermet coated steel substrates taken in turn as working electrode. All the electrochemical tests were performed at 25°C with 5% NaCl solution as electrolyte. Polarization phenomena of the steel and the coated steel structures were studied at a scan rate of 5mV/s. Before starting measurements; all the specimens were immersed in the 5% NaCl solution for 1h to reach steady state condition. The open circuit potential (OCP) was measured after reaching a steady state and then the polarization measurements were done. The corrosion potential (E_{corr}) and corrosion current density (i_{corr}) were calculated from the intersection of the cathodic and anodic Tafel curves using the Tafel extrapolation method. The polarization resistance (R_p) was determined using Stren–Geary equation [1].

$$R_p = \frac{\beta_a \beta_c}{2.303 i_{\text{corr}} (\beta_a + \beta_c)} \quad (1)$$

where β_a and β_c are the anodic and cathodic Tafel slopes. The corrosion rate (r_{corr} in millimeter per year) was calculated through the following equation.

$$r_{\text{corr}} = \frac{0.00327 (i_{\text{corr}} M)}{nd} \quad (2)$$

where M, n, and d are molar mass, electronic charge number, and density of tested metal respectively.

2.5 Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) measurements of the coated samples were performed between the frequency range of 10 mHz and 100 kHz using CH660C electrochemical workstation at the room temperature. The amplitude of the initial sinusoidal voltage signal was 10 mV. The measurements were done against open circuit potential. The equivalent circuit was used to determine the results by fitting using software available in the workstation and the Nyquist plot is obtained [1, 7].

2.6 Weight loss method

The weight loss method is used to find the rate at which the material is getting depleted in different corrosive media. For this, three corrosive media namely 0.1N solutions of HCl and H₂SO₄; 10% NaCl solution were taken and the substrates were immersed in each one of the said corrosive media respectively for 24 h. After that the substrate was removed, washed with distilled water and dried at room temperature. The change in weight of the substrates was measured, from which the percentage of material loss is calculated.

III. RESULTS AND DISCUSSION

3.1 XRD analysis

The structural features of Cu-20TiO₂ and Cu-25TiO₂ is studied from XRD data. XRD of Cu-20TiO₂ and Cu-25TiO₂ nano composites are shown in Fig.2 (a&b). The XRD patterns reveal well developed reflections of Cu-TiO₂ nanocomposites (JCPDS.No.81-1611). Strong Bragg reflections were seen in the XRD which correspond to the reflection of Cu-TiO₂ composite. The XRD patterns of the samples exhibit the characteristic peak at $2\theta=43.3^\circ$, which corresponds to the (111) plane of Cu. They also exhibit peaks at $2\theta=50.38^\circ$, $2\theta=73.99^\circ$ are indexed as planes (200), (220). The small peaks at $2\theta=24.932^\circ$ appears in both the XRD patterns correspond to the (110) plane of TiO₂ and thus confirm the presence of TiO₂ in the Cu-20TiO₂ and Cu-25TiO₂ samples [1, 5]. It is confirmed that, the intensity of TiO₂ (110) is different for both samples. The intensity variation of the peaks of TiO₂ (110) is due to the weight ratio difference of TiO₂ in the nano composite samples.

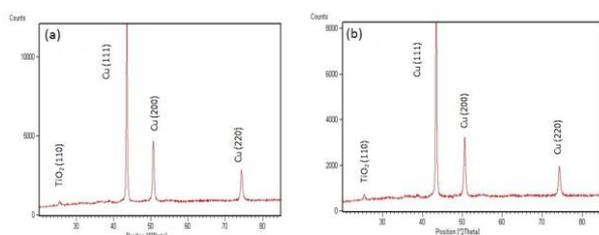


Fig.2 XRD pattern of mixed powder sample (a) Cu-20TiO₂ (b) Cu-25TiO₂

3.2 SEM analysis

Surface morphology of Cu-20TiO₂ and Cu-25TiO₂ films obtained after RF sputtering were examined using SEM analysis. Fig.3 (a&b) is the respective images of Cu-

25TiO₂ nanocomposites coatings recorded in the secondary electron mode. From the figure it is clear that, the mild steel substrate has been covered with the nano structured Cu-TiO₂ particles. The particle size found over the specimen were approximately in the range of about 100-150 nm. Fig.3 (b) shows good dispersion throughout the cross section when compared to Fig. 3(a) of 125nm coating thickness.

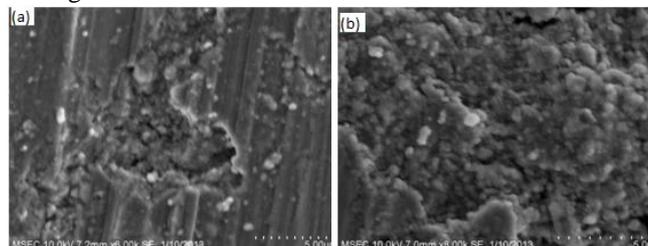


Fig.3 SEM image of Cu-25TiO₂ nano composite coatings of thickness (a) 125nm (b) 150nm

3.3 AFM analysis

AFM is a tool used to evaluate the surface topography of the sputter coated steels. Fig.4 is the 3D AFM images of the Cu-25TiO₂ nano composite coating. The shape and thickness of the coatings can be found from the AFM images. The image reveals that the thickness of the coating lies in the range of 100 - 150 nm. Fig.5 (a) is the 2D AFM image of Cu-25TiO₂ coating in which a line is drawn vertically at a point around 7.5 μm . Figs. 5 (b) and 5(c) are the corresponding line diagram and histogram got with regard to the afore said vertical line. In the line diagram in Fig.5 (b) the line lying on 100nm shows that the coating is evenly distributed around 100nm thickness. Similarly Fig. 5(c) reveals that the coating thickness is around 0 - 200nm.

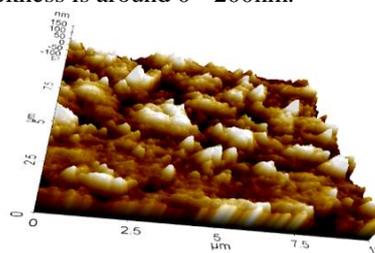


Fig.4 AFM image of Cu-25TiO₂ nano composite coating of thickness 150nm

3.4 Polarization resistance test

Generally, the corrosion resistance coatings developed using sputtering are inert to chemical attacks due to their higher position in the electrochemical series. However, these coatings exhibit galvanic and crevice corrosion between the coatings and the metal substrate because of the presence of defects such as micropores and the potential difference between coatings and the metal substrate. The electrolyte penetrates inside the substrate through these defects present between the coating and metal interface. If there is less porosity, then the sample behaves like the good coating. Moreover, if there is more porosity in the coatings, then the galvanic corrosion occurs, in which the steel substrate acts as anode and the coating material as the cathode, hence the corrosion current is a good measure of the coating porosity [1].

The corrosion behaviour of Cu-TiO₂ nano composite coatings on mild steel substrates were

investigated using potentiometric polarization in 5% NaCl solution at room temperature. Tafel plots obtained for mild steel substrate coated with Cu-20TiO₂ and Cu-25TiO₂ nano composite are shown in Fig.6 (a&b). The corrosion potential (E_{corr}), the corrosion current density (I_{corr}) and polarization resistance (R_p) obtained from the measurements are given in (Table I).

coating thickness. The E_{corr} value has been shifted to more positive side from -0.413V to -0.385V with increase in thickness, which shows the increase in corrosion resistance. Similarly the i_{corr} value decreases from 7.731 (A) to 7.656 (A) which indicates the increase in corrosion resistance; the polarization resistance (R_p) increases from 2005 Ω to 2396 Ω which is also an evidence of increase in corrosion resistance for the increase of coating thickness. The Cu-25TiO₂ nano composites coatings exhibits good corrosion resistance for the increased coating thickness, since the E_{corr} value of steel has been shifted from -0.413V to -0.377V and i_{corr} value has been reduced from 7.731 (A) to 7.359 (A) which shows the increase in corrosion resistance. Further, the polarization resistance (R_p) increases from 2005 Ω to 2818 Ω . By using the electrochemical data, the corrosion rates (r_{corr}) of various coatings are evaluated and tabulated in Table II.

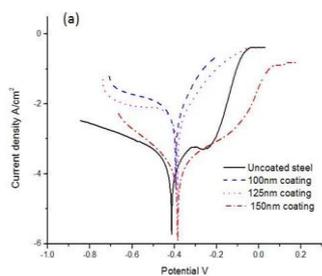
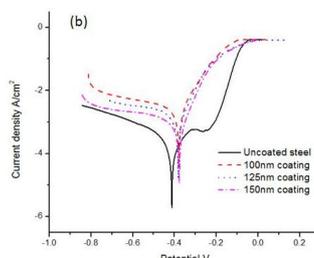


Fig.6 Tafel polarization curves for nano composite coatings (a) Cu-20TiO₂ (b) Cu-25TiO₂



From the data, it is clear that the corrosion potential (E_{corr}) of uncoated mild steel (-0.413V vs. Ag/AgCl) is shifted towards positive side while the surface of steel has been coated with the composite films of Cu-20TiO₂ (150nm: -0.385V) and Cu-25TiO₂ (150nm: -0.377V). While comparing the E_{corr} values of these two coatings Cu-25TiO₂ coated steel shows more positive E_{corr} values than those of Cu-20TiO₂ coated steel. The open circuit potential values do not change sensibly before and after the testing. It is evident that with increasing of TiO₂ nanoparticle content in coating decreases the corrosion current and the corrosion potential shifts to a more positive potential.

Table II Corrosion rate (mpy) for Cu-20TiO₂ and Cu-25TiO₂ nano composite coatings

| Coating thickness | Corrosion rate (mpy) | |
|-------------------|-----------------------|-----------------------|
| | Cu-20TiO ₂ | Cu-25TiO ₂ |
| Uncoated steel | 4.45 | 4.45 |
| 100nm | 4.21 | 4.19 |
| 125nm | 4.03 | 3.97 |
| 150nm | 3.13 | 3.12 |

Table I Corrosion characteristics obtained from potentiodynamic polarization measurements

| Thickness of coating | E_{corr} (V) | | Polarization resistance, R_p (Ω) | | I_{corr} (A) | |
|----------------------|-----------------------|-----------------------|---|-----------------------|-----------------------|-----------------------|
| | Cu-20TiO ₂ | Cu-25TiO ₂ | Cu-20TiO ₂ | Cu-25TiO ₂ | Cu-20TiO ₂ | Cu-25TiO ₂ |
| Uncoated | -0.413 | -0.413 | 2005 | 2005 | 7.731 | 7.731 |
| 100nm | -0.396 | -0.383 | 2094 | 2392 | 7.701 | 7.650 |
| 125nm | -0.394 | -0.380 | 2138 | 2726 | 7.674 | 7.646 |
| 150nm | -0.385 | -0.377 | 2396 | 2818 | 7.656 | 7.359 |

From the data, it is clear that the corrosion rate decreases from 4.45 to 3.12 mpy for Cu-25TiO₂ when compared to 3.13 mpy for Cu-20TiO₂ nano composite coatings. By having these outputs, comparatively the Cu-25TiO₂ nano composites coating shows more corrosion resistance when compared to Cu-20TiO₂ [1, 6].

3.5 Electrochemical impedance spectroscopy

The Nyquist diagrams for the Cu-TiO₂ nano composites obtained using electro chemical impedance spectroscopy (EIS) in 5%NaCl solution is shown in Fig.7 (a&b). The Nyquist diagram was obtained by fitting the experimental data to the proposed equivalent circuit model. The capacitive loop between R_{ct} and C_{dl} can be recognized to the charge transfer reaction. R_{ct} is the charge transfer resistance which is a measure of electron transfer across the coating surface and R_{ct} is inversely proportional to rate of corrosion. The proposed equivalent circuit to obtain Nyquist diagram is shown in the Fig.8. The equivalent circuit consists of solution resistance (R_s), double layer capacitance (C_{dl}) and charge transfer resistance (R_{ct}), in which the C_{dl} and R_{ct} are parallel to each other has been used to simulate the coated steel/solution interface. The Charge transfer resistances in 5% NaCl solution is listed in Table III.

The data further clearly reveals that the improvement in anti corrosive properties is due to the presence of TiO₂ nanoparticles in the composite coatings. It shows that the TiO₂ nanoparticles in Cu matrix increase the corrosion resistance in NaCl, HCl and H₂SO₄ solutions. Obviously, the TiO₂ nanoparticles have more positive potential than the copper and steel, hence the presence of TiO₂ in the Cu matrix improves the corrosion resistance [1]. The Cu-20TiO₂ nano composites coating shows increase in corrosion resistance with an increase in

Table III Charge transfer resistance obtained from EIS

| Thickness of coating | Charge transfer resistance (R _{ct}) Ω | | Double layer capacitance (C _{dl}) F | |
|----------------------|---|-----------------------|---|-----------------------|
| | Cu-20TiO ₂ | Cu-25TiO ₂ | Cu-20TiO ₂ | Cu-25TiO ₂ |
| 50nm | 75 | 80 | 0.0303 | 0.0296 |
| 100nm | 115 | 125 | 0.00380 | 0.00357 |
| 125nm | 220 | 240 | 0.00362 | 0.00292 |
| 150nm | 465 | 475 | 0.00215 | 0.00175 |

data fitting by equivalent circuit model

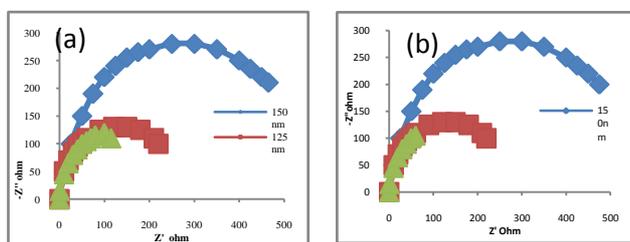


Fig.7 Nyquist impedance diagrams for nano composites coating in 5% NaCl solution (a) Cu-20TiO₂ (b) Cu-25TiO₂

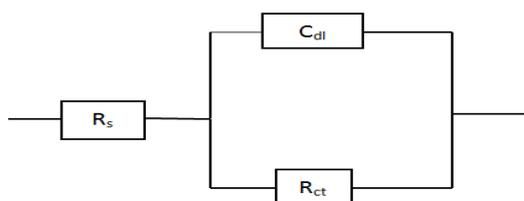


Fig.8 The Equivalent circuit model

R_{ct} increases with increasing of TiO₂ nanoparticle content in coating and also increases with an increase of coating thickness. The Nyquist plots of the entire coatings exhibit a single semicircle and they differ in their size based on the coating thickness. The experiments were carried out in the frequency range of 10 kHz to 0.01 Hz [6-7]. The charge transfer resistance (R_{ct}) values of different coatings of varying thickness shows increase in corrosion resistance irrespective of the percentage of TiO₂ present in the composite. Also in comparison with the two different types of composite, Cu-25TiO₂ possesses higher (R_{ct}) values than the Cu-20TiO₂ composite film. From the above data (Table 3), it is clear that Cu-25TiO₂ nano composite coatings shows better corrosion resistance than the other one. The double layer capacitance (C_{dl})

decreases with an increase in coating thickness also shows the increase in corrosion resistance [5, 14]. The occurrence of a single semicircle in the Nyquist plots indicates that the corrosion process of sputtered Cu-TiO₂ coatings involves a single time constant. Hence it is evident that the sputter coated Cu-TiO₂ nano composite coatings in 5% NaCl solution interface exhibit charge transfer mechanism. The results of electrochemical impedance studies also indicate a similar trend in the anti-corrosive nature of composite coating.

3.6 Weight loss method

The weight loss method is used to analyze the extent of corrosion of uncoated steel and the coated structures in acidic and in brine solutions. In this method the coated substrate is immersed in the acid environments such as HCl, H₂SO₄ and NaCl solutions. The substrate is immersed by keeping the substrate in 0.1N HCl /0.1NH₂SO₄/10%NaCl solutions for 24 hours. Then the substrate was washed and dried at room temperature. The weights of the substrates are measured before and after the immersion, the difference in weight shows the amount of weight loss for particular substrate. The percentage of weight loss was calculated using the following equation.

$$\text{Percentage of weight loss} = \frac{W_i - W_f}{W_i} \times 100 \tag{3}$$

where, W_i = Initial weight, g ; W_f = Final weight, g
Quantity of material lost in different corrosion environment is given in Table IV.

Table IV Weight loss data of Cu-TiO₂ coated steel in different media

| Coating Thickness | % of Weight loss | | | | | |
|-------------------|-------------------------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| | 0.1N H ₂ SO ₄ | | 0.1N HCl | | 10%NaCl | |
| | Cu-20TiO ₂ | Cu-25TiO ₂ | Cu-20TiO ₂ | Cu-25TiO ₂ | Cu-20TiO ₂ | Cu-25TiO ₂ |
| Uncoated | 6.90 | 6.90 | 0.37 | 0.37 | 0.12 | 0.12 |
| 100nm | 2.82 | 2.12 | 0.34 | 0.31 | 0.09 | 0.07 |
| 125nm | 2.27 | 1.75 | 0.22 | 0.21 | 0.06 | 0.04 |
| 150nm | 1.70 | 1.60 | 0.18 | 0.15 | 0.02 | 0.01 |

From the data, it is clear that the weight loss occurred in 150nm coatings is less in comparison with the uncoated substrate irrespective of corrosive media. The amount of TiO₂ content present in the composite film also influencing the rate of corrosion to some extent.

IV . CONCLUSIONS

Cu-TiO₂ nano composite coating on steel was prepared by sputtering process. The corrosion resistance nature of Cu-TiO₂ nano composite coating is studied in different corrosive media. The conclusions derived from the experimentation are as below:

- With increasing of TiO₂ nano particle content in the composite coatings, the corrosion current (I_{corr}) decreases to the much lesser values and the corrosion potential (E_{corr}) shifts to more positive values than the uncoated steel. The potentiometric polarization test reveals that the Cu-25TiO₂ has

higher corrosion resistance. The EIS spectra show that the corrosion rate was controlled by charge transfer resistance. R_{ct} increases with increasing of TiO₂ nano particle content in coating which is an indication of anti-corrosive behaviour.

- The weight loss method shows that the Cu-25TiO₂ nano composite coating provides better corrosion resistance than the Cu-20TiO₂ coatings.
- From this study it is concluded that the Cu-25TiO₂ nano composite coatings shows better corrosion resistance, than Cu-20TiO₂ nanocomposite coatings in steel.

ACKNOWLEDGEMENTS

The authors would like to thank the Management and Principal of Mepco Schlenk Engineering College for their constant encouragement, support and providing all the essential facilities for completing this research work.

REFERENCES

- [1]. P.Bagheri, M. Farzam, A.B. Mousavi, M. Hosseini; 'Ni- TiO₂ nano composite coating with high resistance to corrosion and wear' Surf. Coat. Technol. 2010, 204, 3804 – 3810.
- [2]. Tong Liu, Feifei Zhang, Chaorui Xue, Lan Li, Yansheng Yin; 'Structure stability and corrosion resistance of nano- TiO₂ coatings on aluminium in seawater by a vacuum dip –coating method' Surf. Coat. Technol. 2010, 205, 2335–2339.
- [3]. F.Vargas, H. Ageorges, P. Fournier, P. Fauchais, M.E. López; 'Mechanical and Tribological performance of Al₂O₃ –TiO₂ composite coatings by flame and plasma spraying process' Surf. Coat. Technol. 2010, 205, 2340 –2341.
- [4]. W.X. Zang, Z.H. Jiang, G.Y. Li, Q. Jiang, J.S. Lian; 'Electroless Ni- Sn- P coating on AZ91D magnesium alloy and its corrosion resistance' Surf. Coat. Technol. 2008, 202, 2570 – 2576.
- [5]. Saeed Reza Allahkaram, Setareh Golroh, Morteza Mohammadalipour; 'Properties of Al₂O₃ nano particle reinforced copper matrix composite coatings prepared by pulse and direct current electroplating' Mater.Des. 2011, 32, 4478- 4484.
- [6]. T.S.N. Sankaranarayan, I. Baskaran, K. Krishnaveni, S. Parthiban; 'Deposition of electroless Ni- P graded coatings and evaluation of their corrosion resistance' Surf. Coat. Technol. 2006, 200, 3438–3445.
- [7]. Harish. C, Barshilia, B.Deepthi, A.S.Arun Prabhu, K.S.Rajam; 'Super hard nano composite coatings of TiN/Si₃N₄ prepared by reactive direct current unbalanced magnetron sputtering' Surf. Coat. Technol. 2006, 201, 329 – 337.
- [8]. E. Galvanetto, F. Borgioli, F.P. Galliano, T. Bacci; 'Improvement and corrosion resistance of RPS Ti –TiN coatings by means of thermal oxidation' Surf. Coat. Technol. 2004, 200, 3650 –3655.
- [9]. Fengqun Lang, Zhiming Yu; 'The corrosion resistance and wear resistance of thick TiN coatings deposited by arc ion plating' Surf. Coat. Technol. 2001, 145, 80–87.
- [10]. L.Guzman, M. Adami, W. Gissler, S. Klose, S. De Rossi; 'Vapour deposited Zn – Cr Alloy coatings for enhanced manufacturing and corrosion resistance of steel sheets' Surf. Coat. Technol. 2000, 125, 218 –222.
- [11]. H.A.Jehn; 'Improvement of the corrosion resistance of PVD hard coating– substrate systems' Surf. Coat. Technol. 2000, 125, 212–217.
- [12]. Hu Guoxin, Xu Zhengxia, Liu Jianju, Li Yanhong; 'Microstructure and corrosion resistance of simultaneous Al–Fe coating on copper by pack cementation' Surf. Coat. Technol. 2009, 203, 3392–3397.
- [13]. D. Nickel, G. Alisch, H. Podlesak, M. Hockauf, G. Fritsche, T. Lampke; 'Microstructure, corrosion and wear behaviour of UFG-powder-metallurgical Al-Cu alloys, Al-Cu/Al₂O₃(p) and Al-Cu/SiC(p) composites' Rev.Adv.Mater.sci. 2010, 25, 261–269.
- [14]. . Zambalau, S. Varvara, C. Bulea, L. M. Muresan; 'Corrosion Behavior of Composite Coatings Obtained by electrolytic codeposition of copper with Al₂O₃ nanoparticles' Biochem. Eng. Q. 2009, 23, 43–52.
- [15]. R. A. Antunes, M. C. L. de Oliveira, M. F. Pillis; 'Effect of the Deposition Temperature on the Corrosion Stability of TiO₂ Films Prepared by Metal Organic Chemical Vapour Deposition' Int. J. Electrochem. Sci. 2013, 8, 1487 – 1500.