



PREPARATION AND CHARACTERIZATION OF Cu-ZrO₂ NANOCOMPOSITE BY DC METHOD

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ABSTRACT

Cu-ZrO₂ nanocomposite coatings prepared by electrodeposition method. In bath solution containing different amount of ZrO₂ were studied. The structure, surface morphology, mechanical and corrosion resistance properties of nanocomposite are characterized by varies techniques. Cu-ZrO₂ composite coatings have higher micro hardness, compared to pure copper coating. Surface morphology of both Cu and Cu-ZrO₂ composite coatings were examined through Scanning electron microscopy. The results show that more number of zirconia particles incorporated into copper matrix and then smooth surface, finer grain sized. The incorporation of ZrO₂ particles reduces the particle size. It shows the closer particle-particle contact leads to pore free deposition. The X-ray diffraction was conformed the crystallite size and structure of the electrodeposited Cu and Cu-ZrO₂ composite coatings. The average crystallite size calculated from Scherrer equation was ~105 nm for copper and ~67 nm for Cu-ZrO₂ composites. The structure of electrodeposited Cu and Cu-ZrO₂ composite coatings were crystalline orthorhombic which was confirmed from the JCPDS standard. The corrosion resistance behavior of Cu-ZrO₂ composite is examined through Tafel polarization and impedance measurement studies in 3.5% NaCl. The result shows that the Cu-ZrO₂ composite coatings have more corrosion resistance than pure Cu coating.

Keywords: Electrodeposition, Nanocomposite, Impedance measurement, SEM and Microhardness

1. INTRODUCTION

Composite electroplating is a method of co-depositing insoluble particles of metallic or non-metallic compounds with metals or alloys in a plating bath, to enhance the material coatings properties such as corrosion resistance, lubrication, hardness or wear-resistance. The coatings thus obtained feature the properties of both metal and dispersed particles and can be considered metal-matrix composites (MMC) [1]. Al_2O_3 , TiO_2 , ZrO_2 , SiO_2 , SiC and TiC etc. are the important second phase particles used for the co-deposition and copper, nickel, chromium are commonly used as matrix for the coating. [1,2] Fengyan hou et al reported the effect of the dispersibility of ZrO_2 nanoparticles in Ni- ZrO_2 electroplated nanocomposite coatings on the mechanical properties of nanocomposite coatings [3]. The hardness of all the Ni- ZrO_2 nanocomposite coatings were two-three times higher than that of pure nickel coatings. Wei wang et al reported the fabrication and characterization of Ni- ZrO_2 composite nanocoatings by pulse electrodeposition [4]. Benea et al reported the corrosion study of copper composite coating by impedance spectroscopy method [5-7]. Cu- ZrO_2 composite showed three

times higher corrosion resistance than the copper deposit in sulphuric acid medium. They also reported that the electrodeposition of zirconia particles in a copper matrix. Reza Arghavanian et al describe a microstructure and corrosion resistance of Ni- ZrO_2 composite coatings have been investigated. Lidia Benea described the effect of ZrO_2 dispersed particle co-deposition on nickel electrocrystallisation steps as well as the corrosion behaviour of the composite coatings obtained. This system was selected because nickel is an industrially important coating material on steel and other support materials [1]. ZrO_2 reveals excellent properties such as; high strength, high hardness, excellent chemical resistance, high fracture toughness, and excellent wear resistance. In this study corrosion performance of ZrO_2 -epoxy nanocomposite prepared by up to down approach, on mild steel in 3.5% NaCl solution was studied [8]. Newly ZrO_2/Ni composite coating with different contents of ZrO_2 particles were deposited on super alloy K17 substrate using high speed jet electroplating process [9]. F.Hou et al., studied the polyelectrolyte dispersant containing aromatic rings (PEDA) is used to disperse nanoparticles ZrO_2 in to a Ni- ZrO_2 plating bath and Ni-

ZrO₂ nanocomposite containing mono dispersed ZrO₂ nano particles was prepared from the composite plating bath with monodispersed nanoparticles [10]. W.Wang et al. discuss DC, PC and PRC were used to electrodeposit pure nickel coating and Ni-ZrO₂ composite coatings has been investigated [11]. Direct current (DC) deposition techniques will be employed to deposit Cu-ZrO₂ composite coatings on steel from copper sulphate bath containing CTAB. Plating bath variables like current density, composition like ZrO₂ concentration, pH, temperature would be optimized. The electrocomposites would characterized for their surface morphology, crystalline structure, physicochemical and corrosion resistant properties.

2.Experimental Details

Cold rolled steel plates were degreased with acetone and cathodically electro cleaned in alkaline solution for 2 min and anodically for 30 s in a solution containing a mixture of 35 g/L NaOH and 25 g/L Na₂CO₃ at 30 °C. They were washed in running water and dipped in 5% H₂SO₄ solutions for 10 s. In this chapter, preparation and characterization of Cu-ZrO₂ composite coating by Direct current (DC) method

described in detail, In addition to that, the mechanical properties and corrosion resistance behaviour of Cu-ZrO₂ composite coatings are also studied. Copper specimens were used as base material for the deposition of Cu-ZrO₂ composites. The size of copper specimens 4.5×3.5×0.2 cm cathode was used. The anode used was a copper bar of high purity. All the chemicals used to carry out the experiments were of AnalaR grade. Toshniwal Rectifier Unit (Universal Instruments, Bangalore, India) was used as a current source for all deposition studies. A hot plate with magnetic stirrer was used to keep the uniform dispersion of particles in the plating bath. The chemicals used for the preparation of plating bath are:

Chemicals	Composition	Parameters
Copper sulphate	75 g/l	Current
Conc.	4 ml/l	Density: 7
Sulphuric acid	1 g/l	A/cm ²
CTAB	8 g/l	pH: 2-3
ZrO ₂		Temperature :
		Room
		temperature
		Plating Time
		: 60 min

3. RESULTS AND DISCUSSION

The electrodeposition of inert particles from nickel, copper and other baths have already been well established. The present investigation is on the co-deposition of Zirconia particles with copper and the evaluation of some of their functional properties.

3.1 Structural analysis by XRD measurements

Crystallite size and structure of the electrodeposited Cu and Cu-ZrO₂ composite coatings were determined by X-ray diffraction analysis (Fig. 3.1). Its corresponding XRD data was given in Table 3.1. The average crystallite size calculated from XRD pattern using Scherrer equation and it was ~65 nm for Cu and ~45 nm for Cu-ZrO₂ composite coatings. The structure of electrodeposited Cu and Cu-ZrO₂ composite coating was crystalline cubic and orthorhombic which was confirmed from the JCPDS standard. But, some noticeable differences in the intensity of (111), (200), and (220) peaks were observed for Cu-ZrO₂ composite coatings compared with electrodeposited copper.

Table 3.1
XRD parameters for electrodeposited Cu and Cu-ZrO₂ composite coatings

Material	Miler Indices (hkl)	Average Crystal Size
Electrodeposited Pure copper	(111) (200) (220)	~ 65 nm
Cu-ZrO ₂ composite coating	(111) (200) (220)	~ 45 nm

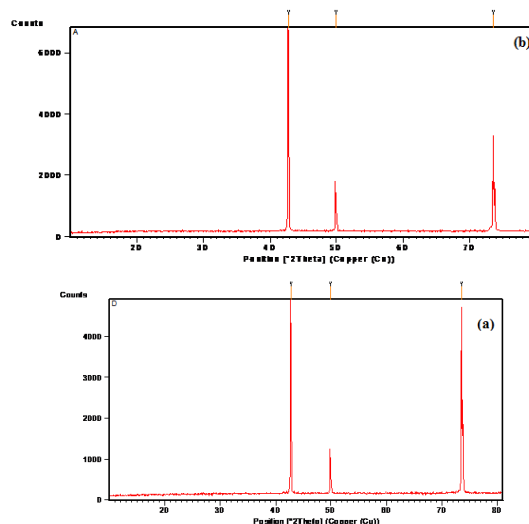


Fig. 3.1 XRD patterns of electrodeposited for (a) Pure Cu and (b) Cu-ZrO₂ composite coatings Using Direct Current

3.2 Surface morphology studies

Scanning electron microscopic (SEM) pictures of the electrodeposited copper and Cu-ZrO₂ composite coatings is shown as Fig. 3.2. Both the coatings were electrodeposited at a current density of 7 A/dm². Cu-ZrO₂ nanocomposite coatings carried out with 8 g/l of ZrO₂ in plating bath. The electrodeposited pure copper showed a regular surface and fine crystallites (Fig. 3.2a) and the ZrO₂ particles are clearly visible on the surface with homogenous distribution in (Fig. 3.2b). The Fig.3.21 a & 3.21 b shows that the EDX spectrum of pure Cu and Cu-ZrO₂ composite coatings. This clearly shows that ZrO₂ were deposited on thin layer of copper. The EDX analysis revealed spectra not only with Zirconium but also with copper

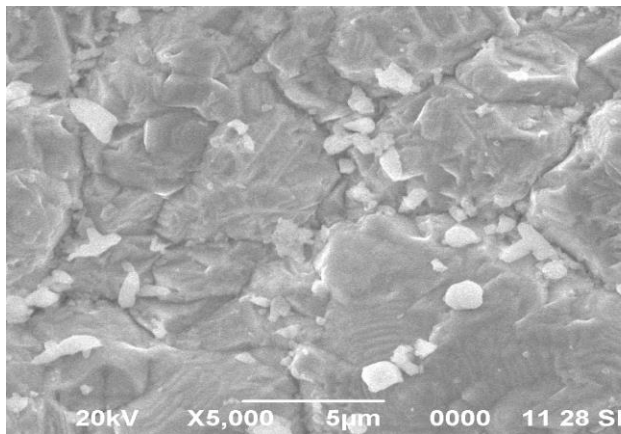
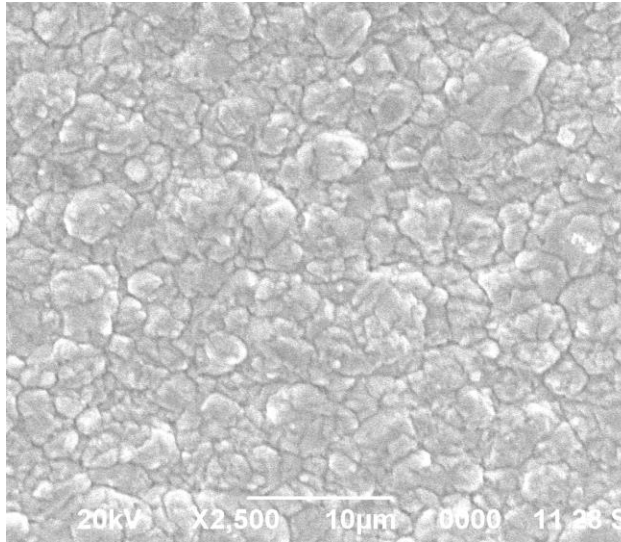


Fig. 3.2 SEM image of the electrodeposited (a) Cu and (b) Cu-ZrO₂ composite coatings

3.3 Micro hardness

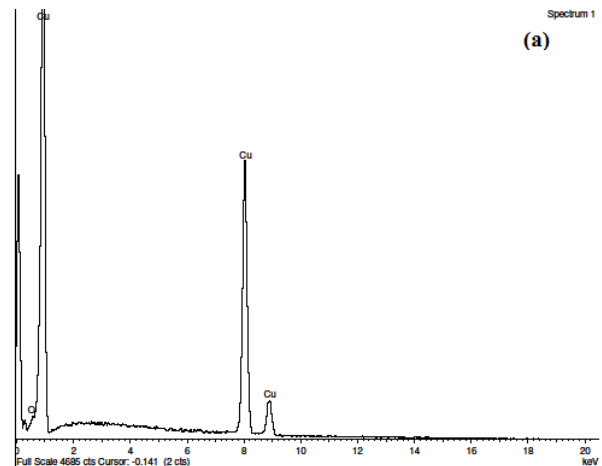
The microhardness, VHN₅₀ of pure copper and Cu-ZrO₂ nanocomposite coatings of thickness 12µm were noted. In case of Cu-ZrO₂ nanocomposite coating, the hardness is found to increase than nickel coating (Table 3.3).

Table 3.3 Micro hardness of Ni and Ni – ZrO₂ nanocomposite coatings using Direct Current

S.No.	System	Vickers Hardness (Load = 50g)
1	Pure Cu coating	225
2	Cu-ZrO ₂ nanocomposite coating	575

3.4.1 Potentiodynamic polarization studies

The polarization behaviours of the pure Cu and Cu-ZrO₂ composite coatings concentration of ZrO₂ particles present 8 g/l in 3.5% NaCl solution are shown as Fig.3.3 and their corresponding corrosion kinetic parameters are given in Table. The linear segments of the polarization curves were extrapolated to OCP to obtain the I_{corr}, and E_{corr} are given as Table- 3.3. It can be seen from the figure that the corrosion current of Cu-ZrO₂ composite is significantly decreased compared to the pure Cu coating.



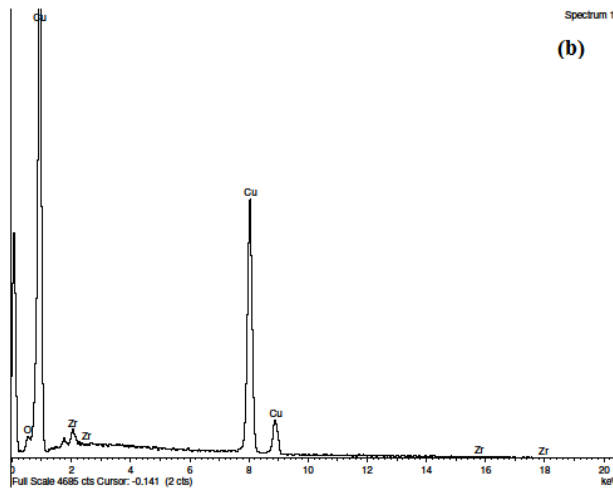


Fig 3.21 EDX spectrum of (a) Copper (b) Cu-ZrO₂ composite using DC

3.4 Corrosion Resistance Characteristics

3.4.2 Impedance measurement

The results of impedance measurements for Cu-ZrO₂ composite coatings concentration of ZrO₂ particles present 8 g/l in 3.5% NaCl solution are shown as Fig.3.4 and their corresponding R_{ct}, and C_{dl} values are given as Table 3.4. It can be seen from the table that the C_{dl} value decreased and the R_{ct} value is increased considerably for Cu-ZrO₂ composite coating compared to the pure Cu coating, confirming the non-porous nature of the deposit. In the case of Cu, the Nyquist plot

is semicircle in nature confirming the charge transfer control of the corrosion process. But in the case of Cu-ZrO₂ composite coating, there is a rising portion at the low frequency end of the Nyquist plot suggesting that incorporation of the partial are mass under transfer control.

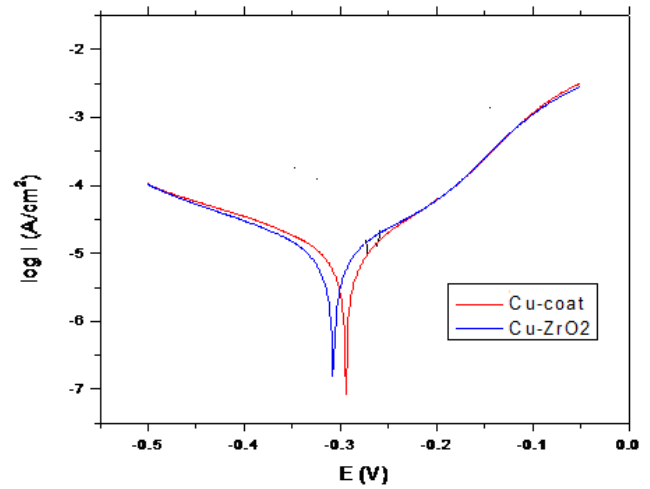


Fig.3.3 Potentiodynamic polarization curves for (a) Pure Cu and (b) Cu-ZrO₂ composite coatings in 3.5% NaCl solution

Table 3.3 Polarization parameters of Cu and Cu-ZrO₂ composite coatings in 3.5% NaCl solution

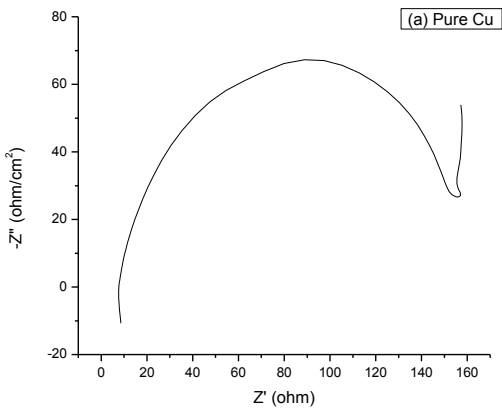


Fig. 3.4 Nyquist plots for (a) Cu and (b) Cu-ZrO₂ composite coatings in 3.5% NaCl solution

Table – 3.4 Impedance parameters of Cu and Cu-ZrO₂ composite coatings in 3.5% NaCl solution

System	Charge transfer resistance (R _t) (ohms)	Double layer capacitance (C _{dl}) (μF)
Pure Cu coating	162	120.75
Cu-ZrO ₂ composite coating	320	48.50

4. CONCLUSION

Cu-ZrO₂ composite coatings were prepared by DC method at 60 min. All the Cu-ZrO₂ composite coatings have higher micro hardness, compared to pure copper coating. The improved hardness is due to the reduction in the crystalline imperfection. Surface morphology of both Cu and Cu-ZrO₂ composite coatings were examined through Scanning electron microscopy. The result show that more number of zirconia

System	E _{corr} (mV vs SCE)	i _{corr} (mA/cm ²)
Pure Cu coating	-0.295	68.25
Cu-ZrO ₂	-0.315	29.03

particles incorporated into copper matrix and then smooth surface, finer grain sized. The incorporation of ZrO₂ particles reduces the particle size. It shows the closer particle-particle contact leads to pore free deposition. The X-ray diffraction is conformed the crystallite size and structure of the electrodeposited Cu and Cu-ZrO₂ composite coatings. The average crystallite size calculated from Scherrer equation was ~65 nm for copper and ~45 nm for Cu-ZrO₂ composites. The structure of electrodeposited Cu and Cu-ZrO₂ composite coatings were crystalline orthorhombic which was confirmed from the JCPDS standard. And also electrodeposited Cu-ZrO₂ composite have a smaller crystalline size than Cu.

The corrosion resistance behavior of Cu-ZrO₂ composite is examined through polarization and impedance measurement studies in 3.5% NaCl. The result shows that the Cu-ZrO₂ composite coatings have more corrosion resistance than pure Cu coating. It can be seen that, the micro hardness and corrosion resistance of Cu-ZrO₂ composite coatings are improved by the DC method.

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