**PRODUCTION OF Zn-Ti ALLOY ELECTRODEPOSITION FOR BIOMEDICAL APPLICATIONS**

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**Abstract:** Acidic sulphate bath having ZnSO4, TiSO4 and sulphamic acid, was optimized for the deposition of bright Zn-Ti coating on mild steel. Bath constituents and operating parameters were optimized by trial-and-error method, for highest performance of the deposit against corrosion. The effect of current density, on deposit characters, such as corrosion rate, thickness, and hardness were discussed. Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) methods were used to evaluate the corrosion properties of the deposit. The composition of deposits was determined by energy dispersive x-ray (EDX) analysis. Surface topography of the deposited film was analyzed by scanning electron microscopy (SEM). Surface roughness was measured by atomic force microscopy (AFM). A new and low-priced sulphate bath, for bright Zn-Ti coatings on mild steel has been proposed, and the results indicate better corrosion resistance properties, and these coatings can be used for biomedical applications.

Keyword: Zn-Ti coating, corrosion, electrodeposition, roughness, SEM,

**Introduction**

Pure zinc coatings are commonly used to protect steel from corrosion; significant attempts are being produced to enhance its corrosion resistance for use in harsher environments [1]. Due to its favorable corrosion resistance, steel is currently used in multiple applications. However, steel is susceptible to corrosion in warm dilute sulfuric acid in certain sectors, such as the synthetic fiber sector, waste heat recovery, and alternative energies (i.e., proton exchange membrane (PEM) fuel cells and water electrolysis hydrogen manufacturing) and biomedical applications. Because steel passivation is not stable, corrosion strength reduces in acidic media [2].

Alloy materials have multiple characteristics such as hardness, resistance to high temperature oxidation, great wear, and resistance to corrosion. The new alloy materials are synthesized by various current techniques because of their significance in many areas. Among these methods, electrodeposition is regarded one of the most significant alloy production techniques due to accurately monitored operation to room temperature, fast deposition rates, and low cost. Several literatures appear in science publications related to Zn-Ni, Zn-Co, Zn-Fe and Zn-Ni-Co alloy electrodeposition [3-8]. XRD and SEM-EDAX techniques researched the structure, morphology and chemical structure of the Zn-Ni coatings, and electrochemical measurements assessed the corrosion resistance [9]. According to Brenner [10], anomalous electrodeposition of Zn-Ni alloys happens (reduction of less noble zinc is preferential), either owing to hydroxide suppression mechanism (release of more noble ions is impeded by the formation of Zn (OH)2 to normal pH increase). In latest years, Zn-Ni alloys have drawn considerable attention due to their greater corrosion resistance and better mechanical properties than pure Zn and other alloy coatings for steel parts based on Zn [11]. For industrial applications, however, demand for Zn-Ni coatings with better mechanical and corrosion characteristics is growing. Recently Zn-Ni composite coatings have been developed to meet industry requirements to improve mechanical and chemical properties [12].

Titanium may lower the cost of destruction, conserve energy, prevent product contamination, and combat corrosion [13]. The first to conduct an exhaustive examination into the electroplating of alloys and related procedures was Kremann [14]. Materials' physical characteristics, wear resistance, corrosion behaviour, and high-temperature stability of substrates can all be improved through surface modification and specialised treatment for a variety of industrial applications [15-17]. Numerous qualities, including biocompatibility, shape memory, improved wear resistance, and strong corrosion resistance, are present in Ni-Ti coatings. Numerous industries, including biotechnology, electronics, aerospace, automotive, etc., use these alloy coating films [18–22]. Many techniques, including spraying [23], laser ablation [24], magnetron sputtering [25], powder metallurgy [26], and electrodeposition techniques [27–29], have been used to create Ni-Ti alloy films. Among these methods, electroplating is particularly significant since it may be used to create a variety of coatings at room temperature, at a cheap cost, and with a high deposition rate. In the present work, to develop an Zn-Ti alloy coatings on mild steel by electrolytic technique and, their corrosion resistances, microstructure of the deposit and mechanical properties have been discussed and used for biomedical applications.

**Experimental method**:

Mild steel substrate was purchased from High-tech corporation, Mangalore. The basic compositions of mild steel are 0.063-C, 0.23-Mn, 0.03-S0.011-P and balance-Fe. The MS specimen was taken in the form of a 5.0 cm×2.0 cm exposed surface areas as a cathode. According to metallographic practice, the specimen was subjected to belt grinding, polishing using different grades of emery and velvet mops to obtain final finish. Then the specimen was cleaned with trichloroethylene followed by distilled water, finally dried, and immediately used for electrodeposition [30].

The electrolyte was prepared by using reagent grade chemicals and distilled water. The bath compositions were optimized by trial-and-error method. All coatings at 30oC and pH of 4.0 were performed, except during their deviation. Plating baths were adjusted to pH 4.0 with dilute solutions of H2SO4 and NaOH whenever necessary. The cleaned MS substrate had exposed area of 10 cm2 was used as a cathode and Zn plate was used as an anode of same area. A 200 ml rectangular poly vinyl chloride cell with a cathode anode distance of ~4 cm has been used. All depositions were galvanostatically performed under the same temperature and pH for 10 minutes (for assessment) using direct current (DC) power analyzer. Sulphamic acid has been used as complexing agent for the deposition. Based on the surface morphology of the deposit, bath compositions and deposit conditions were optimized.

Potentiostat (CH604 E-series, U.S. model with CH instrument beta software) was used to perform electrochemical test results in 5% NaCl solution. The standard arrangement of three-electrode cells was used. The working electrode (WE) was a coated MS with 1 cm2 exposed area. The counter electrode was a platinum foil with a surface area much greater than that of the WE. The reference electrode was a saturated calomel electrode (SCE). The corrosion activities of the deposit were studied by PP method and EIS method. PP measurements were done by polarizing the specimen from −200mV cathodically to +200mV anodically with respect to OCP with a scan rate of 0.1mVs−1 and the potentiodynamic current – potential plots were recorded. Corrosion data such as corrosion potential (*E*corr), corrosion current density (*I*corr), were obtained from the software installed in the CH instrument. The EIS measurements were carried at open circuit potential (OCP) in the frequency range of 100 KHz to 10 MHz and Nyquist plot were analyzed.

Haring–Blum cell was used to determine the throwing power of the plating bath and is given by the relation. Figure 2 shows a schematic of the Haring Blum cell used in this research [31].

Where A is the distance ratio from the anode of far and near cathodes, and B is the mass ratio of deposits on near and far cathodes. Vickers technique was used to determine the microhardness of coated films (~20μm) at a load force of 500 g for 20 sec, at room temperature. For each sample, 10 measurements were taken. The thicknesses of the coatings were determined from Faraday’s equation:

Where x is the thickness of the coating film, E is the equivalent weight, Ic is the coating film current density, A is a current efficiency, Δt is a time period of the deposit, and d is the density coating film and F is Faraday’s constant (96,500 Coulombs). Surface morphology of Zn-Ti coating at optimum current density was carried out by using analytical scanning electron microscope (JEOL JSM-6380L), in the magnification of 1000X. The composition of the Wt.%Ti was analyzed by EDX. The reflectivity of the deposit was measured using gloss meter (Nova-Elite, 600, ASTM D2457).

**Result and Discussion:**

**Optimization of bath:**

Acid bath with ZnSO4, NiSO4 has been optimized using trial and error method. The addition of small quantities (1 g / L) of sulphamic acid has been found to have a significant impact on the deposit properties. As a buffer, citric acid (CA) was used to prevent the formation of hydroxide. Trisodium acetate has been used as a conducting agent to improve the homogeneity of the deposit.

**Table 1.** Working conditions and composition of the bath

|  |  |
| --- | --- |
| **Bath Constituents** | **Amount (g/L)** |
| ZnSO4 | 100 |
| TiSO4 | 25 |
| C6H8O7.H2O | 5.0 |
| CH3COONa.3H2O | 50 |
| H3NSO3 | 1 |

The effect of each component on the appearance, brightness and morphology of the coatings was examined in terms of their impact. Table 1 shows the bath composition and working parameters after optimization.

**Effect of Current density**

Wt. % Ti in the deposit

From optimized baths, wt.% Ti was determined with the effect of ACDs. The wt.% of Ti was determined by EDX. It was revealed that ACD plays a significant role in both surface appearance and corrosion performance of the deposit. The change in the appearance and corresponding wt. % Zn and wt.% Ti over a broad spectrum of 1.0-5.0 A/dm2 is given in Table 2. The bath produced white deposit with ~ 0.13 wt.% Ti at low ACD (1 A/dm2) and a porous bright deposit at high ACD (5 A/dm2) with ~ 1.80 wt.% Ti. A smooth deposit was found at 3.0 A/dm2 with ~ 1.70 wt.% Ti.Increase in Ti content with current density is attributed to the rapid depletion of more readily depositable Zn2+ ions at the cathode coating [32].

**Hardness, Thickness, Glossiness, throwing power of deposit:**

Hardness, thickness, glossiness, of the Zn-Ti alloy coating was found to increase with current density as shown in Table 2. This may be ascribed by the high density of Zn, compared to Ti (dZn= 7.14 g cm–3, and Ti= 4.506g cm-3). The hardness of the alloy coating with increase in ACD as shown in Fig. 1. The practical current density was found to show direct dependency on thickness of deposit as given in Table 2. The observed linear dependency of the thickness of the coating film with applied current density (ACD) may be due to the adsorbed metal hydroxide at the cathode, caused by the stable increase of pH due to hydrogen evolution at the cathode. The glossiness of Zn-Ti coatings at different current densities were tested and it was found that the deposit formed at low current density showed least glossiness, and at the optimum current density, the glossiness was found maximum. At higher current density, glossiness decreased at higher ACD, due to increased porosity [33].

**Table 2.** Effect of ACD on hardness, TP, thickness, glossiness, and corrosion rate

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| ACD  (A/dm2) | TP  (%) | x  (µm) | VH500 | Glossiness | ‒Ecorr  (V) | Icorr  (μA/cm2) |
| 1.0 | 15 | 07.9 | 123 | 105 | 0.710 | 31.22 |
| 2.0 | 23 | 09.1 | 137 | 121 | 0.629 | 26.21 |
| 3.0 | 28 | 16.3 | 145 | 138 | 0.604 | 15.29 |
| 4.0 | 25 | 18.6 | 151 | 146 | 0.649 | 24.91 |
| 5.0 | 20 | 21.8 | 155 | 159 | 0.617 | 28.87 |



**Fig. 1.** Hardness of Zn-Ti coating film at various ACD

Throwing power of the optimized bath at low current density, 1A/ dm2 was found to be very small 15%. Throwing power was found to be good at 3A/dm2 (28 %). Further increase in current density 5 A/ dm2, reduces throwing power to 25% at 5A/ dm2. The throwing power of Zn-Ti alloy coating at different ACDs as shown in Fig. 2. The glossiness of Zn-Ti alloy coatings at different ACDs was tested and it was found that the deposit shows a minimum glossiness at low ACD, but the glossiness was found to be maximum at the optimum ACD (3 A/dm2). The glossiness was decreased at high ACD (5 A/dm2) due to increased porosity [34].



**Fig. 2.** Throwing power of Zn-Ti alloy coating at different ACDs

**Corrosion Study:**

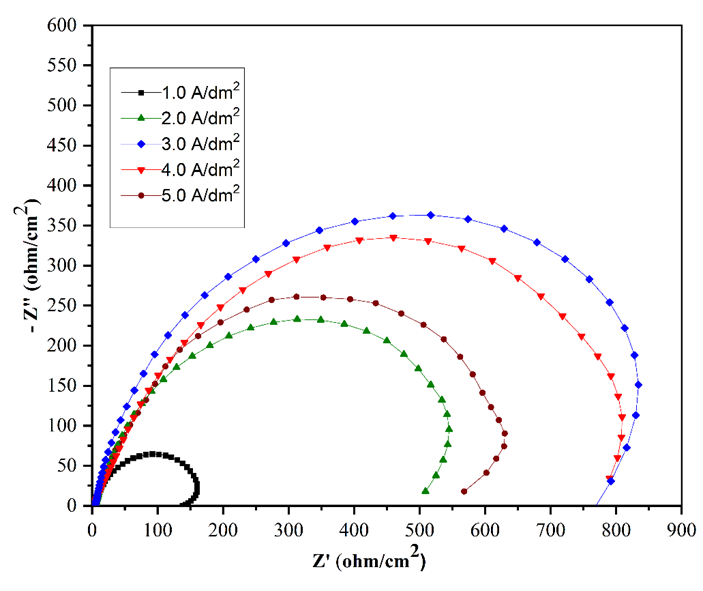
Zn-Ti coated samples were subjected to corrosion study in 3.5% NaCl solution and experimental data are given in Table 2. The corrosion rate of the alloy coatings was determined by potentiodynamic polarization method. Polarization studies have been made at a scan rate of 0.1 mVs-1 in a potential ramp of +0.200V cathodic and -0.200V anodic from open circuit potential (OCP). The calculated Ecorr, andicorr at different current densities are shown in Table 2. The observed results showed that, the coating at 3.0 A/dm2 shows least corrosion current density icor = 16.360 µA/dm2. Potentiodynamic polarization curves for Zn-Ti alloy coating at various ACD as shown in Fig. 3. This is further supported by its dense, smooth, and uniform surface topography of the coating (Fig. 5b). Further at higher ACD, increase in Ti content, however, led to an increase in corrosion rate, i.e., due to its thick porous structure of the coating.



**Fig. 3.** Potentidynamic Polarization curves of Zn-Ti alloy coating at different ACD

**EIS analysis:**

A corrosion measurement technique called electrochemical impedance spectroscopy (EIS) examines the features and dynamics of the electrochemical process at the electrode/solution interface in corrosive solutions. The form of a semicircle is matched by the polarization resistance in Nyquist plots [35, 36]. The electrochemical impedance spectroscopy (EIS) is carried out to identify the electrocatalytic influences on the zinc-Ti alloy coating. The EIS of Zn-Ti alloy coating at different ACD as shown in Fig. 4. It was observed that the radius of the semicircle increases with ACD and decease in semicircle at higher ACD. At low ACD, smaller the semicircle as observed, this may be due thin Zn-Ti coating (Fig. 4). At higher ACD, decrease in the radius of the semicircle, this may be due to the porosity of the alloy coating, but at optimum ACD radius of the semicircle increases, this may be due to the uniform Zn-Ti alloy coating onto the MS substrate.



**Fig. 4.** EIS of Zn-Ti alloy coating at different ACD

**Surface analysis:**

The surface structure of the deposit at different ACD can be observed from the SEM analysis. Fig. 5(a-c) shows the surface topography of Zn-Ti alloy coating at three different ACDs. At low ACD, (1 A/dm2) the deposit was very thin, light grey, semi bright as shown in Fig. 5(a). At high ACD, (5 A/dm2) the deposit was thick, porous bright, and large grain size as shown in Fig. 5(c) and at optimum ACD, (3 A/dm2) the deposit was bright, uniform, and smooth as shown in Fig 5(b). The wt. % Zn and wt.%Ti at optimum CD = 3A/dm2 was determined by EDX analysis (Fig. 6) and the coated sample confirms the presence of Zn (95.99%), Ti (1.70%), and O (2.31%) elements.

The mean roughness Ra was calculated using Atomic Force Microscope (AFM, Nanosurf Flex AFM, and Switzerland) based on AFM images (AFM). Fig. 7 shows the 3D image of Zn-Ti alloy coating at optimized (3A/dm2) ACD and average roughness (Ra) value is 33.1nm. Thus, it can be decided that the Zn-Ti alloy film was less coarse and smooth, homogeneous, and showed small peaks of regular grain size, resulting in higher corrosion resistance (3A/dm2) and has a lower roughness value as shown in Fig. 7.

**Fig. 5(a-c)** surface morphology of Zn-Ti alloy coating at three different ACD



**Fig. 6.** EDX analysis of Zn-Ti alloy film at optimized ACD



**Fig. 7.** AFM image of Zn-Ti alloy coating (3 A/dm2)

**Conclusion:**

To produce highly corrosion-resistant Ni-Ti alloy coatings, the process parameters have been optimized. The optimum ACD (3 A/dm2), the corrosion current density was 15.29 µm/cm2 and shows highest corrosion resistance. The potentiodynamic polarization and EIS measurements show that Ni and Ti play a key role in the deposit by reducing the rate of corrosion. The quantity of Ni and Ti in the coatings directly relates to both the hardness and thickness of the deposits. SEM and AFM examination verified the surface topography and roughness of Zn-Ti coatings, elucidating the reasons for the enhanced corrosion resistance of the coatings. Therefore, it is abundantly clear that Ni-Ti alloy coatings may have potential uses in the aerospace and biomedical industries.

**Conflict of Interest**: The author declares that no conflict of interest.

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