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Influence on Transitional Rare Earth Metal Composite on the Ternary Based Sulphate Rich Coatings

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Abstract

Pure zinc coatings have been widely reported for surface modification on metallic materials for industrial applications. However their major setbacks are their average anticorrosive properties and instability at high-temperature applications. In this study, an attempt was made to incorporate MoO_2 into sulphate bath to produce a ternary $Zn-Ni-MoO_2$ coating at varied voltage. The microstructural characteristics of these produced series composite coatings were investigated using scanning electron microscope coupled with energy dispersive spectroscopy (SEM-EDS). The corrosion degradation properties in 3.5% NaCl medium were studied using potentiodynamic polarization technique and characterized with Optical Microscope. The average micro-hardness and thermal properties were determined with diamond based Vickers hardness tester and isothermal furnace at 350 ˚C respectively. The study revealed that the obtained coating provided enhanced thermal stability characteristics, improved morphology and corrosion resistance.

Keywords: Thermo-mechanical properties; structural modification; Corrosion

1. Introduction

The virtually exceptional properties of mild steel such as world wide availability at affordable cost and good mechanical properties has rendered mild steel a candidate of most engineering structural, as well as domestic applications [1,2]. These types of steel are also eminent for their good tensile strength and ease of fabrication [3]. However, the efficacy and durability of mild steel is questionable as a result of mechanical deterioration, formation of oxide products and susceptibility to damage by heat [4].

In order to protect the substrate of the alloy from the failing conditions, different coatings [5] such as organic

coatings, electrochemical plating, conversion coatings, hydride coatings, anodizing, gas-phase deposition processes, laser surface alloying, DC plating and pulse plating have been developed. Electroplating is one of the most cost effective and simplest processes for the formation of uniform metallic coatings with good corrosion resistance, electrical conductivity and solderability.

Different binary and ternary sacrificial coatings of iron group metals such as Zn, Fe, Co, Ni have been considered to replace cadmium coatings in the aerospace and automotive applications since they were posing environmental impact. [6]. Zn-Ni coating alloys possessing sufficient corrosion resistance and improved mechanical properties are the foremost ecological candidates [7]. Zn-Ni alloys co-deposition is considered to be of anomalous plating type in which the electrochemically less noble zinc metal deposits preferentially on the cathode with respect to the more noble metal; nickel [8]. Alloying with Zn-Ni brings the cell potential of the coating closer to that of the mild steel substrate (E° =0.42V), thus potentially increasing the durability of the coating [9].

The corrosion resistance of coatings fundamentally depends on the organic additives and the type of bath. The incorporation content and the uniform dispersion of nanoparticles in coatings are the important determinants of high performance [11]. The ability to achieve the objectives of electrodeposition depends upon the solution chemistry and the operating parameters [10]. Ternary coatings have been found to exhibit enhanced corrosion resistance and surface properties compared to the binary Zn–Ni and Zn– Fe alloys [8]. This is due to the addition of third enhancing nano-particle such as molybdate since it was reported as a promising compound for corrosion protection of metals and alloys for use on composite coatings and for decoration purposes [12]. When used as coating additive, it provides enhanced ductility on the surface.

In this study, the influence of the incorporation of MoO_2 in ternary Zn-Ni sulphate electrolyte on the properties and microstructures of the produced coatings was investigated. The produced coatings went through post-plating treatment and was analysed for the micro-hardness change; in addition morphological characterization were done using SEM-EDS and Optical microscopic studies.

2. Experimental Procedure

2.1 Substrate Preparation and formation of deposited coating

Commercially sourced mild steel specimen of (40 mm × 20 mm × 2 mm) sheet was used as the cathode substrate for the study. The substrate was prepared by mechanical polishing of the surface using successive grades of emery papers. These were pre-treated in 3.5% NaCl solution prior to deposition and rinsed in distilled water. The anode was 99. 99 % pure zinc of (60 mm × 40 mm × 10 mm) dimension. The Zn-Ni Sulphate Electrolyte consisting of 150 g/L $ZnSO_4$, 60 g\L $NiSO_4$, 20 g\L NH_3SO_4, 10 g\L $NaSO_4$, 10 g\L H_3BO_3, and 10 g\L $C_2H_5NO_2$, was formulated and left overnight for concentrated amalgamation of the MoO_2 powder particulate. Deposition took place for 20 minutes at room temperature and while stirring at 250 rpm to prevent agglomeration of the electrolyte. Table 1 shows the deposition parameters used for the experiments. After electro-deposition, the coatings were rinsed in de-ionised water and then sun-dried.

Table 1: Electro-deposition parameters

Sample order	Matrix	% Weight MoO_2	Time of deposition (min)	Voltage
As-Received	-	0	-	-
1	Zn-Ni-10MoO$_2$	10	20	0.5
2	Zn-Ni-10MoO$_2$	10	20	1.0
3	Zn-Ni-15MoO$_2$	15	20	0.5
4	Zn-Ni-15MoO$_2$	15	20	1.0

2.2 Post-plating treatment

The coated artefacts were heat-treated in a CWF General Purpose Chamber Furnace model E84-J4 at 350 ˚ C for a period of 2 hours.

2.3 Electrochemical studies

µAUTOLAB Potentiostat/Galvanostat corrosion analysing equipment was used to study the electrochemical behaviour of the resulting coatings. It was connected to a laboratory computer with installed 1.8 Nova software consisting of saturated calomel electrode as reference electrode, auxiliary graphite electrode and the coated sample as the working electrode. Linear polarization resistance method was used to evaluate the corrosion behaviour of the coating artefacts in 3.5% NaCl solution. The scanning rate was set to 0.01 V/s and the potentiodynamic potential scan was fixed to run between –1.5 V and +1.5 mV.

2.4 Characterization

Microstructural profiles of the resulting coatings were evaluated using Joel JSM5410 Scanning Electron Microscope coupled With Energy Dispersive Spectroscopy (SEM-EDS) while the micrographs before and after corrosion were obtained using Nikon Eclipse LV150 High Resolution Optical Microscope (HR-OM). The average micro-hardness values were determined using the Micromet scientific hardness testing equipment at a load of 200kgf for 5 sec for the coatings before and after heat treatment.

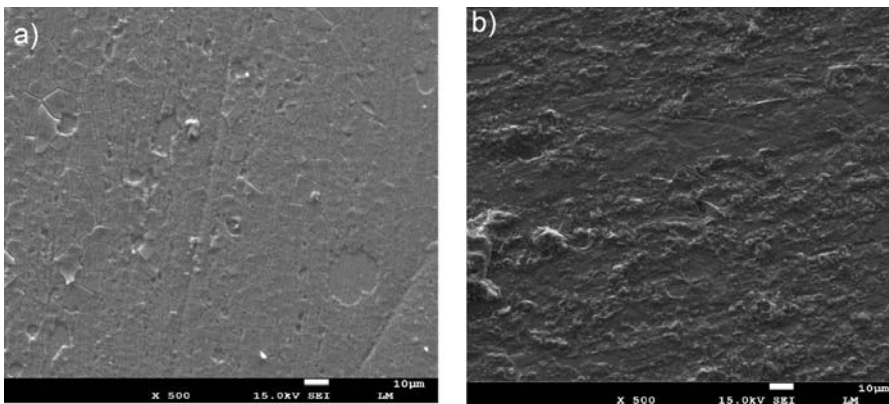### 3. Results and Discussions

3.1 Morphological studies

Figure 1 SEM micrographs results (obtained at × 500 magnification of a) Zn-Ni-10MoO$_2$ b) Zn-Ni-15MoO$_2$ both deposited at 1.0A for 20 min

Figure 1 depict the SEM micrographs of the produced Zn-Ni-MoO$_2$ coating plated at 1.0 V with the concentration variations of MoO$_2$ at 10 (figure 1a) and 15 (figure 1b) .Generally the evaluations of the coatings show uniform adhesion. This could be attributed to the Sulphate electrolyte used in the study since the additives influence the uniformity of the dispersed particles. The effect of the MoO$_2$ can be noticed by good distribution of the grains observed on both SEM micrographs. Zn-Ni-10MoO$_2$ produced a smooth and more stable modification while Zn-Ni-15MoO$_2$ showed wave-like structure. Figure 4 a) and b) show the optical micrographs of the as-deposited samples which depicts better and adhered microstructures at the interface of Zn-Ni-10MoO$_2$ at 1.0V. Altogether bright deposits were expected in the minimum current density of 1 Adm^2, [14] hence bright textures were observed as a result of fabrications.

3.2 Thermo-mechanical studies

Figures 2 respectively show the average micro-hardness results of the as-plated deposited ternary alloys prepared at varying induced additives concentrations of MoO$_2$ at 0.5V and 1.0V for 20 minutes (as listed in Table 1) against

the after heat-treatment valuations. The plotted values are the calculated averages of three values taken per sample. The adsorption of the composite oxide particulates could have a great effect on the strengthening behaviour of the coated metal and formation of the subsequent adhesion [13]. The slight change in hardness of the Zn-Ni-10MoO$_2$ sample deposited at 1.0 V proves that both coatings (15 μm coating thickness) are stable at altered temperatures thereby rendering the coating useful for harsh temperature applications such as engine bolts and other automotive parts that experience high temperature conditions.
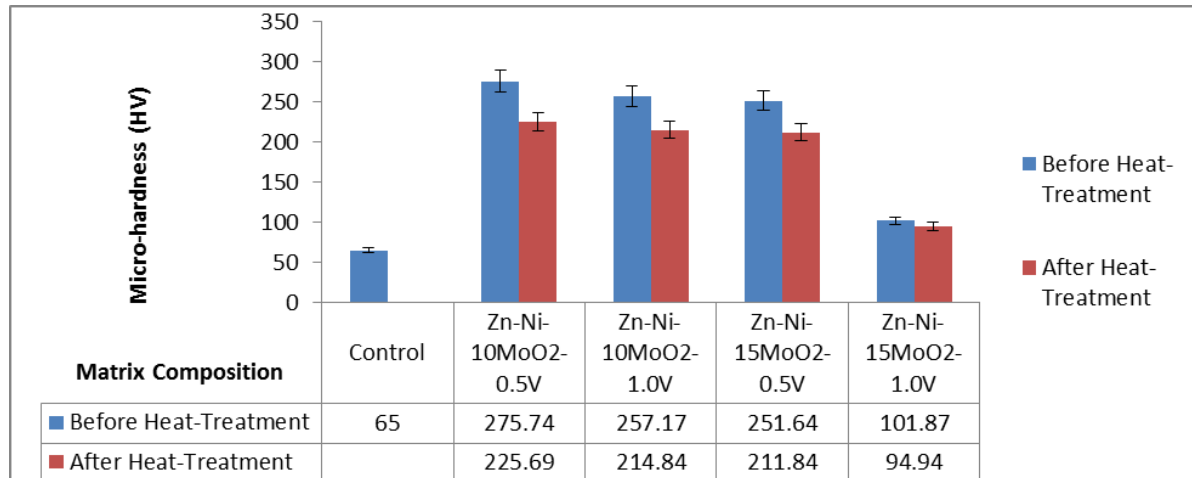

Matrix Composition	Control	Zn-Ni-10MoO2-0.5V	Zn-Ni-10MoO2-1.0V	Zn-Ni-15MoO2-0.5V	Zn-Ni-15MoO2-1.0V
Before Heat-Treatment	65	275.74	257.17	251.64	101.87
After Heat-Treatment		225.69	214.84	211.84	94.94

Figure 2 Variation of micro-hardness of the control versus as-plated and heat-treated Zn-Ni-10MoO$_2$ and Zn-Ni-15MoO$_2$ plated at 0.5V and 1.0V all for 20 minutes

3.3 Corrosion behaviour analysis

Table 2 shows the progression of degradation of the produced coatings Zn-Ni-MoO$_2$ against the as-received mild steel in 3.5% NaCl simulated medium with an induced current propagation examined by potential/current density measurements. The Tafel data shows the current density, polarization resistance and corrosion rate. The observed corrosion rate of the control samples shows that it has less passivation film on its surface and it showed corrosion attack by the chloride medium used in the study. The improvement in potential was discovered significantly for the produced coatings, which is due to the effects of incorporated MoO$_2$ precipitated at the interface of the metal matrix. The Zn-Ni-MoO$_2$ coatings at varied concentrations of 10 and 15 plated at 1.0 V proved to be the best performance since they have the highest polarization resistance potential and low corrosion rate of 27.483 and 30.197 mm/year respectively.

Table 2 Electrochemical corrosion data obtained for Zn-Ni-MoO$_2$ electroplated mild steel in 3.65% NaCl

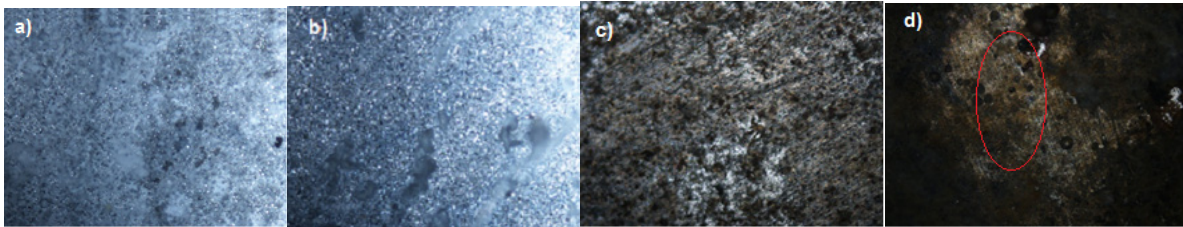| Sample	Additive Concentration (g)	I_{corr} (A/cm^2)	R_P (Ω)	Corrosion rate (mm/yr)
Control		0.038119	11.708	442.94
Zn-Ni-MoO$_2$ – 0.5V	15	0.007833	16.021	91.019
Zn-Ni-MoO$_2$ – 0.5V	10	0.007786	19.308	90.476
Zn-Ni-MoO$_2$ – 1.0V	15	0.002599	32.791	30.197
Zn-Ni-MoO$_2$ – 1.0V	10	-0.00237	462.58	27.483

Figure 3: Optical micrographs obtained at 20 × 0.45 magnification for [a] Zn-Ni-10MoO2 plated at 1.0V [b] Zn-Ni-15MoO2 plated at 1.0V both for 20 minutes OPM analysis of [c] Zn-Ni-10MoO2 at 1.0V [d] Zn-Ni-15MoO2 at 1.0V after the corrosion   .

Figure 3 a), b), c) and d) show the structural micrographs. Observations of the corrosion characteristics tested in 3.5% NaCl are seen for processed surface of (a, b, c) Zn-Ni-10MoO$_2$ and (d) Zn-Ni-15MoO$_2$ both plated at 1.0V for 20 minutes. The structure revealed few black scales at interface of both the coatings but the more transparent view of the Zn-Ni-15MoO$_2$ plated at 1.0V micrograph shows darker areas that look like the coating suffered some burns during analysis in the furnace. The micrograph area indicated by a red oval in figure 3 d) shows reduced thickness of the coating this means the coating is less adhesive after being subjected to a high temperature environment. This could be the reason the sample in question show low micro-hardness values. This indicates the significant effect of increased %weight of MoO$_2$ additive. The Zn-Ni-10MoO$_2$ at 0.5A showed compact and stable grains even after corrosion attack in chloride environment. This implies that effects of electron transfer rate and throwing power are functions of applied potential or current and this assists the possible modification of crystal growth and further penetration of blocking effect of vacancies with the help of particle induced within the cathode site.

Conclusions

The Zn-Ni-MoO$_2$ coatings were successfully done at varying concentrations of 10 and 15 MoO$_2$ at voltages between 0.5 and 1.0 V. The structural micrographs presented an even and uniform deposit. The incorporation of the admixed composite provides more stable and stress relieved coatings and all co-deposits of Zn-Ni-MoO$_2$ improved the corrosion and micro hardness properties.

Acknowledgement

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