Quaternary Zn-Ni-MoO$_2$-NbO$_2$ intermetallic composite deposits on mild steel via electrodeposition route

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Abstract- In majority of industrial applications zinc electrodeposition has been widely used for the corrosion resistant coating on steel due to its unique properties, low cost and sacrificial nature. Steel remains the most widely used material in most applications due to its excellent properties but its faults cannot be over emphasis in term of deterioration. A thin film of Zn on steel substrates was prepared by electrodeposition technique using incorporated rare earth metallic composites to form an optimised bath plating solution. Quaternary Zn-Ni-MoO$_2$-NbO$_2$ alloy coatings, as a potential replacement for Zn-Ni coatings were deposited from an acid sulphate solution. The mechanical wear and corrosion behaviours of Zn-Ni-MoO$_2$-NbO$_2$ Coated Mild Steel in 3.65% NaCl are described; these were studied by means of MTR-300 dry abrasive wear and polarization measurements respectively. The crystal particles present were observed by X-ray diffraction pattern (XRD) and energy dispersive X-ray diffraction spectrometer (EDS). The microhardness of deposited plate were investigated by means of Vickers microhardness. Scanning electron microscope and was used to study the surface morphology, and synergistic influence content in bath on surface morphology revealed that morphological changes observed in presence of additives exhibits synergistic influence on improving corrosion resistance and hardness of the deposit.

Keywords: Inter-metallic, Tafel plot, Micrographs, Zn-Ni-MoO$_2$-NbO$_2$

1. Introduction

Electroplating technology is one of the long-standing surface treatment techniques employed in most industries. This method is useful due to some distinctive advantages such as affordability, operation plainness and coating quality [3-6]. Zn has been functionally coated by different methods and most research studies have focused on Zn electrodeposition [1-6]. This is because of the sacrificial protection that Zn offers to steel components [4]. However the inflexible [7] properties of Zn coatings necessitates further techniques in pursuit for improvement. In the past thick coatings were opted for as an economical enhancement of such but as technology was advancing Zn-M (where M is the iron group metals) alloy coatings were introduced [3]. Zn-Ni co-deposition is promising for obtaining good corrosion resistance and enhanced mechanical properties compared to other Zn-M coatings [1]. For this reason Zn-Ni coatings have been exploited in different industries such as automotive, construction, household, aerospace etc. [4,8].
Molybdenum oxide additive improve properties of metallic coatings including hardness, wear resistance and corrosion resistance; it can be co-deposited especially with iron group metals [8-9]. The melting and boiling temperatures of zinc and molybdenum are different and in a study by [8] it was stated that electrodeposition can be one of the ways to obtain such environmentally friendly alloys. The present study aims to prepare Zn-Ni-MoO$_2$-NbO$_2$ quaternary inter-metallic coatings onto mild steel and evaluate and study the microstructure, micro-hardness, wear and corrosion resistance properties. To the best of author’s knowledge, no work was reported on the quaternary Zn-Ni-MoO$_2$-NbO$_2$ intermetallic composite deposits on mild steel by electrodeposition route.

2. Experimental

Table 1: Compositions of the electrolyte

| Composition   | Mass Concentration (g/l) |
|---------------|--------------------------|
| ZnSO$_4$      | 150                      |
| Na$_2$SO$_4$  | 10                       |
| H$_3$BO$_3$   | 20                       |
| (NH$_4$)$_2$SO$_4$ | 20                  |
| Glycine       | 10                       |
| Nickel powder | 60                       |
| pH            | 5                        |
| Voltage       | 0.5V and 1.0V            |
| Time          | 20mins                   |

Table 1 shows the compositions of the electrolytic bath of Zn-Ni alloy optimized without using any additives. Zn–Ni–MoO$_2$–NbO$_2$ alloy coatings were deposited from a sulphate bath with the addition of MoO$_2$ and NbO$_2$ in varying contents. The deposition operating parameters and additive contents under optimal conditions are shown in table 2. The plating solutions were freshly prepared from de-ionised water and analytical grade reagents. The pH of the electrolytes was adjusted to 4.8. The coatings were deposited on an exposed surface area of (4×4×0.02) cm of the disc electrodes made of mild steel (sourced in
Johannesburg, South Africa) which served as a cathode. The anode used was two pure Zn electrode (99.9%) with a surface area of (8×4×2) cm and both were placed at a maintained distance of 5 cm away from the cathode on the centre of the 250 mL deposition vessel. Before each experiment the surface of electrode was mechanically polished with successive grades of abrasive paper, degreased and rinsed with de-ionised water. Electrodeposition was done in room temperature (25°C) while stirring at 250 rpm for 20 minutes with an adjustable DC power source at Voltage of 0.5 to 1.0 V.

Table 2: electrolyte Summarized Bath Formulation (Zn–Ni–MoO$_2$–NbO$_2$)

| Sample order | Matrix           | % Weight MoO$_2$ | Time of deposition (min) | Voltage |
|--------------|------------------|------------------|--------------------------|---------|
| As-Received  | -                | 0                | -                        | -       |
| 1            | Zn-Ni-5NbO$_2$-5MoO$_2$ | 10               | 20                       | 0.5     |
| 2            | Zn-Ni-5NbO$_2$-5MoO$_2$ | 10               | 20                       | 1.0     |
| 3            | Zn-Ni-10NbO$_2$-10MoO$_2$ | 15               | 20                       | 0.5     |
| 4            | Zn-Ni-10NbO$_2$-10MoO$_2$ | 15               | 20                       | 1.0     |

Surface morphology of the coatings was characterized using scanning electron microscopy (SEM, JSM–7610F), energy dispersive spectroscopy (EDS) and Optical Microscope. The wear resistance towards abrasion was evaluated using the modification of MTR-300-ASTM-G-65 dry sand rubber wheel abrasion test on prepared sample of 10x10mm. Micro-hardness studies were carried out using a Diamond pyramid indenter EMCO Test Dura-scan micro-hardness testers at a load of 10 g for a period of 20 s before and after heat treatment at 250 °C and 350 °C. The electrochemical behaviour of intermetallic coatings was monitored in 3.65 wt.% NaCl solution by potentiodynamic polarization using Linear Polarization Resistance (LPR) techniques; the equipment used was metrohm AUTOLAB electrochemical workstation utilizing NOVABO software. All electrochemical measurements were made using three electrode set up with developed coating (1 cm$^2$ exposed surface area) as working electrode, graphite as counter electrode and saturated calomel electrode (SCE) as reference. The corrosion currents were obtained from the tafel’s extrapolation method.
3. Results and discussion

3.1. SEM/EDS analyses of deposition

Figure 1: SEM/EDS Spectra showing the Surface Morphology of Zn-Ni-5NbO2-5MoO2-1.0V

Figure 1 and 2 shows the SEM-EDS spectra of the Zn-Ni-5NbO2-5MoO2-1.0V and Zn-Ni-10NbO2-10MoO2-1.0V intermetallic composite coating deposited for 20 minutes respectively. The EDS pattern of the developed coatings confirms the crystalline nature of the thin film developed while showing the elemental presence (in appreciable amounts) of the induced MoO2 and NbO2 with visible peaks for both the samples analysed.

Figure 2: SEM/EDS Spectra showing the Surface Morphology of Zn-Ni-10NbO2-10MoO2-1.0A Sulphate Deposition
Generally, good surface appearances and smooth orientation was obtained as a result of the proposed quaternary enhancements. Uniform arrangement of the surface was noticed with sprinkles of dispersed particles. Much smaller scattering grains were noticed for increased content Zn-Ni-NbO$_2$-MoO$_2$ deposit in figure 2 (a). This might be due to the increased ions [2] of MoO$_2$ and NbO$_2$ on the morphology and thus sows surface modifications. No visible pores or cracks were revealed on the interface of the coatings and therefore one can state that good adhesion was obtained for the optimized deposition parameters in the study. Therefore the presence of molybdenum and niobium oxide has a significant effect on obtained smooth morphology of the alloy coating surface.

3.2. Micro-hardness Behavior

![Figure 3](image)

Figure 3 shows the micro-hardness variations of the deposited coatings against the as-received sample for different temperature subjection (25, 250 and 350 °C) respectively. Alloying zinc coatings with nickel can enhance their corrosion resistance, micro-hardness and thermal stability [7], this might be even better for co-deposition with refractory oxide particles such as MoO$_2$ and NbO$_2$. The presence of MoO$_2$ and NbO$_2$ improves the micro-hardness [4] for all the co-deposited coatings obtained, but it has negative influence on the corrosion and wear for the Zn-Ni-10MoO$_2$-10NbO$_2$-0.5V sample proving to be the unstable sample by a sharp decrease (44 HV) after heat treatment. The thermal diffusion characteristics were analysed by heat treatment (at 250 °C and 350 °C) subjection and the micro-hardness variations were evaluated. Highest wear results were obtained for Zn-Ni-10NbO$_2$-10MoO$_2$-1.0V this can be explained by the lowest micro-hardness obtained, therefore it can be attested that the micro-hardness values obtained affirms both the wear and corrosion results. This statement is further confirmed by sample Zn-Ni-5NbO$_2$-5MoO$_2$-1.0V which
proved to be the best sample in the deposition matrix in terms of corrosion, wear and micro-hardness. Generally as the temperature was increased there was a slight decrease in the micro-hardness values. These Zn-Ni alloyed coatings can be useful for fasteners of car engines, because they retain their properties at temperatures variations [7].

3.3. Electrochemical Behaviour of Deposition

Table 3: Potentiodynamic Polarization Data

| Sample                  | $I_{\text{corr}}$ (A/cm²) | $R_p$(Ω) | $E_{\text{corr}}$(V) | Corrosion rate (mm/yr) |
|-------------------------|---------------------------|----------|----------------------|------------------------|
| Control                 | 0.038119                  | 11.708   | -1.3065              | 442.94                 |
| Zn-Ni-5NbO₂-5MoO₂-0.5V  | 0.002557                  | 66.787   | -1.3867              | 29.717                 |
| Zn-Ni-5NbO₂-5MoO₂-1.0V  | 0.000159                  | 471.1    | -1.0286              | 11.8422                |
| Zn-Ni-10NbO₂-10MoO₂-0.5V| 0.004758                  | 31.71    | -0.95087             | 55.288                 |
| Zn-Ni-10NbO₂-10MoO₂-1.0V| 0.003523                  | 52.692   | -0.60053             | 40.932                 |

Data on the corrosion potential ($E_{\text{corr}}$), corrosion current density ($I_{\text{corr}}$) and corrosion rate (CR) and polarization resistance ($R_p$) of Zn–Ni-NbO₂-MoO₂ alloys is summarized in Table 3.

Figure 4: Potentiodynamic Polarization Curves for Zn-Ni-NbO₂-MoO₂ Deposition
The polarization curve of the Zn-Ni-NbO\textsubscript{2}-MoO\textsubscript{2} matrix deposition is shown in figure 4. The enhanced corrosion behaviour of the quaternary alloy deposited is attributed to the chemical composition and the synergistic effect of MoO\textsubscript{2} and NbO\textsubscript{2}. Again additive increase seemingly increases with the corrosion rate thus reducing the polarization rate. In the case of deposited coatings the lowest obtained corrosion rate was 11.8422 mm/year for Zn-Ni-5NbO\textsubscript{2}-5MoO\textsubscript{2} characterized coatings deposited at 1.0V and this implies that the deposition parameters resulted in strongest passive layer on the coating’s surface. It is known from literature [2] that MoO\textsubscript{2} co-deposition enhances the properties of Zn or rather iron group metallic coatings. Generally it can be said that there is a passive film on all the coatings but there is a possibility of passivity breakdown for Zn-Ni-10MoO\textsubscript{2}-10NbO\textsubscript{2} and Zn-Ni-5NbO\textsubscript{2}-5MoO\textsubscript{2} both deposited at 0.5 V.

![Image of optical micrographs](image-url)

**Figure 5:** Optical Micrograph of (a) Zn-Ni-5NbO\textsubscript{2}-5MoO\textsubscript{2} at 0.5A (b) Zn-Ni-5NbO\textsubscript{2}-5MoO\textsubscript{2} at 1.0A (c) Zn-Ni-10NbO\textsubscript{2}-10MoO\textsubscript{2} at 0.5A (d) Zn-Ni-10NbO\textsubscript{2}-10MoO\textsubscript{2} at 1.0V after corrosion

From all indications, uniform attack by aggressive chloride anions can be seen from figure 5 which shows the optical micrographs obtained after corrosion for all the coating. The corrosion resistance of these coatings depends on the additives [7] contents and deposition parameters. The corrosion reactions rendered the rough surface observed.
Figure 6: Variation of the wear rate with time (Zn-Ni-NbO$_2$-MoO$_2$ deposition)

The wear loss ranges from the highest to the lowest is indicated by: Zn-Ni-10NbO$_2$-10MoO$_2$-1.0V, Zn-Ni-5NbO$_2$-5MoO$_2$-0.5V, Zn-Ni-10NbO$_2$-10MoO$_2$-0.5V, Zn-Ni-5NbO$_2$-5MoO$_2$-1.0V. This is graphically represented in figure 6. Higher voltage of 1.0V yielded both the highest and lowest wear loss with time. Correct adjustment could distinguish the better performing sample this can be attributed to a statement by [3] about specific bath additives.

4. Conclusions

In conclusion the Zn-Ni-NbO$_2$-MoO$_2$ intermetallic matrix was successful deposited. The induced co-deposited oxides synergistically improved the corrosion, wear, micro-hardness and surface properties of mild steel. Energy Dispersive Spectroscopy results confirmed the deposition of both NbO$_2$ and MoO$_2$ on the surface interface. The coated samples prove to retain thermal stability at temperature variations.

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