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ORIGINAL ARTICLE

The effect of nanoparticulate loading on the fabrication and characterization of multi-doped Zn-Al2O3-Cr2O3 hybrid coatings on mild steel

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Abstract Nanoparticle Al2O3/Cr2O3 was successfully incorporated into Zn rich by electrodeposition technique to produce Zn-Al2O3-Cr2O3 ternary coatings. The morphology and structural characteristics of the fabricated electrodeposits were characterized by scanning electron microscopy (SEM) affixed with energy-dispersive spectroscopy and X-ray diffraction. The electrochemical behavior of the coatings was studied by potentiodynamic polarization. The wear and microhardness properties of the coatings were tested using ball-on-disk sliding wear tester and diamond base microhardness indenter, respectively. The results showed that the incorporation of the nanoparticles into the Zn matrix refines the morphology and modifies the crystallographic orientation of the Zn coatings. The nanocomposite coatings exhibited improved microhardness properties, wear resistance, and thermal stability. Corrosion studies revealed that the incorporation of the mixed-oxide nanoparticles has no significant effect on the corrosion resistance of Zn coatings.

Keywords Electrodeposition · Zn-Cr_2O_3-Al_2O_3 nanocomposite coatings · Corrosion · Thermal stability · Wear

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1 Introduction

Advancement in industrial applications of coatings has drastically increased over the last few decades. These increasing demands for coatings that can withstand aggressive environments have led to the search of new coating materials and improvement of existing techniques for fabrication of surface coatings. The required materials need to exhibit excellent anticorrosive, wear resistance, biocompatibility, thermal stability, and printability properties. Incorporation of nanosized particles into metal matrixes poses a promising solution to combat the demand. This is due to the unique and exotic properties possessed by these materials and their ability to perform better than their micron/submicron-sized counterparts [1–3].

Zinc electrodeposition is one of the techniques that have attracted several researchers for the development and fabrication of new novel coatings with functional properties. This owes to the cost-effectiveness, versatility, and simplicity of this technique in the fabrication of surface coatings. Inert nanoparticles such as Al_2O_3, SiO_2, TiO_2, ZrO_2, CeO_2, etc., have been successfully co-deposited with Zn to form Zn nanocomposite coatings [3–6]. Several studies investigated the incorporation of Al_2O_3 and Cr_2O_3 into metal matrixes, and the results showed a positive effect on the surface properties of the coatings. Al_2O_3 and Cr_2O_3 possess excellent corrosion resistance, high hardness, low thermal expansion, and coefficient of friction [6–11].

Inclusion of Al_2O_3 particles into a metal matrix proved to improve the hardness properties of Zn coatings [7]. Blejan et al. investigated the corrosion behavior of Zn-Ni-Al_2O_3 nanocomposite coatings. The presence of alumina nanoparticles in the composite coating showed improved corrosion resistance [9]. The mechanical properties of the composite coatings were also improved when compared to plain Zn coatings [7]. Cr_2O_3 particles alter the surface morphology, increase the hardness, and reduce the corrosion rate of the Ni matrix [11].

Srivastava et al. studied the co-deposition of nickel with Cr_2O_3 nanoparticles in an additive free bath and found that the incorporation of these nanoparticles had no effect on the corrosion resistance of the matrix, but improved the tribological and mechanical properties [8]. The contradictory results obtained for the corrosion resistance of Cr_2O_3 composite coatings indicate that the quality depends on the optimization of the plating parameters.

The inclusion of A_2O_3 and Cr_2O_3 nanoparticles into the metal matrix is available in the published literature. However, investigation of the incorporation of these nanoparticles in a Zn metal matrix is scanty. Therefore, this research seeks to synthesize Zn-Al_2O_3-Cr_2O_3 nanocomposite coatings and study the synergetic effect of Al_2O_3 and Cr_2O_3 nanoparticles in a Zn matrix. The morphology, microstructure, electrochemical, mechanical, and tribological properties of the fabricated coatings were studied.

2 Experimental

2.1 Sample preparation

Zn and Zn-Cr_2O_3-Al_2O_3 nanocomposite coatings were prepared by electrodeposition technique using mild steel plates as cathodes. The mild steel plates were sectioned using a cutting wheel to sections of dimensions of 25 × 40 mm. Emery papers of grit sizes of 180 and 400 grits were used to grind, polish, and remove the unwanted material such as rust on the mild steel substrate. The polished samples were then dipped into ethanol to remove the grease or oil on the mild steel followed by suspension into 1 M HCl to activate the surface prior to plating. The plating solutions were mechanically stirred using a magnetic stirrer for 18 h to keep Cr_2O_3 (100 nm) and Al_2O_3 (50 nm) nanoparticles in suspension (Table 1). During electrodeposition, two Zn plates were used as anodes and the pH was kept constant at 3.8. The deposition time for the experiments was 20 min under ambient conditions while stirring at a speed of 300 rpm. The samples were rinsed in water for 5 s to remove loosely adhered particles and were air-dried after electrodeposition (Table 2).

2.2 Surface characterization

JEOL-JSM-5800V scanning electron microscope was used to study the microstructural characteristics of the as-received powder and electrodeposited samples. The compositional analysis of the samples was done using energy-dispersive spectrometry (EDS) affixed to the microscope. X-ray diffraction (XRD) patterns of the samples were obtained with an XPertPro PANalytical, LR 39487C XRD diffractometer using Cu Kα radiation (40 kV, 40 mA). Stepwise increase for small angle was 0.01° over the range of 1 to 8° and wide angle rate of 1° 2θ min^{-1} over the range of 8 to 90° (2θ). High-resolution 5500LS AFM analytical technique was used to examine the adhesion and topography of fabricated crystalline materials. The topographical images are captioned in 3D dimension through a scanning probe. The amplitude is demonstrated in order of fractions of a nanometer. The methodologies operate at the material interface with a mechanical and piezoelectric probe which facilitates command and enables very precise scanning.

Table 1 Bath composition and operating condition

Composition	Parameters
$ZnCl_2$—150 g/L	Cathode—mild steel
KCl—50 g/L	Anode—Zn
Boric acid—30 g/L	Temperature—25 °C
Glycine—30 g/L	pH—3.8
Thiorea—10 g/L	Current—1.5 A
Cr_2O_3—2.5, 5, 7.5 g/L	
Al_2O_3—2.5, 5, 7.5 g/L	

2.3 Microhardness testing

Diamond indenter microhardness tester was used to investigate the microhardness properties of the samples. The values reported are an average of three indentation measurements made at different locations. The values reported are an average of three indentation measurements made at different locations for a 15-s dwell time with a 100-g load.

2.4 Electrochemical behavior

Electrochemical measurements were performed using μAutolab pontentiostat/galvanostat to investigate the corrosion properties of the samples in a 3.65 % NaCl environment. Saturated calomel electrode was used as a reference and graphite rod as counterelectrode, which were employed for the measurements in a conventional three-electrode electrochemical cell. All the tests were conducted under ambient conditions with specimen of area 1 cm^2 which was exposed to corrosive medium. The potentiodynamic potential scan was fixed from −1.5 V to +1.5 mV with a scan rate of 0.012 V/s. The electrochemical corrosion test was performed at room temperature.

Table 2 Electrodeposited sample codes

Sample code	Description
ZAC1	Zn-2.5 g/L Al_2O_3–7.5 g/L Cr_2O_3
ZAC2	Zn-5 g/L Al_2O_3–5 g/L Cr_2O_3
ZAC3	Zn-7.5 g/L Al_2O_3–2.5 g/L Cr_2O_3