Research Article

Electrodeposition and Corrosion Resistance Properties of Zn-Ni/TiO₂ Nano composite Coatings

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Nano sized TiO₂ particles were prepared by sol-gel method. TiO₂ nano particles were dispersed in zinc-nickel sulphate electrolyte and thin film of Zn-Ni-TiO₂ composite was generated by electrodeposition on mild steel plates. The effect of TiO₂ on the corrosion behavior and hardness of the composite coatings was investigated. The film was tested for its corrosion resistance property using electrochemical, weight loss, and salt spray methods. The paper revealed higher resistance of composite coating to corrosion. Microhardness of the composite coating was determined. Scanning electron microscope images and X-ray diffraction patterns of coating revealed its fine-grain nature. Average crystalline size of the composite coating was calculated. The anticorrosion mechanism of the composite coating was also discussed.

1. Introduction

Composite materials have various properties such as dispersion hardening, self-lubricity, high-temperature oxidation resistance, excellent wear, and corrosion resistance. Because of their importance in many fields, the newer composite materials are synthesized through different existing methods. Among these methods, the electrodeposition is considered to be one of the most important techniques for producing composites, owing to precisely controlled near room temperature operation, rapid deposition rates, and low cost. A number of the literatures appear in scientific journals connected to the codeposition of SiC, ZrO₂, Al₂O₃, TiO₂, and PTFE with single metal and alloy electrodeposition [1–4].

So, generated composite coatings on steel exhibited excellent atmospheric corrosion resistance property and thus reducing or eliminating its chromium passivation. Further the corrosion resistance property is enhanced by codeposition of nano materials like CNT, MWCNTs, TiO₂, Fe₂O₃, and so forth, with metals. The size of nano structural materials ranging from 1–100 nm, are used widely in electrodeposition. Thus, these materials enhance the mechanical and

physical properties of the coatings due to their extremely small size [5–7].

Significant progress has been made in various aspects of synthesis on nano scale materials. The focus is now shifting from synthesis to manufacture of useful structures and coatings having greater wear and corrosion resistance. Because of large availability of nano particles, nowadays they are generally used in composite coating for achieving good mechanical and corrosion resistance properties. Gomes et al. adopted pulse deposition method for preparing Zn-TiO₂ and Zn-Ni-TiO₂ composites [8]. In our method, simple electrodeposition method was adopted for preparing these composites.

In this paper Zn-Ni-TiO₂ composite coating on steel was prepared by electrodeposition process. The electrolyte was aqueous solution containing zinc and nickel salts with uniformly dispersed TiO₂ nano particles. The study also examined the corrosion resistance property of composite with reference to alloy coating.

2. Experimental

Titanium oxide nano particle was synthesized by a sol-gel method according to a procedure reported elsewhere [9].

FIGURE 1: SEM image of TiO_2 Particles.

Titanium isopropoxide, $\text{Ti}(\text{OiPr})_4$ (8 mL 27 mmol) dissolved in absolute ethanol (82 mL) under nitrogen blanket was added dropwise to a solution of ethanol/water 1 : 1 (250 mL) under rapid stirring for 10 minutes, then filtered to obtain a white precipitate, which was dried at 100°C for 15 hours. The prepared TiO_2 particles are in 100–200 nm range and it was confirmed by scanning electron micrograph (SEM) in Figure 1.

Zn-Ni and Zn-Ni- TiO_2 coatings were electrolytically deposited from sulphate bath. Analytical-grade chemicals and distilled water were used to prepare the plating solution. The constituents of the bath were 160 g/L ZnSO_4 , 40 g/L Na_2SO_4 , 12 g/L H_3BO_3 , 16 g/L NiSO_4 , 1.5 g/L cetyl trimethyl ammonium bromide, and 3 g/L TiO_2 . While in solution, the nano particles may get agglomerated due to their high surface energy. The agglomeration was minimized by the addition of surfactant cetyl trimethyl ammonium bromide. Also the bath solution was subjected to stirring for 10 hours for uniform dispersion of TiO_2 particles in the bath. The cathode was mild steel panel and anode was pure zinc (99.99%). The mild steel plates were polished mechanically, and degreased by trichloroethylene in degreaser plant followed by water wash. Before each experiment, the zinc (anode) surface was activated by dipping in 10% HCl for few seconds followed by washing with water. The same surface area of anode and cathode was used for electrodeposition process. The bath temperature was 300°K and pH was 4. The cathodic current density was controlled at 2 A/dm^2 . The electrodeposition process was carried out under galvanostatic condition using a regulated DC power source.

The porous nature of the coated specimens were examined by adopting porosity test. The steel samples of Zn-Ni coated and Zn-Ni- TiO_2 coated samples of $5 \times 5\text{ cm}^2$ area were taken for this study. The porosity of the deposit was assessed by ferroxyl test [10]. The deposited plates were subjected to continuous spray of neutral 5% sodium chloride vapors, by using ASTM B 117 standard [11]. The specimens surfaces were observed carefully and the duration of time for the formation of white rust was noted.

The mild steel plates, electrodeposited with Zn-Ni and Zn-Ni- TiO_2 composites, were used for investigating their corrosion behavior in aggressive media by weight loss method. In each experiment, five samples were used to ensure the reproducibility. The corrosion experiments were

performed in 3.5% NaCl solution by immersing the coated articles. After specified hours of immersion the mass loss incurred by them was determined by using Vibra HT-220E Analytical balance with 0.1 mg weight scale accuracy.

A conventional three-electrode electrochemical cell was used for polarization studies. The steel samples coated separately with Zn-Ni alloy and Zn-Ni- TiO_2 nano particles composite with surface area of 1 cm^2 were employed as working electrodes. Saturated calomel and platinum were used as reference and counter electrodes, respectively. The electrolyte used for this study was 3.5% NaCl solution. The electrochemical measurements were performed using AUTOLAB from Eco-Chemie (The Netherlands) and the polarization curves were recorded at a sweep rate of 0.1 mV/s. The corrosion rate was obtained from Tafel extrapolation method by using five samples per condition.

The Vickers microhardness of the deposit was determined by an indentation technique with a weight of 50 g for 10 seconds using Clemex microhardness tester, made in Japan. The average of five replicated values was recorded.

The surface morphology of the coatings was examined using a JEOL-JEM-1200-EX II scanning electron microscope (SEM). X-ray diffraction patterns of the deposits were recorded by Philips TW 3710 X-ray recorder and Nickel-filtered $\text{Cu-K}\alpha$ radiation was used.

3. Results and Discussion

3.1. Optimization of Bath Constituents. Basic bath constituents concentrations were selected based on the appearance of coating obtained at different concentrations of all the constituents in the bath except TiO_2 . Its concentration was optimized by generating composite coating from the bath solution containing different amount of TiO_2 . The concentration of TiO_2 was varied from 0.5 g/L to 5 g/L. The coating obtained from this bath solution was subjected to anodic polarization. The results indicated that, lower current densities were achieved at 3 g/L and above this concentration corrosion current is increased. So, it was chosen as optimum concentration for further experiments.

3.2. Weight Loss Measurements. Figure 2 shows the variation of corrosion rate during 15 days of immersion in 3.5% NaCl solution for both coatings (Ni-Zn alloy and composite). Corrosion rate of composite-coated sample was less than the alloy-coated sample. It indicated that the TiO_2 in the coating reduced its corrosion rate. This reveals that the presence of TiO_2 hinders the dissolution rate of zinc and nickel of the alloy coating [12]. In other words the TiO_2 particles in the coating reinforce the Zn-Ni grains and thus behave as good reinforcing agent. Ultimately the corrosion resistance property of composite was increased.

3.3. Electrochemical Measurements. The electrochemical polarization was carried out separately for Zn-Ni and Zn-Ni- TiO_2 coating which were generated at different conditions of the bath. potentiodynamic polarization curves for the steel samples coated with the Zn-Ni alloy and the composite

FIGURE 2: Corrosion rate with immersion time for Zn-Ni coating and composite coating samples in 3.5% NaCl solution.

FIGURE 3: Tafel plots of composite-coated and alloy-coated samples.

are shown in Figure 3. The polarization curves were shifted towards more positive and negative potentials in case of composite-coated samples in anodic and cathodic direction, respectively. In cathodic direction, this shift reduced the hydrogen reduction process and the corrosion rate. So, the polarization curves show that there is a decrease in corrosion rate when using TiO_2 in the coating. It produces good corrosion inhibition property than simple alloy coating. This coating can be easily commercialized because TiO_2 particles were prepared by simple sol-gel method and composite coatings are obtained by simple electrodeposition method.

3.4. Salt Spray Test. Salt spray test was conducted by spraying 5% NaCl solution vapors on coated articles hang freely in a closed chamber. The fog of NaCl got accumulated on surface of the articles and facilitates the corrosion resulting in the formation of zinc salts called white rust. The

(a)

(b)

FIGURE 4: SEM images of alloy-coated (a) and composite-coated samples (b).

higher corrosion resistance property of coating delays the generation of white rust. In the present case the white rust appeared after 30 hours on Zn-Ni-coated sample and Zn-Ni- TiO_2 composite showed white rust after 45 hours.

3.5. Microhardness Measurements. Microhardness values of composite-coated and alloy-coated samples were 170 and 135 HV, respectively. It indicates that grain size of composite-coated sample was smaller than alloy-coated sample. The higher hardness of the coating was due to the fine-grained structure of the deposit. During hardness measurements, the dispersed particles in the fine-grained matrix may obstruct the easy movement of dislocations, which was shown by higher hardness values of composite-coated samples.

The TiO_2 particles were codeposited in the Zn-Ni matrix and restrained the growth of the Zn-Ni alloy grains and the plastic deformation capacity of the matrix under a load. The introduction of a harder reinforcing phase in the alloy matrix reduced the weight loss. Thus the microhardness of the composite coatings were significantly higher in presence of TiO_2 . Because of higher mechanical properties the coating surface behavior changes and poses certain degree of resistance to corrosion and surface deterioration.

3.6. Surface Morphology. Figure 4 shows the SEM images of composite-coated sample and alloy-coated sample respectively. In composite-coated sample crystal size was reduced appreciably when compared with the alloy-coated sample. The grain size of the composite-coated sample was calculated by XRD (Figure 5). The grain size was 30 nm. The small peak at $27.04 (2\theta)$ corresponds to TiO_2 . It gives the evidence for the presence of TiO_2 in the coating. This peak is highest

FIGURE 5: XRD images of composite-coated sample.

intensity peak of TiO_2 in JCPDS file. All remaining peaks are matched with Zn-Ni alloy sample. Microhardness, SEM and XRD studies inferred that crystal size was minimized and more uniform crystals were observed in composite-coated sample. This improves the corrosion resistance property to coating.

The metal surface always possesses defects, cracks, gaps, crevices, and microholes which were generally larger than micron. It was obvious that the nano particles easily enter and fill these defects. In the present case also the TiO_2 enters and fills these gaps of the surface of zinc and nickel. Moreover this microhole behaves as active sites for dissolution of metal during corrosion. Thus these holes were covered in by TiO_2 thereby bringing down the corrosion rate. The results of the present paper revealed that the corrosion resistance property of composite coating can be improved by selecting proper preparation technique, monitoring its grain size along with the microhardness.

4. Conclusions

- (1) Nano sized TiO_2 particles were prepared, and they were used for generating Zn-Ni- TiO_2 composite coating from sulphate bath.
- (2) The incorporation of TiO_2 in the coating was confirmed by XRD.
- (3) Lower corrosion current and higher microhardness of composites exhibited higher corrosion resistance property than the alloy coating.
- (4) The enhancement in the corrosion resistance may be due to physical barriers produced by TiO_2 to the corrosion process by filling crevices, gaps, and micron holes on the surface of the alloy coating.
- (5) SEM studies inferred that crystal size of the composite-coated sample was smaller compared to alloy coating.

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