

Investigation of corrosion protection performance of epoxy coatings modified by ZnO-Cr₂O₃ nanocomposites on mild steel surfaces

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Abstract

In this study, ZnO-Cr₂O₃/epoxy nanocomposites are employed to protect mild steel corrosion in 3.5% NaCl solution. The corrosion performances of the nanocomposites coatings were evaluated by using electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization measurements. Electrochemical measurements show that ZnO-Cr₂O₃ nanocomposite coated has good inhibitive properties with PE% of ~99% at 0.04 gr/L concentration on mild steel corrosion in 3.5% NaCl solution. The results indicated that the incorporation of ZnO-Cr₂O₃ nanoparticle into epoxy resin coating significantly decrease the corrosion current as well as the hardness of epoxy coatings. ZnO-Cr₂O₃ nanoparticles are able to cure the defect in epoxy resin and prevent the diffusion of corrosive electrolyte to mild steel substrate.

Keywords: Corrosion, ZnO-Cr₂O₃ nanoparticle, Epoxy coating, Mild steel.

1. Introduction

Industries depend heavily on the use of metals and alloys. One of the most challenging and difficult tasks for industries are the defense of metals from corrosion. Corrosion is a ubiquitous problem that continues to be of great relevance in a wide range of industrial applications and products; it results in the degradation and eventual failure of components and systems both in the processing and manufacturing industries and in the service life of many components. Corrosion control of metals and alloys is an expensive process and industries spend huge amounts to control this problem [1]. Corrosion, an increasingly serious issue, is the deterioration of metal by chemical interaction with their surrounding environment, which would cause substantial damage to society and industry all over the

world [2, 3]. To address this issue, several methods for the protection of metal substrates have attracted huge attention in recent decades, such as cathodic protection, anodic protection, corrosion inhibitors, coating, and alloying [4, 5]. Among the various approaches, polymer coatings are regarded as most effective method to prevent metals from corrosion [6]. Epoxy resins, the conventional coating, are widely used as polymeric coatings, composite matrix, adhesives, and structural materials due to their anticorrosion properties, chemical stability, low shrinkage, excellent adhesion, thermal stability, and electrical resistance [7-9]. Unfortunately, epoxy resins also have some undesirable properties, such as brittleness, poor flexibility and impact resistance [10], resulting in plentiful tiny pores easily

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produced when fabricating the high temperature curing epoxy solvent-borne coatings, which may attenuate their barrier properties.

In the latest years, the efforts have been achieved to use nano sized pigments to improve the corrosion resistance behavior of epoxy coatings [11-13]. The Utilization of neat epoxy resin (without pigments) cannot give long period corrosion protection performance [14]. Where the corrosive species can diffuse to metal/epoxy coating interface through epoxy coating porosities [15, 16]. However, epoxy resins are inherently shortcoming, fabricating the high temperature curing epoxy solvent-borne coatings, which makes them inevitably produced micro-pores via solvent evaporation [17, 18]. The corrosive liquid medium can quickly permeate the coating into the protected substrate using micro-pores generating poor corrosion resistance. Extensive studies have thus been conducted to toughen epoxy resins using nano fillers [19, 20]. Epoxy resins containing film nano fillers have shown the greatest barrier property arising from the sheet-like a no material which has a more efficient obstruction for micro-pores than others and GO owns the property. With the purpose of stick nano-TiO₂ to sheets, nanoparticle could be a useful method for forming reactive activity on its surface [21]. Organic coatings have been commonly used on the metal substrates to protect them against corrosion. In fact, the organic coating acts as a physical barrier between the

2. Experimental procedure

2.1. Materials

In this study, acetone and sodium chloride and ethanol from merck Co. were used. Also, mild steel metal, circularly cut to 1 cm in diameter and 1 mm in length, is used as a working electrode. The nanoparticles (ZnO/Cr₂O₃) produced by the research group Professor Masoud Salavati were used as inhibitors. Catalysts with different Zn:Cr ratios were prepared by a co-precipitation procedure adapted from Kurtz et al [34]. A metal salt solution (1 M) consisting of zinc and chromium nitrates with the desired Zn:Cr ratio was added drop wise into a vessel, which contained 50 ml HPLC water heated up to 65°C. The precipitation was performed under continuously stirring at a constant pH

metal surface and the corrosive environment. However, water and oxygen can penetrate through all polymeric coatings to some extent [22-24].

Nanoparticles in anticorrosive polymeric coatings, remarkably improve the protection ability of polymer coatings. The inorganic and organic (polymer) hybrid nanocomposite coatings possess synergistic properties, i.e., the plasticity, adhesion, water and chemical resistance properties contributed by organic (polymer) constituents, while good scratch hardness, impermeability, impact and bend resistance properties are induced by inorganic materials[25]. Nanocomposite coatings such as polymer-clay, polymer-silica, polymer-graphene, etc. have potentially been used to combat corrosion [26-28]. Alumina (Al₂O₃), silicon oxide (SiO₂), zinc oxide (ZnO), iron oxide (Fe₂O₃) and clay nanoparticles are being used as fillers, extenders and pigments in polymeric coatings [29-33].

The aim of this work is studying the effects of pre-dispersed nano-ZnO/Cr₂O₃ particles on the anticorrosion performance of an epoxy coating. In this regard, nanocomposites were prepared using loading of nanoparticle. The morphology was investigated by atomic force microscope (AFM). Electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization measurement tests were utilized in order to investigate the anticorrosion properties of the nanocomposites.

of 7 by simultaneous addition of Na₂CO₃ solution (1.2 M) using an auto titrator while the precipitation temperature was constantly kept at 65°C. The suspension after precipitation was aged at 65 °C for 2 h. Subsequently, the precipitate was filtered and washed with HPLC water and then dried for 18 h at 120 °C. The dried precipitate was granulated and calcined in synthetic air for 3 h with a heating rate of 2 °C min⁻¹ to 320 °C and keeping this temperature for 3 h.

2.2. Preparing the working electrode

The mild steel (with the chemical composition (wt.%) of: C (0.027), Si(0.0027), P (0.009), Al (0.068), Mn (0.340), S (0.007), Nb (0.003), Cu (0.007), Ni (0.030), Ti (0.003), Cr (0.008), V (0.003) and Fe (balance) cutting plate is soldered to a thick wire and soldered

wire to mild steel in a pre-assembled cube to be dimensioned (1cm×1cm×1cm) then added inside the cube with a mixture of resin and hardener, which is pre-mixed with a ratio of 10:1. The cube containing the electrode and the mixture of resin and hardener remains intact for 24 hours until it becomes firm. The mild steel electrode was abraded by emery papers with different grades (320, 400, 800, 1000, 1200 and 2000) and at the end of the work its surface is washed with deionized water and ethanol.

2.3. Epoxy resin coating on the working electrode

First, weigh 1.8 g of resin with a weighbridge and add 0.2 g of hardener, we then weigh the specified amount of nanoparticle and add to the mixture, to reduce the viscosity of the mixture, add ratio 1:1 to acetone (2 g acetone). Acetone is added to the mixture and the man's lid is covered with aluminum foil and put in ultrasonic bath for 24 minutes to disperse the solution then, with a 100 µlit micro sampeller, we pour a certain volume of the mixture onto the pre-prepared electrode so that it covers the surface of the electrode completely evenly. We then allow the electrode to remain in the environment for one day and dry the glue.

2.4. Electrochemical experiments

The electrochemical measurements were carried out using an AUTOLAB PGSTAT 35 model potentiostat-galvanostat. A three-electrode cell, consisting of mild steel working electrode (WE), a platinum counter electrode (CE) and a saturated silver-silver chloride (3.0 M) (Ag/AgCl) electrode as a reference electrode, was used for measurements. All experiments were performed in atmospheric condition without stirring. Before electrochemical measurements, the mild steel electrode was immersed into the corrosive solutions for 1 h in order to establish a steady-state open circuit potential (E_{ocp}). Then, EIS and potentiodynamic polarization measurements were carried out subsequently. Before polarization and EIS measurements, the working electrode was immersed into the test solution and left for 60 min at the open circuit potential (OCP). A scan rate of potential was 0.5 mV/s and potential was scanned in the range of -900 to +900 mV relative to the corrosion potential. In the case of electrochemical impedance spectroscopy, a.c. signals of 10 mV amplitude and various frequencies from 100 kHz to 0.01 Hz at open circuit potential were impressed to the mild steel electrode

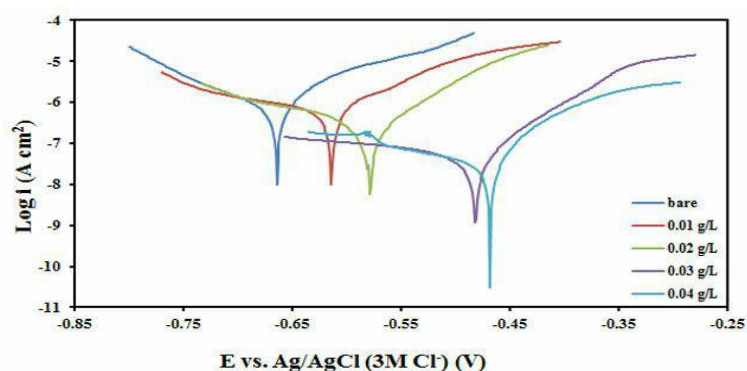


Fig. 1. Polarization curves of mild steel in absence and present coatings in 3.5% NaCl media.

Table1: Corrosion parameters of ZnO-Cr₂O₃/epoxy nanocomposite coated on mild steel in 3.5% NaCl media.

Extract (g/L)	i_{Corr} ($\mu\text{A}/\text{cm}^2$)	E_{Corr} (mV)	β_a (V/dec)	β_c (V/dec)	CR (mm year ⁻¹)	PE%
Blank	1.90	-651.2	0.08807	0.14827	0.02	-----
0.01	0.62	-454.8	0.15077	0.33681	0.02	67.2
0.02	0.24	-318.5	0.23735	0.17164	0.005	87.3
0.03	0.033	-295.0	0.26439	0.25609	0.002	98.3
0.04	0.004	-202.4	0.11549	0.08765	0.001	99.7

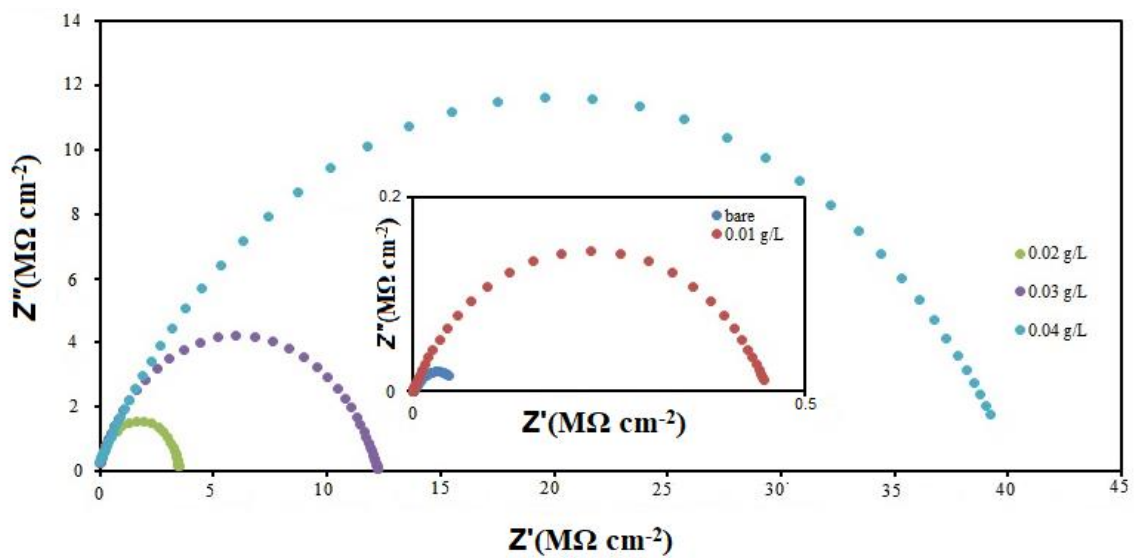
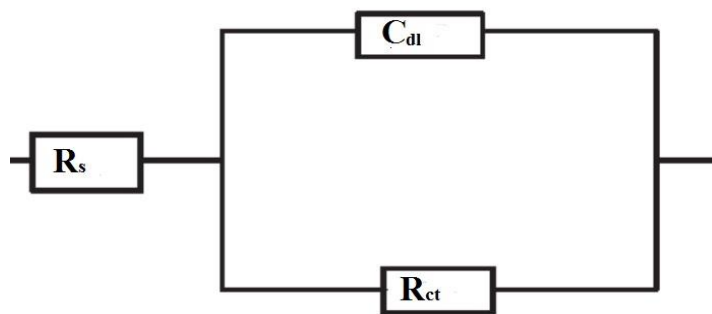
**Fig2:** Impedance spectra of mild steel in 3.5% NaCl solution with and without the nanocomposite coating.**Fig3:** Equivalent electrical circuit for the corrosion of mild steel in 3.5% NaCl solution.

Table2: Electrochemical impedance parameters for mild steel in 3.5% NaCl in absence and presence of ZnO-Cr₂O₃ nanocomposite coating.

Etract (g/L)	R _s (Ω cm ⁻²)	R _{ct} (MΩ cm ⁻²)	C _{dl} (μF)	PE _{EIS} %
Blank	0.002	0.08	0.795	-----
0.01	0.038	0.45	0.104	82.22
0.02	0.040	3.78	0.0098	97.88
0.03	0.056	12.50	0.00089	99.36
0.04	0.080	40.10	0.00015	99.80

3. Results and discussion

3.1. Potentiodynamic polarization studies

Fig. 1 demonstrates the potentiodynamic polarization curves of the ZnO-Cr₂O₃/epoxy coatings on the mild steel. The electrochemical data extracted from the polarization curves are also summarized in Table 1. The lowest corrosion current density (*I*_{corr}) is related to a mild steel coating containing 0.04g/L ZnO/Cr₂O₃ nanoparticles. Therefore, ZnO/Cr₂O₃ nanoparticles coatings exhibit the lowest corrosion rate. The percentage protection efficiency (PE%) for each ZnO-Cr₂O₃/epoxy nanocomposite coating was calculated using the relationship given below and their values are mentioned in Table 1[35, 36]:

$$PE\% = \frac{I_{corr} - I_{corr(c)}}{I_{corr}} \times 100 \quad (1)$$

Where, *I*_{corr} and *I*_{corr(c)} are the corrosion current densities without and with the ZnO-Cr₂O₃/epoxy nanocomposite, respectively.

From Fig. 1, it is clear that the presence of ZnO-Cr₂O₃/epoxy nanocomposite coatings causes a prominent decrease in the corrosion rate i.e. shifts both anodic and cathodic curves to lower values of current densities. Namely, both cathodic and anodic reactions are drastically retarded by ZnO-Cr₂O₃/epoxy nanocomposite coatings in 3.5% NaCl [36]. Inspection of Table 1 reveals that *I*_{corr} decreases considerably in the presence of ZnO-Cr₂O₃/epoxy nanocomposite

coatings with increasing concentration of ZnO/Cr₂O₃ nanoparticles. Correspondingly, PE% increases with the ZnO-Cr₂O₃ nanoparticles concentration. PE% of 0.04 g/L of ZnO-Cr₂O₃ nanoparticles reaches up to a maximum of 99.7%. Table 1 shows a slight change in anodic and cathodic Tafel slopes for all of nanocomposite coatings in all concentrations. This means that the presence of nanocomposite coatings in the test solution does not modify the process mechanism and act as adsorptive inhibitor, retarding both cathodic and anodic reaction by blocking the active sites [38]. From Table 1 also can find that the corrosion potential of coatings changed slightly towards the positive direction. It was apparent that the current values of the coated sample are lower than that of the bare sample and corrosion potential of the coated sample is shifted to anodic direction. This result was pointed out the protective property of the coating against corrosive medium [39].

3.2. EIS analysis

The electrochemical impedance spectroscopy (EIS) measurement was conducted to compare and investigate the anticorrosion performance of ZnO-Cr₂O₃/epoxy nanocomposite coatings. Before electrochemical test, the samples were immersed in 3.5% NaCl solution for 1 h to obtain a stable open circuit electrode.

Fig. 2 shows the Nyquist plots of the composite coatings corresponding to ZnO-Cr₂O₃/epoxy nanocomposite and the uncoated mild steel after 1 h of immersion in 3.5%

NaCl aqueous solution. The radius of impedance arc of uncoated mild steel was smaller than nanocomposite coatings. The size of the radius delegated the size of impedance thus the impedance of uncoated mild steel was the lowest amongst the four nanocomposite coatings.

The Nyquist plot contains a depressed semicircle with the center under the real axis, such behavior is characteristic for solid electrode which is attributed to surface roughness and inhomogeneities of metalelectrodes. The existence of a single semicircle shows the presence of single charge transfer process during dissolution, which is unaffected by the presence of an inhibitor molecule. The corresponding equivalent circuit for this behavior is reported in Fig. 3 [16]. This circuit consists of solution resistance (R_s), charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}).

The protection efficiency obtained from the charge-transfer resistance is calculated by the following relation [40]:

$$PE(\%) = \frac{R_{ct(c)} - R_{ct}}{R_{ct(c)}} \times 100 \quad (2)$$

Where, $R_{ct(c)}$ and R_{ct} are the charge-transfer resistances in the presence and absence of the ZnO-Cr₂O₃/ epoxy nanocomposite coating.

The mild steel surfaces coated with ZnO-Cr₂O₃/Epoxy nanocomposite show the similar Nyquist plot and the proposed equivalent circuit as observed for neat epoxy resin. This means that ZnO-Cr₂O₃ nanoparticles cannot retard the diffusion of corrosive electrolyte to the interface of coating and substrate completely. The fitted EIS parameters are shown in Table 2. Generally, the fitted data match the experimental, with an average error of about 4.0%. From Table 2, the higher coating resistance and the lower coating capacitance values of epoxy coating containing ZnO-Cr₂O₃ nanoparticles indicate the more protection ability of ZnO-Cr₂O₃/Epoxy nanocomposite [16, 41]. The best protection efficiency was achieved by epoxy resin containing 0.04 g/L ZnO-Cr₂O₃ nanoparticles. The PE%

calculated from EIS data is found to be 99.5 % for 0.04g/L ZnO-Cr₂O₃/epoxy nanocomposite-coated mild steel, which is in agreement with the potentiodynamic polarization results.

3.4. AFM characterization

AFM is a powerful technique to investigate the surface morphology and study the influence of nanocomposite on the generation and the progress of the corrosion at the metal/solution interface. AFM images (Fig 4) of the polished mild steel and mild steel after immersion for 60 min in 3.5% NaCl solution in absence and presence of ZnO-Cr₂O₃/epoxy nanocomposite coating. It can be seen from Fig. 4 that the mild steel samples before immersion seem smooth and appear some abrading scratches on the surface. After immersion in uninhibited 3.5% NaCl solution for 1 h, the mild steel surface appears an aggressive attack of the corroding medium as shown in Fig.4. These images showed that decrease surface roughness for mild steel immersed in chloride solution in presence ZnO-Cr₂O₃/epoxy nanocomposite coatings.

4. Conclusion

Incorporating nano ZnO-Cr₂O₃ particles into epoxy amine coatings improves the anti-corrosive properties, water barrier properties and abrasion resistance properties of coatings. In this work the best performance of the ZnO-Cr₂O₃ coating is observed at 0.04 g/L concentration of nano ZnO-Cr₂O₃ inside epoxy matrix. Maximum protection corrosion found at a very specific concentration of 0.04 g/L of nano ZnO-Cr₂O₃. AFM image confirmed the exfoliation and better embedded ZnO-Cr₂O₃ nanoparticles inside epoxy at high concentration of 0.04g/L. Comparative surface topographs and surface profiles of neat epoxy and ZnO-Cr₂O₃ nanoparticles confirm regular profile and protrusion of particles, respectively, analyzed by AFM.

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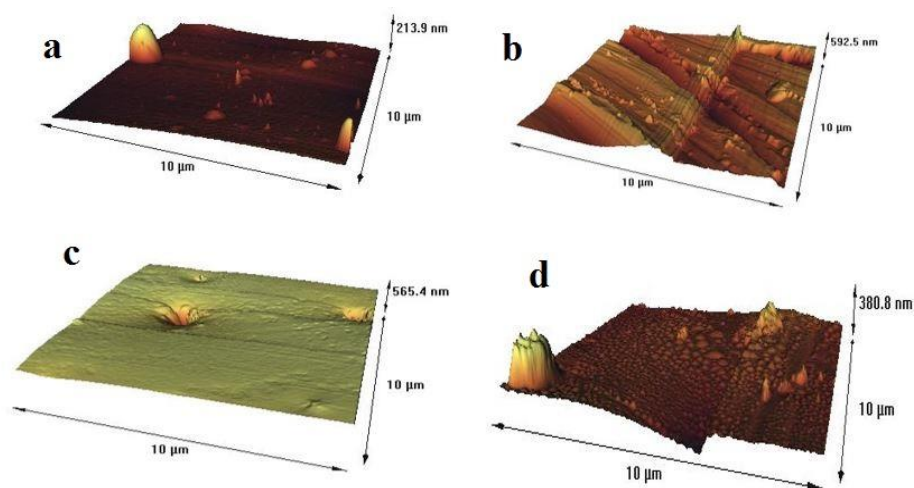


Fig4: AFM images of specimens: a) polished mild steel electrode b) pre-treated mild steel after corrosion c) ZnO-Cr₂O₃/epoxy nanocomposite (0.04 g/L) coated on mild steel d) ZnO-Cr₂O₃/epoxy nanocomposite (0.04 g/L) coated on mild steel in corrosion media.

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