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Corrosion protection of magnesium ZM 21 alloy with polyaniline–TiO_2 composite containing coatings

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Abstract

A polyaniline–TiO_2 composite (PTC) was prepared by oxidative polymerization of aniline in phosphoric acid with ammonium persulphate, in the presence of TiO_2. The composite was characterized by spectroscopic methods. An acrylic paint containing the PTC was prepared and the coating formed on magnesium alloy was evaluated by electrochemical impedance spectroscopy after exposure to salt spray test for a period of 250 h. The coating containing the PTC was found to protect the magnesium alloy more efficiently than the coating containing polyaniline.

Keywords: Polyaniline; Polyaniline–TiO_2 composite; Magnesium alloy; Corrosion; EIS

1. Introduction

Magnesium and its alloys are extensively used in automobile and aerospace components due to their high strength, weight ratio, thermal conductivity, good electromagnetic shielding characteristics and high damping characteristics [1]. But magnesium and its alloys have poor corrosion and wear resistance, poor creep resistance and high chemical reactivity. Besides, magnesium alloys undergo severe galvanic and pitting corrosion. To minimize the corrosion of magnesium and its alloys, electrochemical plating, conversion coatings, anodizing, gas-phase deposition, laser surface alloying, cladding and organic coatings are employed [2]. The organic coatings for magnesium alloys are based on resins such as polyvinyl butyral, acrylic polyurethane, vinyl, epoxy and baked phenolic containing zinc chromate or strontium chromate [3,4]. Due to high carcinogenic nature of chromate, other pigments such as zinc phosphate and zinc molybdate have been used in the organic coating system [5]. In recent years, it has been shown that conducting polymers such as polyaniline (PANI), polypyrrole can be applied on steel as corrosion protective coatings and the mechanism of protection is formation of passive film on the metal surface. The reviews summarize the application of conducting polymers for corrosion control of ferrous and non-ferrous metals [6–9]. The use of conducting polymers for corrosion protection of magnesium is not well studied. Truong et al. [10] have shown that the paint containing polypyrrole coated magnesium samples show insignificant corrosion protection in salt spray test and the pitting potential is shifted to noble direction. The authors [11] have studied the corrosion resistant property of PANI—acrylic coating on magnesium alloy and found that the PANI containing coating is able to protect magnesium alloy in 0.5% NaCl solution up to 75 days. In this paper, the performance of acrylic coating containing polyaniline-TiO_2 composite (PTC) on the protection of magnesium ZM 21 alloy is reported.

2. Experimental

2.1. Preparation of PTC pigment

One mole of distilled aniline was dissolved in 500 ml of 1 M solution of phosphoric acid containing 25 gm of TiO_2. Pre-cooled 500 ml of 1 M solution of ammonium persulfate was added drop wise to the pre-cooled aniline–acid mixture for about 1.5 h with constant stirring. The reaction was conducted at $5 \pm 1\,^{\circ}C$. After the addition, the stirring was continued for 2 h for ensuring complete polymerization. A dark green coloured conducting PTC thus formed was filtered and repeatedly washed with distilled water to remove excess acid content. The polymer was dried in oven at about 80 °C for 2 h. The dried polyaniline was fine grinded using mortar and then used as pigment.

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2.2. Characterization of PTC pigment

The X-ray diffraction pattern of PANI–phosphate pigment powder was taken with an Analytical (Model PW3040/60) X-ray diffractometer using Cu Kα radiation in the 2θ range 5–75° at the scan range of 0.0170° 2θ with continuous scan type with scan step time of 15.5056 s. The infrared spectra of the polymer were recorded on NICOLET 380 FTIR spectrometer in KBr medium at room temperature in the region of 2000–500 cm^{-1}. The morphology of the pigment was analyzed at a magnification of 1 k using Hitachi (Model S3000 H) scanning electron microscope by spreading the pigment over a copper block over which gold was sputtered. The electrical conductivity of the pigment was found by four-probe resistivity meter.

2.3. Preparation of PTC pigmented paint

A commercially available acrylic resin (Kondicryl 166, Pidilite, India) was used for formulating acrylic primer. The primer was formulated with 30% volume solids and 35% pigment volume concentration using titanium dioxide and polyaniline conducting polymer doped with phosphate as main pigments.

Polyurethane topcoat was prepared by taking acrylic polyol (Pidilite, India) as base. The paint was prepared in a lab attritor with 40% volume solids. The pigments were premixed before mixing with the resin. The mixture of xylene and butyl acetate was taken as solvent. The attritor was run for 45 min. The paint was transferred to an airtight container. The paint was mixed with aliphatic polyisocyanate curing agent in the mix ratio of 2:1 and applied over the primer after 24 h as topcoat.

- The formulation details of the primer and the topcoat are:
  - Volume of solids: 30%;
  - Pigment volume concentration: 35%;
  - Pigments: PTC, TiO_2, talc, silica and aluminium sterate;
  - Specific gravity: 1.01 g/cm^3;
  - Dry film thickness: 55 ± 2 μm.
- The details of the top coat are:
  - System: Acrylic-polyurethane;
  - Volume of solids: 40%;
  - Pigment volume concentration: 18%;
  - Pigments: TiO_2, talc, mica, silica;
  - Specific gravity: 1.08 g/cm^3;
  - Dry film thickness: 35 ± 2 μm.

2.4. Water uptake studies of coating

The total paint system was applied over 5 cm × 7.5 cm glass plates by means of brush and allowed to cure for seven days at ambient temperature. Triplicate samples were prepared for this test. These coated glass panels were weighed in an electronic balance (Shimadzu, Model AX200) with an accuracy of 0.1 mg and immersed in a 500 cm^3 beaker containing 400 cm^3 of distilled water. The panels were reweighed after regular time intervals after removing the surface water by means of a filter paper. The average weight gain was measured up to 10 days.

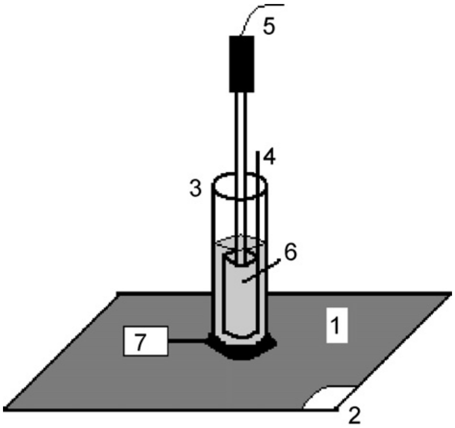


Fig. 1. Experimental cell setup. (1) Painted magnesium alloy panel, (2) paint removed area for making working electrode contact, (3) Teflon tube, (4) platinum counter electrode, (5) SCE reference electrode, (6) test electrolyte, (7) silicon grease.

2.5. Evaluation of corrosion resistant properties of the coating

Magnesium alloy (ZM 21) specimens of size 5 cm × 5 cm × 0.1 cm were polished and degreased with trichloroethylene and coated with PTC pigment containing paint. The total thickness of the coating was 100 ± 5 μm. The coated panels were exposed to salt spray of 5% NaCl solution as per ASTM B117.

The panels exposed to salt spray fog was periodically removed and after air drying a Teflon tube of inner diameter 1.2 cm was fixed over the coated panel using silicone vacuum grease. 3% NaCl solution was poured into the tube and a platinum foil and saturated calomel electrode (SCE) were placed inside. The schematic diagram of the experimental cell assembly is shown in Fig. 1. The assembly was connected to electrochemical impedance analyzer (Model 6310, EG&G). Impedance measurements were carried out for a frequency range of 100 KHz to 0.01 Hz with an ac amplitude of 20 mV for different immersion time up to 75 days. Higher amplitude of 20 mV is used since the impedance of the system is very high. Using Z view software, the impedance data were analysed. The impedance values are reproducible ±2–3%. From the impedance plots, the coating resistance (R_c) and the coating capacitance (C_c) values were calculated using the equivalent circuit shown in Fig. 2. In the equivalent circuit, R_s is the solution resistance, R_c is the coating resistance and CPE is the constant phase element of the coating capacitance (C_c).

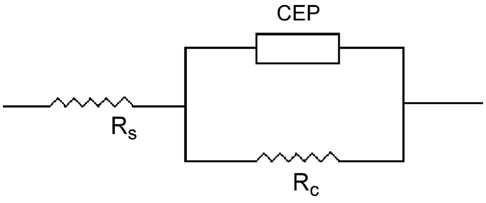


Fig. 2. Equivalent circuit for painted magnesium alloy panel.

Assumption of a simple R_c–C_c is usually a poor approximation. For the description of a frequency independent phase shift between an applied ac potential and its current response, a constant phase element (CPE) is used which is defined in impedance representation as

$$Z(\mathrm{CPE}) = Y_0^{-1}(\mathrm{j}\omega)^{-n}$$

where Y_0 is the CPE constant, ω the angular frequency (in rad s^{-1}), $\mathrm{j}^2 = -1$ the imaginary number and n is the CPE exponent. Depending on n, CPE can represent resistance ($Z(\mathrm{CPE}) = R$, $n = 0$), capacitance ($Z(\mathrm{CPE}) = C$, $n = 1$),inductance ($Z(\mathrm{CPE}) = L$, $n = -1$) or Warburg impedance for ($n = 0.5$) [12]. The following equation used to convert Y_0 into C_c is [13],

$$C_c = Y_0(\omega''_m)^{n-1}$$

where C_c is the coating capacitance and is ω''_m the angular frequency at which Z'' is maximum. After the measurements were over, the Teflon tube was removed and the painted surface was degreased using trichloroethylene and put back into the salt spray chamber.

3. Results and discussion

3.1. Characterisation of PTC pigment

3.1.1. XRD analysis

Fig. 3 shows the XRD pattern of PTC. It confirms that the polyaniline deposited on the surface of TiO_2 particles has no effect on the crystallization behaviour of TiO_2 particles. Xu et al. [14] and Lee et al. [15] have recorded similar observation on the XRD pattern of polyaniline-nano TiO_2 composites.

3.1.2. Infrared analysis

Fig. 4 shows the FTIR spectra of PANI–TiO_2 composite (PTC). The main characteristics of bands of polyaniline are found, i.e., the bands at 1574 and 1484 cm^{-1} are the stretching mode of C=N and C=C, the bands at 1297 and 1245 cm^{-1} are to C–N stretching mode of benzenoid ring and the band at 1109 cm^{-1} is assigned to a plane bending virbration of C–H mode which is found during protonation [16]. These peaks when compared to that of pure polyaniline [17] are found to be shifted slightly due to strong attraction of TiO_2 particle with polyaniline. Similar observation has been reported by Lee et al [14]. In the case of TiO_2, strong absorption around 670 cm^{-1} due to Ti–O stretching [15] is observed while this band is found to be weak in PTC due to the presence of PANI.

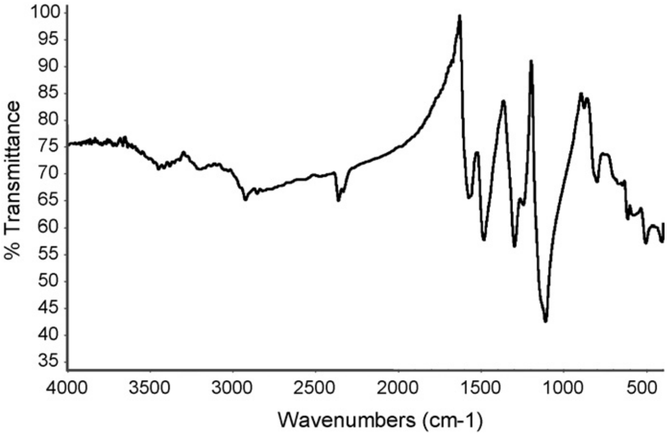


Fig. 4. FTIR spectra of PANI–TiO_2 composite.

3.1.3. Conductivity studies

The electrical conductivity of PANI–TiO_2 composite is found to be 0.0125 $\mathrm{S\,cm}^{-1}$. The reported values of the conductivity are $2.4 \times 10^{-3}\ \mathrm{S\,cm}^{-1}$ [14], 0.04 $\mathrm{S\,cm}^{-1}$ [15] and 0.16 to 7.0 $\mathrm{S\,cm}^{-1}$ [18].

3.1.4. SEM studies

Fig. 5 shows the morphology of the PTC pigment. It is found that PTC pigment shows a globular structure consisting of small globules and pores.

3.2. Evaluation of coating

3.2.1. Water uptake studies

Fig. 6 shows the water uptake values with immersion time. The average value is 1.0 ± 0.2 mg in the case of PANI coatings and 0.6 ± 0.2 mg in the case of PTC coatings.

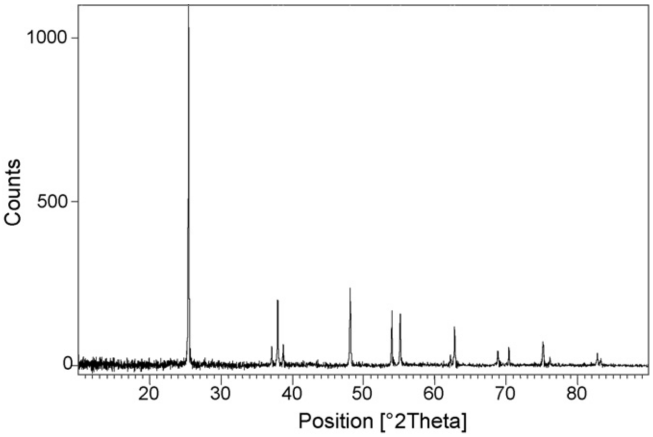


Fig. 3. XRD pattern of PANI–TiO_2 composite.

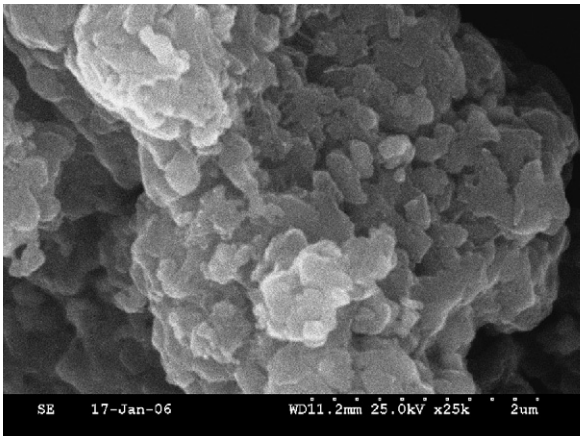


Fig. 5. Scanning electron micrograph of PTC.

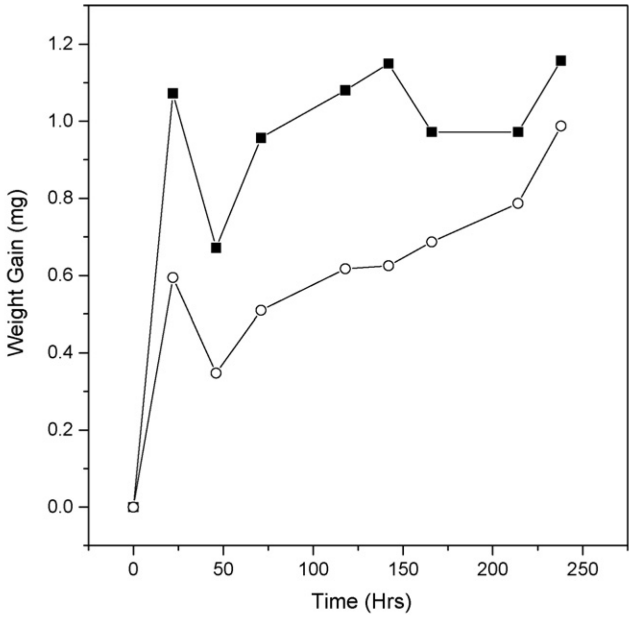


Fig. 6. Water up-take of paint films (■) PANI + TiO_2; (○) PTC.

3.2.2. EIS studies of coated magnesium alloy after salt spray exposure test

The corrosion protection performance of the polyaniline and PTC containing coating on magnesium alloy has been found out by salt spray exposure test as per ASTM B117. The specimens were visually examined periodically and even after 250 h of salt spray exposure, it has been found that there is no corrosion product observed on the coated surface. Besides the visual inspection, the coatings performance has been periodically found out by EIS. Figs. 7–9 show the impedance variation of magnesium alloy coated with polyaniline, 25% PTC and 40% PTC containing coatings after salt spray exposure test, respectively. The variation of coating's resistance and capacitance with time is given in Tables 1–3.

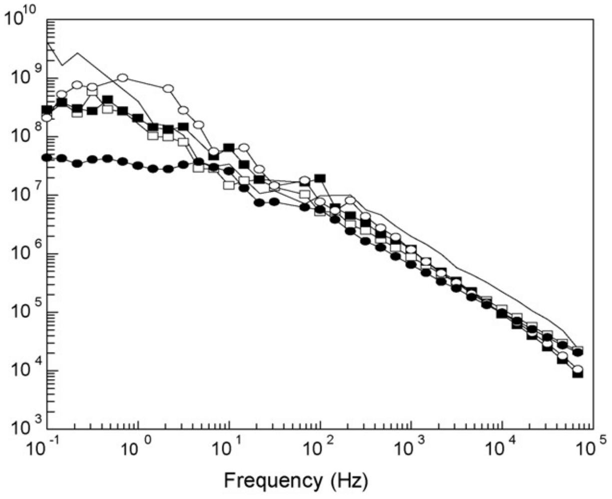


Fig. 7. Impedance plots of PANI + TiO_2 containing paint coated magnesium alloy in 3% NaCl after salt spray exposure. (—) Initial; (□) 24 h; (■) 50 h; (○) 100 h; (●) 250 h.

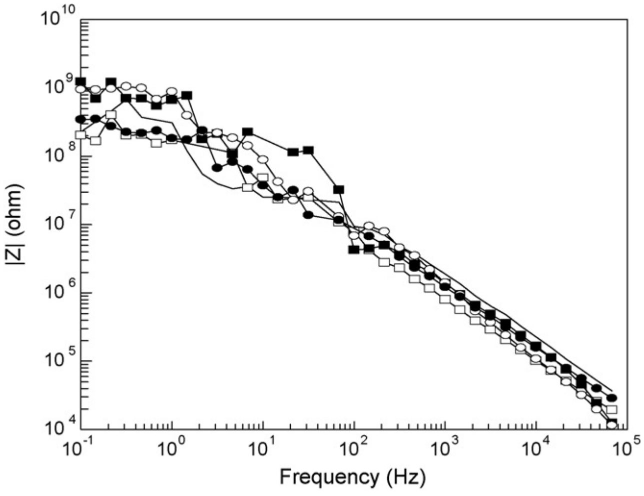


Fig. 8. Impedance plots of 25% PTC containing paint coated magnesium alloy in 3% NaCl after salt spray exposure. (—) Initial; (□) 24 h; (■) 50 h; (○) 100 h; (●) 250 h.

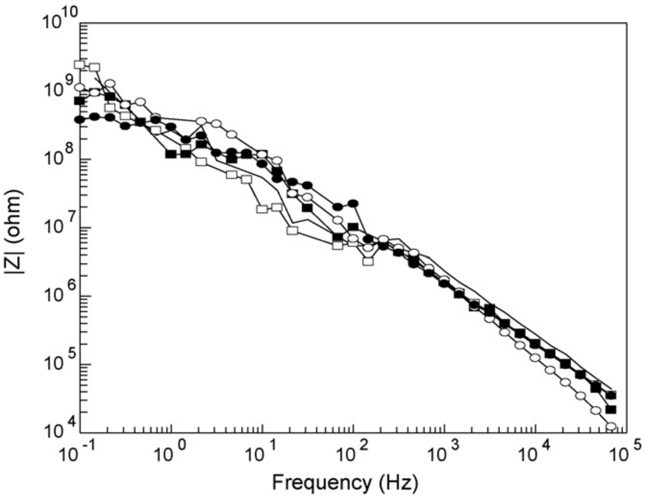


Fig. 9. Impedance plots of 40% PTC containing paint coated magnesium alloy in 3% NaCl after salt spray exposure. (—) Initial; (□) 24 h; (■) 50 h; (○) 100 h; (●) 250 h.

In the case of PANI containing coating, the initial resistance value of the coating is found to be $2.08 \times 10^8\ \Omega\,cm^2$. After 250 h of salt spray test, the resistance value of the coating is $3.09 \times 10^7\ \Omega\,cm^2$. It can be seen that PANI containing coating is

Table 1
Impedance parameters of PANI + TiO_2 containing paint coated magnesium in 3% NaCl after salt spray exposure

Time (h)	R_c ($\Omega\,cm^2$)	Y_0 ($\Omega^{-1}\,s^n$)	n	C_c ($F\,cm^{-2}$)
Initial	2.08×10^9	4.33×10^{-10}	0.85	2.86×10^{-10}
4	1.89×10^9	1.49×10^{-10}	0.95	1.63×10^{-10}
24	3.33×10^8	5.16×10^{-10}	0.88	5.26×10^{-10}
50	3.12×10^8	1.28×10^{-10}	1	1.28×10^{-10}
75	4.26×10^8	1.56×10^{-10}	1	1.56×10^{-10}
100	1.13×10^8	1.26×10^{-10}	1	1.26×10^{-10}
200	3.02×10^7	5.18×10^{-10}	0.88	2.93×10^{-10}
250	3.09×10^7	9.76×10^{-10}	0.84	5.17×10^{-10}

Table 2
Impedance parameters of 25% PTC containing paint coated magnesium in 3% NaCl after salt spray exposure

Time (h)	R_c ($\Omega\,cm^2$)	Y_0 ($\Omega^{-1}\,s^n$)	n	C_c ($F\,cm^{-2}$)
Initial	9.94×10^9	4.14×10^{-10}	0.83	2.42×10^{-10}
4	9.16×10^9	4.82×10^{-11}	1	4.82×10^{-11}
24	2.34×10^9	1.72×10^{-10}	0.98	1.66×10^{-10}
50	1.12×10^9	8.05×10^{-11}	1	8.05×10^{-11}
75	1.77×10^9	1.44×10^{-10}	0.96	1.35×10^{-10}
100	1.01×10^8	1.20×10^{-10}	1	1.20×10^{-10}
200	2.84×10^8	3.49×10^{-10}	0.88	2.54×10^{-10}
250	2.91×10^8	4.05×10^{-10}	0.87	2.95×10^{-10}

able to protect magnesium alloy since the variation in resistance value is low. During the period of testing, the capacitance values of the coating are in the range 1.2 to $5.1 \times 10^{-10}\,F\,cm^{-2}$ which indicates the low amount of water absorption by the coating.

From the Table 2, the resistance value of the 25% PTC containing coating after 250 h of salt spray exposure is found to be $2.91 \times 10^8\,\Omega\,cm^2$ which is not much different from that of initial value $9.94 \times 10^8\,\Omega\,cm^2$. On comparing the resistance value of PANI containing coating, the resistance value of PTC containing coating is nearly one order high which indicates the high protection ability of the composite containing coating. The capacitance values of the coating containing 25% PTC are in the range of 0.4 to $2.9 \times 10^{-10}\,F\,cm^{-2}$ during the test period. The low value of the capacitance values indicates the absence of corrosion reaction.

The value of resistance of coating (Table 3) of 40% PTC containing coating is $5.81 \times 10^9\,\Omega\,cm^2$ initially and after 250 h of sal spray exposure, it is $3.63 \times 10^8\,\Omega\,cm^2$. This value is also one order high when compared to that of PANI containing coating. Besides the capacitance values are not changed markedly.

The above studies indicate that the polyaniline–TiO_2 composite containing coating is more corrosion resistant than that of PANI containing coating. This may be due to uniform distribution of PANI in the coating containing composite which felicitates the passivation of magnesium alloy more uniformly.

The results obtained from the impedance values of coated magnesium alloy after salt spray test indicate the protective nature of the coating containing polyaniline and PANI composite. In general, the magnesium corrosion reaction in neutral media can be given as follows:

Table 3
Impedance parameters of 40% PTC containing paint coated magnesium in 3% NaCl after salt spray exposure

Time (days)	R_c ($\Omega\,cm^2$)	Y_0 ($\Omega^{-1}\,s^n$)	n	C_c ($F\,cm^{-2}$)
Initial	5.81×10^9	8.43×10^{-11}	0.97	1.26×10^{-10}
4	1.09×10^9	5.93×10^{-11}	1	5.93×10^{-11}
24	3.14×10^9	2.42×10^{-10}	0.90	2.35×10^{-10}
50	1.53×10^9	1.29×10^{-10}	0.96	1.51×10^{-10}
75	2.58×10^8	1.61×10^{-10}	0.92	1.23×10^{-10}
100	1.13×10^9	1.18×10^{-10}	0.99	1.17×10^{-10}
200	1.13×10^9	1.72×10^{-10}	1	1.72×10^{-10}
250	3.63×10^8	1.76×10^{-10}	0.93	1.41×10^{-10}

Anodic reaction:

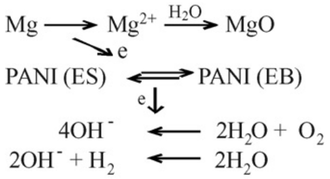
$$Mg \rightarrow Mg^{2+} + 2e$$

Cathodic reactions:

$$O_2 + 2H_2O + 4e \rightarrow 4OH^-$$

$$2H_2O + 2e \rightarrow H_2 + 2OH^-$$

However, the presence of PANI in the coating maintains the passive state on the metal surface by the reduction of the PANI (Emeraldine salt). The reduced PANI (Leuco Emeraldine base) is again oxidized to original form by the oxygen reduction reaction occurring on PANI. Due to this cyclic reaction, the metal is also covered with a passive film. The mechanism of protection is shown schematically as follows. This type of mechanism has been proposed by several workers [19–23] for the protection of steel by PANI.



4. Conclusion

The chemically prepared polyaniline and polyaniline–TiO_2 composite containing coatings are able to protect magnesium alloy from corrosion. The corrosion protection ability of PTC containing coating is found to be more than that of PANI containing coating due to the uniform distribution of PANI which can protect the metal surface more uniformly.

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