Corrosion resistant properties of polyaniline–acrylic coating on magnesium alloy

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Abstract

The performance of the paint coating based on acrylic–polyaniline on magnesium alloy ZM 21 has been studied by electrochemical impedance spectroscopy in 0.5% NaCl solution. The polyaniline was prepared by chemical oxidative method of aniline with ammonium persulphate in phosphoric acid medium. The phosphate-doped polyaniline was characterized by FTIR and XRD methods. Acrylic paint containing the phosphate-doped polyaniline was prepared and coated on magnesium ZM 21 alloy. The coating was able to protect the magnesium alloy and no base metal dissolution was noted even after 75 days exposure to sodium chloride solution.
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1. Introduction

Magnesium and its alloys have got potential applications in automobiles, electronics, aerospace and aviation. Due to their high corrosion activity, their applications are limited. Various types of protective coatings are applied to magnesium and its alloys in order to reduce the corrosion [1,2]. The primers for magnesium alloys are based on resins such as polyvinyl butyral, acrylic, polyurethane, vinyl, epoxy, baked phenolic with zinc or strontium chromates and titanium dioxide pigments [3–5]. Due to high toxicity and carcinogenic nature of chrmoates, alternate inhibiting pigments such as zinc molybdate and zinc phosphate have been considered [6]. In recent years, studies have shown that conducting polymers such as polyaniline and polypyrrole have been found to offer corrosion protection of iron, steel [6–13], aluminium [14,15] due to its higher stability in air, adhesion and redox properties with the substrate.

The use of polypyrrole as pigment for the protection of magnesium alloy has been reported recently by Truong et al. [16] and Yfantis et al. [17] in acrylic coating system. Their studies have shown that the corrosion protection by the coating containing polypyrrole is superior to the sample coated without polypyrrole. In the earlier study [18] by the authors, the performance of the polyaniline (PANI) in epoxy containing coating on magnesium alloy has been compared with that of strontium chromate in epoxy and found that PANI containing coating has performed equal to that of chromate containing coating. In this paper, the results of the study of the acrylic coating containing PANI on magnesium alloy ZM 21 are reported.

2. Experimental

2.1. Preparation of PANI–phosphate pigment

One molar of distilled aniline was dissolved in 500 ml of 1 M solution of phosphoric acid. 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 $5 \pm 1\,°C$. After the addition, the stirring was continued for 2 h for ensuring complete polymerization. A dark green coloured conducting polyaniline 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 morter and then used as pigment.

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2.2. Characterization of PANI–phosphate pigment

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}. X-ray diffraction pattern of PANI–phosphate pigment powder was taken with analytical (Model PW3040/60) X-ray diffractometer using Cu Kα radiation in the 2θ range 5–75° at the scan rage of 0.0170° 2θ with continuous scan type with scan step time of 15.5056 s. The morphology of the pigment was analyzed at a magnification of 1k 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 PANI–phosphate pigmented paint

A commercially available acrylic resin (Kondicryl 166, Pidilite, India) is 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 pre mixed before mixing it 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 polyisocyante 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 concentraiton: 35%,
pigments: PANI–phosphate, TiO_2, talc, silica and aluminium state,
specific gravity: 1.01 g cm^{-3},
dry film thickness: 55 ± 2 μm.

The details of the topcoat 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 $\times$ 7.5 cm glass plates by means of brush and allowed to cure for 7 days at ambient temperature. These coated glass panels were weighed and immersed in a 500 cm^3 beaker containing 400 cm^3 of distilled water. The panels were reweighed after regular time
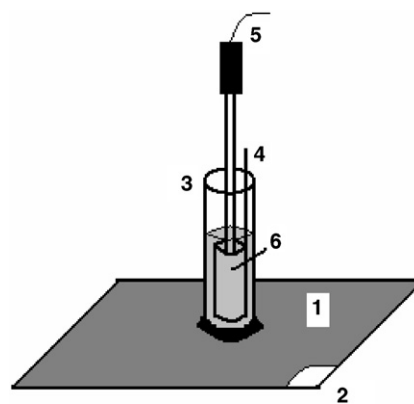

Fig. 1. Experimental cell setup: (1) painted Mg alloy, (2) paint removed area for making working electrode contact, (3) glass tube, (4) platinum counter electrode, (5) SCE reference electrode, (6) test electrolyte.

intervals after removing the surface water by means of a filter paper. The weight gain was measured up to 75 days.

2.5. Evaluation of corrosion resistant properties of the coating

Magnesium alloy (ZM 21) specimens of size 5 cm $\times$ 5 cm $\times$ 0.1 cm were polished and degreased with trichloroethylene and coated with PANI–phosphate pigment containing paint. The total thickness of the coating was 100 ± 5 μm. A glass tube of 0.9 cm diameter of length 3 cm was fixed on the coated aluminium with adhesive (m seal) and the exposed area was 0.64 cm^2 to the solution. The solution of 0.5% NaCl was taken in the glass tube. A platinum foil and a saturated calomel electrode were placed inside the glass tube. 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.

3. Results and discussion

3.1. Characterisation of PANI–phosphate pigment

3.1.1. Infrared analysis

Fig. 2 shows the infrared spectrum for PANI–phosphate pigment. The peak at 820 cm^{-1} is due to the 1,4-para substituted benzene ring. The peaks at 1120 and 620 cm^{-1} are due to in plane and out of plane C–H bending motion of quinoid and benzenoid rings, respectively. The peaks at 1250 and 1350 cm^{-1} are characteristic of aromatic amines. The peaks at 1560 and 1490 cm^{-1} are due to benzenoid and quinoid groups, respectively [19,20]. The peak around 1000 cm^{-1} has been assigned to $H_2PO_4^-$ peak [21]. Further it has been reported that the dopant anions present on PANI/H_3PO_4 are dihydrogen phosphate anions $H_2PO_4^-$ [22,23].
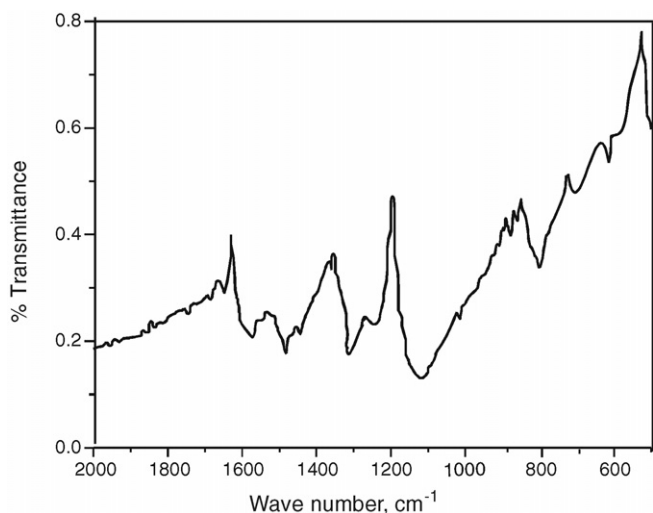
Fig. 2. FTIR spectra of PANI–phosphate pigment.

Fig. 4. Scanning electron micrograph of PANI–phosphate pigment.

3.1.2. XRD analysis

The XRD pattern of the PANI–phosphate pigment is shown in Fig. 3. The intense peak at 2θ around $25°$ has a similar profile as that of free polyaniline reported in literature [24,25]. The diffraction pattern also matches well with the PANI standard pattern (00-053-1890).

3.1.3. Conductivity studies

The conductivity of the pigment has been found to be $2.5\,S\,cm^{-1}$. This value is some what less from the value reported in literature ca. 15.5 [26].

3.1.4. SEM studies

Fig. 4 shows the morphology of the PANI–phosphate pigment. It is found that PANI–phosphate pigment shows a globular structure consisting of small globules and pores. Earlier studies [27] have shown that the morphology of polyaniline–phosphate polymer is dependent on the pH of the solution from which the polymer is prepared.
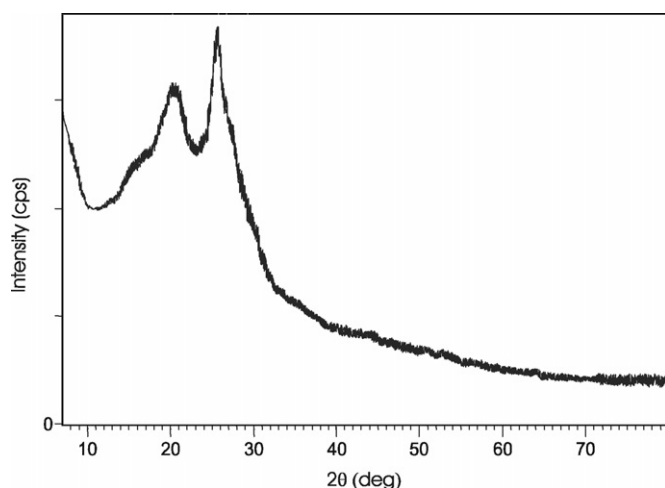
3.2. Evaluation of coating

3.2.1. Water uptake studies

Fig. 5 shows the water uptake values with immersion time. It can be seen that the coating absorbs very low quantity of water and the water uptake is not increased markedly with immersion period. The average value is 0.100 ± 0.025 mg.

3.2.2. Open circuit potential measurements

The variation of the open circuit potential of the coated magnesium alloy in 0.5% NaCl solution is given in Table 1. It can be seen that the potentials are in noble values (i.e. < -0.800 V versus SCE) in comparison to that of bare magnesium alloy (≈ -1.5 V). This shows that the coating is able to offer corrosion protection of magnesium alloy for the

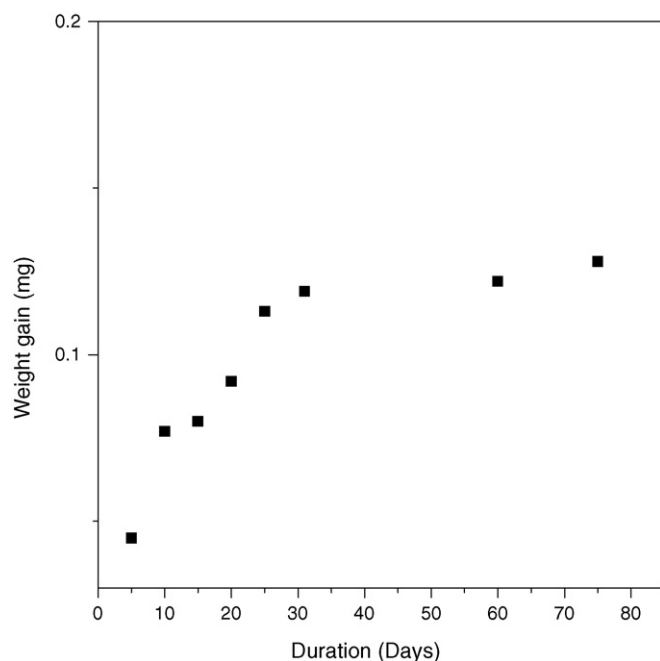Fig. 3. X-ray diffraction pattern of PANI–phosphate pigment.

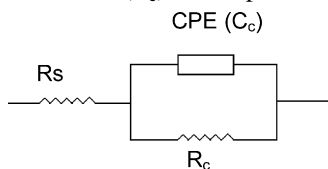Fig. 5. Water up take plot of PANI–phosphate pigment containing coating.

Table 1
Impedance parameters of PANI–phosphate pigmented acrylic coated magnesium ZM 21 alloy in 0.5% NaCl

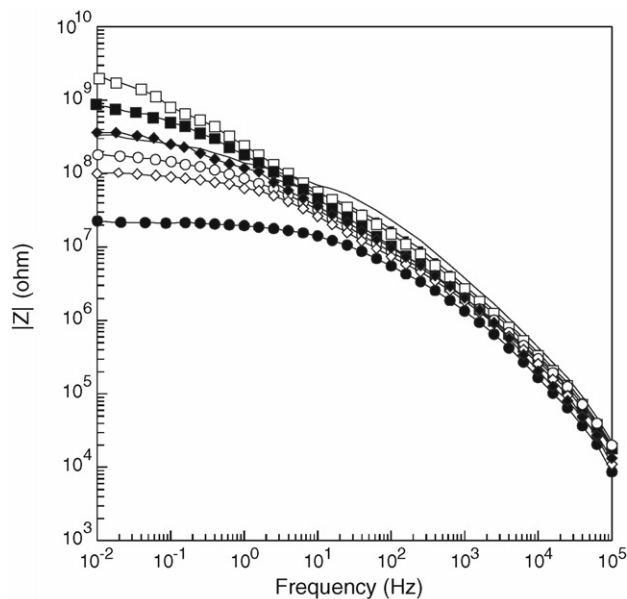| Duration (days)	Open circuit potential V vs. SCE	Coating resistance R_c (Ω cm^2)	Y_0 (Ω^{-1} s^n cm^{-2})	n	Coating capacitance C_c (F cm^{-2})
Initial	−0.272	3.7×10^8	6.72×10^{-10}	0.80	5.55×10^{-10}
1	−0.090	3.5×10^8	2.62×10^{-10}	0.80	1.51×10^{-10}
4	−0.782	2.3×10^9	1.55×10^{-9}	0.80	0.21×10^{-10}
7	−0.419	8.1×10^8	1.31×10^{-9}	0.80	0.13×10^{-10}
15	−0.864	1.8×10^8	1.09×10^{-9}	0.80	0.82×10^{-10}
28	−0.116	2.3×10^7	3.86×10^{-10}	0.80	1.56×10^{-10}
38	−0.535	1.0×10^8	7.52×10^{-10}	0.80	4.76×10^{-10}
75	−0.740	2.5×10^8	9.45×10^{-10}	0.80	7.29×10^{-10}

Fig. 6. Impedance plots of PANI–phosphate pigmented acrylic coated. Magnesium ZM 21 alloy in 0.5% NaCl. (—) Initial; (●) 1 day; (□) 3 days; (■) 7 days; (○) 15 days; (●) 28 days; (◇) 38 days; (◆) 75 days.

studied period. If corrosion of magnesium alloy takes place, the open circuit potential will be around −1.5 V versus SCE. It has been reported [16] that for the defect area in an acrylic paint coated magnesium sample the open circuit potential fluctuates between −1.65 and −1.56 V versus SCE due to the initiation of corrosion.

3.2.3. EIS studies

The impedance behaviour of coated magnesium alloy in 0.5% NaCl solution is shown in Fig. 6. It can be seen that the impedance values decrease upto 28 days and after words, they are found to be increasing. The spectra show a single time constant due to coating behaviour. Absence of second time constant indicates the absence of any corrosion reaction. Hence the following equivalent circuit was used to obtain the resistance (R_c) and capacitance (C_c) of the coating,

where R_s is the solution resistance, CPE the constant phase element of the capacitance of the coating and R_c is the resistance of the coating. Since the impedance of the metal/coating interface did not behave as an ideal capacitor, a constant phase element (CPE) was used as a substitute for the equivalent circuit to fit more accurately the impedance behaviour of coating capacitance. The admittance of CPE is described as

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

where Y_0 is the CPE constant, ω the angular frequency (in rad s^{-1}), $j^2 = -1$ the imaginary number and n is the CPE exponent. Depending on n, CPE can represent resistance ($Z(\text{CPE}) = R$, $n = 0$), capacitance ($Z(\text{CPE}) = C$, $n = 1$), inductance ($Z(\text{CPE}) = L$, $n = -1$) or Warburg impedance for ($n = 0.5$) [28,29]. The correct equation to convert Y_0 into C_c is [30],

$$C_c = Y_0(\omega_m'')^{n-1} \tag{2}$$

where ω_m is the frequency at which Z'' is maximum. The resistance (R_c) and capacitance (C_c) values of the coating

derived from Fig. 6 are given in Table 1. It is found that the resistance values of the coating exposed to 0.5% NaCl are found to be greater than 1.0×10^8 Ω cm^2 and the value is not significantly changed. The higher coating resistance values show the protective nature of the coating. Besides, the resistance of the coating has started increasing after 28 days of immersion, which shows the passivation effect of the polyaniline pigment. In general, the resistance of the coating decreases with time of exposure due to ingress of water and corrosive ions. However in this case, an increase in coating resistance is observed after 28 days. Similar results have been reported for polyaniline pigmented coating on steel surface due to passivaiton effect of polyaniline [13,31]. However, the studies by Truong et al. [16] on the corrosion protection of magnesium by polypyrrole paint coating have shown that the impedance values of the polypyrrole containing paint coated sample has got low coating resistance values in comparison with the values of the sample coated without polypyrrole due to electrochemical activity. Further no corrosion is observed during the period of study. Besides, the capacitance values of the coating are in the range of 1×10^{-9} to 8×10^{-10} F cm^{-2}, which indicate the coating is intact and no corrosion reaction is initiated.

Earlier studies by Scully and Hensley [32] on the corrosion performance of epoxy polymide coated magnesium alloy ZE41AT5 in 0.5% NaCl solution have shown that the coating with the resistance value greater than 10^8 Ω cm^2 has been found to be protective in nature. In this study also, it has been found that the resistance of the coating is greater than 10^8 Ω cm^2 in 0.5% NaCl solution. This shows the protective nature of the coating. In general, there are four possible mechanisms have been postulated to explain the effectiveness of the corrosion protection of metals by conducting polymers [16]:

(a) the conducting polymer could act as a barrier coating,
(b) the conducting polymer could function to cathodically protect the metal (a sacrificial anode),
(c) the conducting polymer could act as a reservoir for releasing corrosion inhibiting ions, and
(d) the conducting polymer could function to stabilize a passive (oxide) layer similar to chromate compounds.

In this study, it is found that the polyaniline containing paint-coated sample shows an increase in impedance values with time of exposure, which indicates the mechanism of protection is passive film formation.

4. Conclusion

A corrosion protective coating for magnesium alloy ZM 21 comprised of phosphate doped polyaniline in acrylic binder have been described. The coated magnesium alloy showed the open circuit potential values in the noble direction due to passivation ability of the polyaniline. The resistance of the coating is found to be greater than $100\,M\,\Omega\,cm^2$, which indicates the highly protective nature of the coating.

Acknowledgements

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