Corrosion protection by acrylamide treatment for magnesium alloy metal matrix composite (MMC) reinforced with titanium boride

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Using potentiodynamic polarisation, polarisation resistance and electrochemical impedance spectroscopy measurements, the effect of amide treatment to magnesium metal matrix composite in 0.6 N sodium chloride medium has been studied. The corrosion potential $E_{\rm corr}$, corrosion current $I_{\rm corr}$, polarisation resistance $R_{\rm p}$ and charge transfer resistance $R_{\rm ct}$ were determined from the corresponding plots. $E_{\rm corr}$ shifted towards more negative values while $I_{\rm corr}$ decreased with increasing treatment time. Surface analysis with SEM and AFM showed an improvement in surface due to formation of a film. X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) studies confirmed the film formation and the coordination of magnesium to the oxygen in the amide compound.

Keywords: Corrosion, Acrylamide, Magnesium alloy, Coatings, Surface film, Smooth

Introduction

Magnesium is an attractive metal due to its low density, high specific strength and good machinability.¹ As a structural material, it is used in automotive, aerospace, electronic and telecommunication industries. The poor corrosion resistance of magnesium limits its wide application. Protective coatings, mainly organic coatings, have been used to protect magnesium from environmental damage.

Organic coatings serve the primary functions of surface decoration and protection.² The coating process involves two steps: attachment of a bifunctional reagent containing a vinyl group to the surface and extension of the anchored groups through polymerisation. The wide range of applications and the increasing environmental requirements for the coatings indicate the need for developments in organic coating technology to protect magnesium.

Huang *et al.* investigated the improvement in tribological performance of magnesium alloy using amide compounds.³ The film formed on the magnesium alloy was a stable polymer by reaction between magnesium and amide compounds. Mahjani *et al.* have evaluated the corrosion behaviour of organic coatings with electrochemical noise and electrochemical impedance spectroscopy.⁴ Electrolytic penetration through the coating, changes in the characteristics of resistance of the coating and extent of protection were a function of time. Itagaki *et al.* have studied the organic film degradation by impedance measurements.⁵ The equivalent circuit for impedance spectra obtained led to identification of the deterioration mechanism. Hara *et al.* reported the formation and breakdown of surface films on magnesium and its alloys in aqueous solutions.⁶ The current density decreased and the breakdown potential increased with increasing thickness of film formed. The corrosion properties of polyaniline-acrylic coating on magnesium alloy were studied by Sathiyanarayanan *et al.*⁷ These coatings are able to protect the magnesium alloy as a barrier. Han and Park investigated the corrosion under an organic coating.⁸ By analysing the temperature on the surface of the specimen, the location, shape and size of the corroded area were estimated.

Gray and Luan evaluated the protective coatings on magnesium and its alloys used in automotive and aerospace applications.⁹ Magnesium surfaces have to be free of surface contamination, oxides and intermetallic compounds.¹⁰ The magnesium surfaces before the application of an organic coating are treated with an aqueous solution containing an organic compound resulting in increased adhesion of further coating.¹¹ Another process also improves paint adhesion and corrosion resistance for magnesium, where an ester cross-linked polymeric coating is formed by reaction between a polymer rich in carboxyl groups and in hydroxyl groups.¹² Another process demonstrates that the addition of zinc chromate to a phenolic resin primer can significantly improve corrosion resistance.¹³

The corrosion protection of magnesium is improved by addition of a leachable pigment in the form of small spherical aluminium particles.¹⁴ These coatings offer protection by providing resistance to transport of ions, water and oxygen through the film to the substrate.^{15,16} Coating systems consisting of an epoxy primer followed by a polyurethane topcoat yielded a service life of approximately 4–6 years.¹⁷ This layer had excellent

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 Coating weight calculated by weight difference method in magnesium metal matrix composite

adhesion and chemical resistance. The topcoat was flexible and chemically resistant. Use of a multiple layer system ensures that the substrate is completely coated.¹⁸ Another process for eliminating pinholes in organic coatings involves the application of an organic sealant to the coating.¹⁹

In the present work, feasibility of using polyacrylamide for surface treatment of magnesium was investigated. Polyacrylamide is a condensation polymer. The structure of polyacrylamide is similar to that of polyethylene,²⁰ but having hydrogen on every other carbon replaced by an amide group $-CO-NH_2$. The $CONH_2$ group from one molecule can react with the same group of another molecule, forming a link between them with the structure -CONHCO-. This produces a polymer chain. The free, unlinked amide group can bond to form a protective film. This property favours the use of polyacrylamide.

Experimental

The specimens of the magnesium alloy containing 5% titanium boride (Mg MMC) were polished using different grades of emery paper. Then they were degreased with acetone and dried. The specimens were weighed. The specimens were then treated in 10% acryl amide bath for different durations, from 60 to 3600 s. Then the specimens were dried and weighed. The difference in weight was used as a measure of the coating formed. Then, 1×10^{-4} m² area of the sample was marked and the remaining area was covered with lacquer for electrochemical characterisation. The specimens were tested in triplicate for determining the coating weight and for electrochemical characterisation. The data obtained were averaged and reported.

The treated samples were subjected to potentiodynamic polarisation, linear polarisation and electrochemical impedance tests in 0.6 N sodium chloride. The polarisation curves of amide treated magnesium metal matrix composite (MMC) specimens were obtained with Voltalab PGP 201 Potentiostat/Galvanostat. Potentiodynamic polarisation measurements were carried out at ± 0.25 V with respect to open circuit potential. The scan rate was 0.001 V s⁻¹. Impedance curves were obtained with Solartron SI 1280 B. The electrochemical impedance measurements were evaluated over the frequency range 10 000–0.01 Hz. All the experiments were controlled by PC, which was also used for the acquisition,





storage, plotting and analysis of data. The different parameters obtained such as corrosion potential, corrosion current density and charge transfer resistance were averaged and reported.

Fourier transform infrared spectroscopy (FTIR, Model Nexus 670; Thermo Electron Corporation, USA) analysis was conducted for the amide treated samples to identify the surface film formed. The treated samples were also analysed using SEM (Model S-3000H, Hitachi), XRD (Model X'per Pro, PAN Analytical) with Cu K_{α} (2·2 kW) source and AFM (Model Picoscan, PicoSPM) to understand the changes in structure and topography resulting due to this treatment.

Results and discussion

Coating weight

Figure 1 shows the coating weight calculated by weight difference method for magnesium MMC treated in amide bath for different durations. As the treatment time increases from 60 to 3600 s, the weight of film formed also increases. A fourfold increase in coating weight with increasing treatment time, from 0.22×10^{-2} to 0.90×10^{-2} kg m⁻², is observed.

Potentiodynamic polarisation

The potentiodynamic polarisation behaviour of magnesium MMC subjected to different durations of amide treatment in 0.6 N sodium chloride medium is shown in Fig. 2. The Tafel extrapolation method is used to determine the polarisation parameters. It can be seen from this figure that when the treatment time increases, the polarisation curves shift towards more negative corrosion potentials and lower current densities. The results show similar changes in the corrosion potential and the corrosion current values for magnesium MMC with different treatment durations. Such shift in corrosion potential and corrosion current density values is also reported by Montemor, with increasing treatment time,²¹ which is attributed to the surface film formed.

This indicates that the dissolution rate of magnesium in sodium chloride is decreased with increasing treatment time. It can be inferred that due to the amide treatment, a film formation on the magnesium surface occurs. A complex formation occurs in which the metal Mg is coordinated through oxygen.²² The direct reaction of metal ions with acrylamide to form metal complexes



3 Corrosion potential of acrylamide treated magnesium MMC in 0.6 N sodium chloride

of acrylamide is also reported by Angus *et al.* and others.^{23–27}

The effect of amide treatment on the corrosion potential of the magnesium MMC, in 0.6 N sodium chloride medium, is shown in Fig. 3. It can be seen from this figure that the corrosion potentials shift towards more negative direction with increasing treatment time. The corrosion potential value for 60 s amide treated magnesium MMC is -1.515 V. It shifts to -1.601 V for 3600 s treated magnesium alloy MMC sample. The corrosion potential shifts to more negative values by -0.086 V with increasing treatment time. The shift in polarisation curves towards more negative values and reduction in corrosion current densities is generally encountered with cathodic inhibition.

Figure 4 illustrates the variation in corrosion current density for amide treated magnesium MMC, in 0.6 N sodium chloride medium. The corrosion current value is decreased from 0.8×10^1 A m⁻² for 60 s treated magnesium MMC to 0.275×10^1 A m⁻² for 3600 s treatment. There is nearly 66% reduction in current density when treatment time increases from 60 to 3600 s. The 60 s treated sample exhibits higher current density when compared with that of 3600 s treated sample. In the presence of sodium chloride, for 60 s treated sample, due to the shorter treatment time, the film formed is thinner and therefore, surface activation occurs earlier. The 3600 s treated sample has lower corrosion current density since it is covered by a thicker film which is more protective and hence prevents the dissolution process.

Figure 5 shows the effect of treatment time on the polarisation resistance of amide treated magnesium



4 Corrosion current density of acrylamide treated magnesium MMC in 0.6 N sodium chloride



5 Polarisation resistance of acrylamide treated magnesium MMC in 0.6 N sodium chloride

MMC, in 0.6 N sodium chloride medium. As the treatment time increases, the polarisation resistance is also increased. It can be seen from this figure that the polarisation resistance value is increased by four times as the treatment time is increased from 60 to 3600 s.

The decrease in corrosion current density and the increase in polarisation resistance can be attributed to the thickening of the film formed on the surface with increasing treatment time and its protective ability against corrosion.

Electrochemical impedance spectroscopy

The electrochemical impedance behaviour of amide treated magnesium MMC, in 0.6 N sodium chloride medium, is described in Fig. 6. These diagrams show a single semicircle for each curve, indicating the occurrence of a single charge transfer reaction for each treatment duration. These curves are depressed in nature, similar to that reported.²⁸ This is due to the origin of microroughness and other inhomogeneities of the solid electrode/solution interface formed during the reaction at the interface.^{29–31}

Figure 7 shows the charge transfer resistance values for magnesium MMC specimens subjected to surface treatment in amide bath for different durations, in 0.6 N sodium chloride medium. It can be seen from this figure that the charge transfer resistance increases with increasing treatment time by one order of magnitude due to this treatment. The charge transfer resistance value of amide treated magnesium alloy is 12 Ω for 60 s treatment. It is increased to 128 Ω for 3600 s treatment. In earlier studies,³² the charge transfer resistance values



a 60 s; b 900 s; c 1800 s; d 3600 s

6 Effect of treatment time in acrylamide on impedance behaviour of magnesium MMC in 0.6 N sodium chloride medium



7 Charge transfer resistance of acrylamide treated magnesium MMC in 0.6 N sodium chloride

for cast AZ61 and Mg–Al–Zn–Y alloys, immersed in sodium borate solution, are reported to be 140 and 165 Ω respectively. The charge transfer resistance

obtained in the present work is in the reported range. This indicates that adsorption at the electrode/solution interface increases leading to the formation of a thicker surface film for longer treatment time.

The corrosion resistance is directly proportional to $R_{\rm ct}$. Hence, the higher the value of $R_{\rm ct}$, the higher the corrosion resistance. This shows that the protection offered increases with increasing treatment time. The initial low value of charge transfer resistance for the 60 s treatment may be due to the thin film formed on the substrate. The subsequent growth of the surface film results in the increase in $R_{\rm ct}$ value as reported by Srinivasan *et al.* and others.^{33–37}

Surface characterisation

Scanning electron microscopy

Figure 8 shows the SEM images of magnesium MMC after surface treatment for different durations in amide bath. Microstructure of untreated sample is shown in Fig. 8a.



a untreated; b 60 s; c 900 s; d 1800 s; e 3600 s 8 Micrographs (SEM) of acrylamide treated magnesium MMC with increasing treatment time



a 60 s; b 900 s; c 1800 s; d 3600 s

9 Atomic force microscopy for magnesium MMC, subjected to different durations of surface treatment in acryl amide bath

Figure 8*b* reveals a rough surface for 60 s treated specimen. The surface is smoother for 900 s treated specimen as shown in Fig. 8*c*. Figure 8*d* illustrates the surface of the specimen subjected to 1800 s treatment in amide bath where it is observed to be smoother than that of the 900 s treated specimen. For 3600 s treated specimen, a much smoother surface is observed (Fig. 8*e*). It is known that a surface with less heterogeneity is less susceptible to corrosion. Earlier studies⁷ have shown that treatment with PANI-phosphate pigment yields a surface with very little heterogeneities which increases the resistance to corrosion. Here also the surface becomes smoother with increasing treatment time, with the formation of the film on the surface.

Atomic force microscopy

The surface profile obtained with atomic force microscope for magnesium MMC subjected to 60 s amide treatment is illustrated in Fig. 9*a*. The profile exhibits a variation of $247 \pm 32 \times 10^{-9}$ m. The surface is observed to be relatively rough. Figure 9b shows the topography of the specimen subjected to 900 s treatment in amide bath. The variation in the surface profile is $184 \pm 29 \times 10^{-9}$ m. This surface is still rough but less than that obtained for 60 s treatment. The specimen treated in amide bath for 1800 s is observed to exhibit a surface with much less roughness as illustrated in Fig. 9c. The roughness varies in the range $145 \pm 34 \times 10^{-9}$ m. Figure 9d shows that the surface roughness is significantly reduced for the specimen treated in amide bath for 3600 s, which varies in the range $78 \pm 26 \times 10^{-9}$ m. The improvement in the quality of surface with increasing treatment time further reinforces the observed improved electrochemical characteristics, offered by this treatment.

Fourier transform infrared spectroscopy

Figure 10 shows the FTIR spectra of magnesium MMC samples subjected to amide treatment for different durations. Metal complexes of acryl amide are formed



10 Spectra (FTIR) of different durations of acrylamide treated magnesium MMC

by direct reaction of metal ions with acryl amide. The complex formation of metal ions occurs with carbonyl oxygen.²² The C=O absorption of amides occurs at lower frequencies than normal.³⁸

The carbonyl (C=O) absorption frequency decreases to 1599×10^{-2} m⁻¹ with 91% of transmittance intensity for 1 min treatment. It also occurs for other treatment times with 90, 86 and 82% of reduction in transmittance respectively. The feature at 1684×10^{-2} m⁻¹ is related to the $\gamma_{c=o}$ and this value decreases to 1594×10^{-2} m⁻¹ as treatment time increases. This may be due to the fact that formation of a thicker surface film decreases the transmittance. It indicates the metal complexes with carbonyl oxygen of acryl amide.³⁹ The treated samples also exhibit absorption frequency corresponding to N–H bend at 688×10^{-2} m⁻¹.

Hence, it can be inferred that the most important effect in this case involves decreasing the carbonyl force constant by draining π electron density, out of the carbonyl group.³⁹ This causes the decrease in the carbonyl frequency and indicates oxygen coordination with magnesium. As the treatment time increases, the stronger absorption occurs. The decrease in carbonyl frequency from 1684×10^{-2} to 1594×10^{-2} m⁻¹ confirms the complexing with metal ions on the surface. From the above analysis, the compound formed is inferred to be the complex



This causes the deactivation of the surface and hence increases the resistance to corrosion. The formation of a similar compound is reported by Huang *et al.*³

Conclusions

From the above studies, the following conclusions can be inferred:

1. Thickness of poly acryl amide film formed on the Mg MMC sample increases as the treatment time increases from 60 to 3600 s.

2. With increasing treatment time, the corrosion potential shifts towards more negative values.

3. The corrosion current density is observed to decrease with increasing treatment time.

4. As the treatment time increases, the polarisation resistance and the charge transfer resistance also increase.

5. These indicate that the film formed is protective in nature.

6. The film is inferred to be a complex formed by the coordination of magnesium with oxygen from the amide supported by the decrease in the carbonyl frequency.

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