Polymer Plating of 6-Substituted-1, 3, 5-Triazine-2, 4-Dithiols on Magnesium Alloys and Applications of the Plated Alloys

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Polymer plating of triazine dithiols on magnesium alloys and applications of the plated alloys were investigated, focusing on important factors for improvement of corrosion resistance and adhesion properties of magnesium alloys. Three kinds of triazine dithiols; 6-dihexylamino-1,3,5-triazine-2,4-dithiol monosodium salts (DHN), 6-diallylamino-1,3,5-triazine-2,4-dithiols (DAN), and 6-mercapto-1,3,5-triazine-2,4-dithiol (TTN), were prepared for imparting functions such as corrosion resistance and direct adhesion to magnesium alloys. In polymer plating of DHN, film thickness initially increases with current density, reaches a maximum at 1 A/m², and then decreases. Film thickness initially increases with DHN concentration, reaches a maximum at 8 mol/m³, and then decreases. Polymer plating of DAN yields good polymer film on magnesium in terms of adhesion when 10 mol/m³ NaOH/Na₂CO₃ aqueous solution is used as an electrolytic solution. An 8 mol/m³ DHN aqueous solution was found to impart the best corrosion resistance for reaction resistance and corrosion current density. In direct adhesion of EPDM to polymer-plated magnesium alloys, a film thickness of near 100 nm imparts the highest peel strength. In injection molding adhesion of PPS polymer to polymer-plated magnesium alloys, high tensile shear strength is obtained when mold temperature exceeds 140°C.

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1. Introduction

Magnesium alloys are considered important for next-generation metallic materials. Recently, the application of magnesium alloys has increased in various industrial areas.¹⁻³⁾ Although a wide variety of applications can be envisaged for magnesium alloys, their use is limited, mainly due to lack of studies on surface properties, although studies have been performed recently. In order to satisfy the increasing demand for magnesium alloys, surface characteristics must be improved.

The authors have developed effective surface finishing technology that improves surface characteristics such as corrosion resistance,^{4,5)} adhesion properties,⁶⁻⁸⁾ and application of paint on metals, through polymer plating^{9,10)} 6-substituted-1,3,5-triazine-2,4-dithiols (triazine dithiols). Polymer plating is a method for coating metal surfaces and results in deposition of triazine disulfide polymers by electrochemical processing of triazine dithiols at the anode surfaces. Formation of various deposited films seems to have an effect of improving various surface properties of magnesium alloys.

In this study, the authors investigated important factors which are effective for improving corrosion resistance and adhesion of magnesium alloys in polymer plating of triazine dithiols. Corrosion resistance and adhesion properties of the deposited films were evaluated.

2. Experimental

2.1 Materials and reagents

Magnesium alloy test samples (1 mm × 10 mm × 50 mm) of AZ91 and AZ31¹²⁾ were prepared by cutting pieces off a commercial ingot or plate of magnesium alloy.¹¹⁾ These samples were sanded with emery paper (#3000, 5 μm) and then

finished with polishing paste (particle, 2 μm). The average surface roughness after processing fell in the range of 0.05–0.1 μm. Before use, the AZ91 and AZ31 test plates were degreased by ultrasonic washing in acetone and drying with a hot-air drier.

Three kinds of triazine dithiols; 6-dihexylamino-1,3,5-triazine-2,4-dithiol monosodium salts (DHN), 6-diallylamino-1,3,5-triazine-2,4-dithiols (DAN), and 6-mercapto-1,3,5-triazine-2,4-dithiol (TTN), were prepared by reacting 6-R-1,3,5-triazine-2,4-dichloride with NaSH, according to the method described in a previous paper.¹²⁾ NaOH and Na₂CO₃ were used as supporting electrolytes.

Ethylene propylene diene monomer copolymer (EPDM) and poly (phenylene sulfide) (PPS) were obtained commercially. Some additives for EPDM rubber were also obtained commercially.

2.2 Polymer plating

The electrochemical polymerization of triazine dithiols, also referred to as polymer plating, was performed by use of an electrochemical measurement apparatus (Hokuto Denkou Co. Ltd. HD-3000) as described in a previous paper.^{9,13)} The electrolytic cell was equipped with a working electrode (Magnesium alloy plates), counter electrode (stainless steel plate), and reference electrode (saturated calomel electrode, SCE), and filled with an electrolytic solution containing triazine dithiols and electrolytes in water. Polymer plating was conducted without agitation.

2.3 Corrosion testing

Corrosion tests^{11,14)} were carried out by use of electrochemical methods (electrochemical impedance spectroscopy, EIS) and a polarization curve. The coated magnesium alloy AZ91, which was covered with Kapton adhesion tape

(polyimide type), was used as the working electrode. The counter and reference electrodes were a Pt plate and a saturated calomel electrode, respectively. After immersion for 3 h at 25°C, EIS measurements¹¹⁾ were carried out at E_{ocp} and in the frequency range of 20 kHz to 10 mHz, by use of a frequency response analyzer, a potentiostat/galvanostat, and a data processor. After the coated AZ91 samples were immersed in a 0.1 kmol/m³ NaCl solution for 3 h at 25°C, polarization curves were obtained by polarization from the open-circuit potential in the cathodic potential direction, and then in the anodic potential direction, using the potential step method at 20 mV/min by use of a potentiostat/galvanostat, a function generator, and a zero shunt ammeter.

2.4 Direct adhesion

Direct adhesion of EPDM compounds to DAN polymer-plated magnesium alloy AZ91 was carried out as follows. EPDM compounds were prepared by blending EPDM polymer 100 phr (part per hundred resin), HAF carbon black 50 phr, peroxide (Perhexane 3M-40) 10 phr. EPDM compounds were pressed onto DAN polymer-plated magnesium alloy AZ91 for 20 min at 140°C after both were inserted into a mold.

The procedure of injection molding and the dimensions and shapes of obtained samples are described in our previous paper.⁸⁾ The TTN polymer-plated magnesium alloy AZ31 samples were inserted into molds, after which PPS resin was injected through a gate (1 mm × 30 mm × 50 mm). Injection molding was carried out at an injection rate of 30 cm³/s and an injection pressure of 100 MPa. The cylinder and molding temperatures were within the ranges for ordinary use.

2.5 Measurements

The thickness of the polymer films was determined by use of a JASCO M-150i ellipsometer (Jasco Tokyo Japan). FT-IR spectra were measured by the high-performance reflection absorption spectroscopy method (high-performance RAS) employing a JASCO IR-5500 (Jasco Tokyo Japan). The contact angles of pure water on plated test samples were determined by use of an Elma goniometer-type contact angle measuring apparatus (Elma-type G-1) in a clean area. Droplet diameter was controlled between 0.08 and 0.1 mm. Corrosion tests were carried out by use of electrochemical methods (electrochemical impedance spectroscopy, EIS) and a polarization curve. The coated magnesium alloy, which was covered with Kapton adhesion tape (polyimide type), was used as the working electrode. The counter and reference electrodes were a Pt plate and a saturated calomel electrode, respectively. After immersion for 3 h, EIS measurements were carried out at E_{ocp} and in the frequency range of 20 kHz to 10 mHz at 25°C, by use of a frequency response analyzer, a potentiostat/galvanostat, and a data processor. After the coated alloy was immersed in a 0.1 kmol/m³ NaCl solution for 3 h at 25°C, polarization curves were obtained by polarizing from the open-circuit potential in the cathodic potential direction, and then in the anodic potential direction, through the potential step method at 20 mV/min and by use of a potentiostat/galvanostat, a function generator, and a zero shunt ammeter. Adhesion strength was measured by use of a tensile tester (Shimadzu Autograph ABS-1000) operating at a tensile

rate of 3.33×10^{-3} m/s. As described in our previous paper,⁷⁾ an installing tool was used to fix samples to the tensile tester.

3. Results and Discussion

3.1 Polymer plating on magnesium alloys

In our previous paper,^{11,14)} we described that 6-dihexylamino-1,3,5-triazine-2,4-dithiol monosodium salt (DHN) is the most effective triazine dithiol for inhibiting corrosion of magnesium alloys coated by polymer plating. The corrosion resistance of polymer-plated magnesium alloys was predicted to be influenced by the thickness and minuteness of the formed film. Figure 1 shows the effect of current density on film thickness in the polymer plating of DHN in 1 kmol/m³ NaOH aqueous solution. Film thickness initially increases with current density, reaches a maximum at 1 A/m², and then decreases. The increase in film thickness is due to an increase in reaction rate of polymer plating reaction, which in turn is due to the increase in current density. The decrease in film thickness is due to the diffusion of DHN into the interface between plates and solution being the dominant factor for determining deposition rate at high current density. The diffusion rate is generally considered to increase with the concentration of DHN. Figure 2 shows the effect of DHN concentration on film thickness. The film thickness initially increases with DHN concentration, reaches a maximum at 8 mol/m³, and then decreases. The increase in film thickness is based on the phenomenon that reaction rate generally increases with DHN concentration. The decrease in film thickness with DHN concentration is due to a special reason; many DHN molecules start to form micelles aggregated at a concentration of 8 mol/m³ in the aqueous solution, and residual DHN molecules¹⁵⁾ are present as single molecules. The micelles do not participate in polymer plating, because they are aggregations and therefore have a lower diffusion rate; only single DHN molecules participate polymer plating.¹⁵⁾ Therefore, at concentrations greater than 8 mol/m³, the concentration of

Fig. 1 Effect of current density on film thickness in the polymer plating of 6-dihexylamino-1,3,5-triazine-2,4-dithiol monosodium salt (10 mol/m³) in 1 kmol/m³ NaOH aqueous solution at 20°C. (□) 0.5 A/m², (●) 1.0 A/m², (○) 1.5 A/m², (■) 2.0 A/m².

Fig. 2 Effect of DHN concentration on film thickness in the polymer plating of 6-diethylamino-1,3,5-triazine-2,4-dithiol monosodium salt in 1 kmol/m^3 NaOH aqueous solution at 20°C .

Fig. 3 Effect of the concentrations of Na_2CO_3 on the FT-IR spectra in the polymer plating of 6-diallylamino-1,3,5-triazine-2,4-dithiol monosodium salts (30 mol/m^3) on magnesium alloy AZ91 in 0.1 kmol/m^3 NaOH aqueous solution at a current density of 0.6 A/m^2 for 40 min at 20°C .

single DHN molecules decreases with increasing DHN concentration.

To improve the adhesion properties of magnesium alloys, the functional groups must be introduced on the surfaces.^{7,8} Various functional groups can be introduced by polymer plating, by appropriate selection of the kinds of triazine dithiols. To provide adhesion properties of rubber on magnesium alloy surfaces, 6-diallylamino-1,3,5-triazine-2,4-dithiol (DAN), which has double bonds, was selected. As shown in Fig. 3, in polymer plating of DAN in a 0.1 kmol/m^3 NaOH aqueous solution, the presence of oxygen compounds (3700 cm^{-1} , 600--

Fig. 4 Effect of current density on film mass in the polymer plating of 6-diallylamino-1,3,5-triazine-2,4-dithiol monosodium salt (30 mol/m^3) on magnesium alloy AZ91 in 0.1 kmol/m^3 NaOH/ 0.1 mol/m^3 Na_2CO_3 aqueous solution at 10°C . Current density (A/m^2): (●) 0.1, (□) 0.4, (■) 1.0, (○) 2.0.

700 cm^{-1})^{16,17} of magnesium result in preferable formation of polymer film (1500 cm^{-1}). However, when Na_2CO_3 ¹⁶ is added to the solution, the mass of oxygen compounds decreases in relation to the formation mass of polymer film. In the case of polymer plating of DAN, two component electrolytes, Na_2CO_3 and NaOH, are effective for obtaining thick polymer film to prevent the formation of oxygen compounds of magnesium. The effect of current density on film mass has been investigated by use of the two-component electrolyte system. Film mass increases with current density and plating time, as shown in Fig. 4. Film mass increases with current density because DAN does not form micelles even at a concentration of 30 mol/m^3 ; DAN has no critical micelle concentration in the two-component electrolyte system.

Polymer plating of 6-mercapto-1,3,5-triazine-2,4-dithiol (TTN) enables provision of thiol (SH) and disulfide (S-S) groups on magnesium alloy surfaces. Figure 5 shows the effect of TTN concentration on film thickness in the polymer plating. Film thickness initially increases with TTN concentration, reaches a maximum, and then decreases. The increase in film thickness appears to be generally reasonable, and the decrease in film thickness is related to the structure of polymer film. At low TTN concentration, the polymer film is composed of substantially disulfide groups only, because the charge necessary for the formation of disulfide groups is sufficiently higher than the given charge (current efficiency: 20–60%). As TTN concentration increases, thiol group content increases and disulfide group content decreases. When the proportion of thiol groups to disulfide groups exceeds 1/2, growth of polymer film is suppressed. Figure 6 shows the contact angles of polymer film formed on magnesium alloys. Contact angles decrease with polymer-plating time and TTN concentration. The decrease in contact angle shows an increase in the proportion of thiol groups to disulfide. The de-

Fig. 5 Effect of TTN concentration on film thickness in the polymer plating (current density: 4 A/m^2) of 1,3,5-triazine-2,4,6-trithiol monosodium salt (TTN) in 1 kmol/m^3 NaOH aqueous solution at 20°C on magnesium alloy AZ31. TTN concentration (mol/m^3): (■) 5, (□) 10, (○) 30, (●) 50.

Fig. 6 Effect of contact angles on film thickness in the polymer plating (current density: 4 A/m^2) of 1,3,5-triazine-2,4,6-trithiol monosodium salt (TTN) in 1 kmol/m^3 NaOH aqueous solution at 20°C on magnesium alloy AZ31. TTN concentration (mol/m^3): (■) 5, (○) 30, (●) 50.

crease in contact angle with plating time indicates change in the top surface structure of polymer film. The increase in TTN concentration indicates high thiol group content on top surfaces.

3.2 Corrosion resistance of the polymer-plated magnesium alloy AZ91

The corrosion resistance of magnesium alloy plates coated with a thin film was evaluated from reaction resistance (charge transfer resistance in Cole-Cole plots) and corro-

Table 1 Effect of the concentration of 6-dihexylamino-1,3,5-triazine-2,4-dithiol monosodium salt (DHN) on the corrosion resistance and corrosion current density of polymer-plated magnesium alloy AZ91.

DHN concentration (mol/m^3)	Corrosion resistance ($\Omega \cdot \text{cm}^2$)	Corrosion current density (A/cm^2)
5	5,200	$10^{-5.5}$
7	45,200	$10^{-7.0}$
8	76,000	$10^{-8.2}$
9	62,000	$10^{-7.8}$
10	60,200	$10^{-7.3}$
12	2,100	$10^{-4.5}$

Current density: 1 A/m^2 , Temperature: 20°C , Time: 20 min.

Fig. 7 Corrosion resistance of polymer-plated magnesium alloys AZ91 in 1 kmol/m^3 NaCl aqueous solution at 30°C . Current density: 2 A/m^2 , 1 kmol/m^3 NaOH/ 10 mol/m^3 DHN aqueous solution, 20°C , 20 min.

sion current density (Tafel extrapolation of the polarization curves).^{11,14} Table 1 shows the effect of concentration of 6-dihexylamino-1,3,5-triazine-2,4-dithiol monosodium salts on reaction resistance and corrosion current density. At 8 mol/m^3 DHN aqueous solution was found to yield the highest corrosion resistance for reaction resistance and corrosion current density. This is because the polymer film is thickest and closely packed in the polymer plating condition.¹¹ Figure 7 shows the corrosion resistance of polymer-plated magnesium alloys in 1 kmol/m^3 NaCl aqueous solution at 30°C . Under the corrosion conditions, oxygen compounds of magnesium are formed in 1 kmol/m^3 NaCl aqueous solution, and the formed oxygen compounds are dissolved at the same time. However, the formation and dissolution of oxygen compounds are markedly suppressed by the polymer plating of magnesium alloys. Figure 8 shows the corrosion resistance of polymer-plated magnesium alloys in saturated water vapor at 60°C . Mass gain (W) indicates the formation of MgO and $\text{Mg}(\text{OH})_2$ ^{16,17} under corrosion conditions. Between W and $t^{0.5}$, equation $W = kt^{0.5} + W_0$ applies, where k is a rate constant for corrosion in saturated water vapor at 60°C , and W_0 (about 0.12 kg/m^2) is

Fig. 8 Corrosion resistance of polymer-plated magnesium alloy AZ91 in saturated water vapor at 60°C. Polymer plating conditions: Current density: 1 A/m², Temperature: 20°C, Time: 20 min. DHN concentration (mol/m³): (■) Blank, (□) 5, (●) 8, (○) 10.

the mass of oxide compounds that samples contain on surface before the corrosion test. Application of the equation indicates that corrosion in saturated water vapor at 60°C is determined by diffusion rate. The constant k is related to DHN concentration for polymer plating, and the following order applies: blank ($0.0275 \text{ kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$) > 10 mol/m³ ($0.0018 \text{ kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$) > 5 mol/m³ ($0.0012 \text{ kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$) > 8 mol/m³ ($0.0007 \text{ kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$). Polymer plating film is very effective for preventing corrosion of magnesium alloy AZ91. The 8 mol/m³ DHN concentration yields good corrosion resistance and the thickest polymer film formed on magnesium alloy AZ91.

3.3 Adhesion

Adhesive technology between magnesium alloys and polymers enables productions of various lightweight goods. Thus, development of direct adhesion is important. Figure 9 shows the effect of current density on peel strength in the direct adhesion of ethyl propylene diene rubber (EPDM) to polymer-plated magnesium alloy AZ91. Fundamental adhesion properties are determined by the reactivity between polymer films, magnesium alloys, and rubber. Both polymer films and EPDM contain double bonds. In a peroxide curing system, this combination can form chemical bonds between polymer films, magnesium alloys, and rubber,^{18,19} which is necessary for attaining adhesion. In the polymer plating,¹⁸ low current density provides formation of generally minute polymer film on magnesium alloys. Adhesion properties are related to the properties of polymer films. Low current density yields good polymer films containing few defects, although the formation rate of polymer films is low. The defects in a solid are statistically proportional to thickness or volume. As a result, high peel strength in the adherends is obtained. Increase in polymer plating time brings about a decrease in the film strength

Fig. 9 Effect of current density on the peel strength in the direct adhesion of EPDM rubber to DAN polymer plated magnesium alloy AZ91. Current density (A/m²): (○) 0.4, (●) 1.0.

Fig. 10 Relationship between peel strength and film thickness in the direct adhesion of EPDM rubber to DAN polymer plated magnesium alloy AZ91.

of the top surface, because the three-dimensional structure of polymer films is suppressed. The above findings are substantiated by the results shown in Fig. 10. The highest peel strength is obtained not in a particular range of film thickness, but at a defined thickness. The film thickness of near 10 nm yields the highest peel strength. Peel strength decreases for thicknesses above and below this figure. The first increase in film thickness occurs because polymer film plays a role in suppressing stress concentration at the interface of adherends. Cohesive failure occurs at a peel strength greater than 5 kN/m. In this case, rubber coverage on magnesium alloy plates after peeling tests was always 100%.

Figure 11 shows the relationship between tensile shear

Fig. 11 Relationship between tensile shear strength and TTN concentration in the direct adhesion of PPS polymer to polymer plated magnesium alloy AZ31 during injection molding. TTN concentration (mol/m^3): (■) Blank, (●) 10, (○) 30, (□) 50.

Fig. 12 Effect of mold temperature on tensile shear strength in the direct adhesion of PPS polymer to TTN polymer plated magnesium alloy AZ31 during injection molding.

strength and TTN concentration in the direct adhesion of PPS polymer to polymer-plated magnesium alloy AZ31 during injection molding. In this case, interfacial reaction can occur between the benzene ring of the PPS polymer and the S-S bonds of polymer-plated magnesium alloy AZ31. As a result,

the reaction between the two forms monosulfide bonds between the compounds. Noncoated magnesium alloy AZ31, which is electrochemically treated in 1M aqueous solution without TTN, exhibits very low tensile shear strength in the direct adhesion of PPS polymer during injection molding. In this case, the surfaces of magnesium alloy AZ31 lack functional groups that react with PPS polymer. The TTN concentration of 30 mol/m^3 yields the highest tensile shear strength at the polymer plating time of 3 min. This is because the polymer plating film has surface properties and S-S bonds that are well suited for adhesion with PPS polymer during injection molding. Because of the reaction between polymer plating films and PPS polymer in adhesion during injection molding, mold temperature strongly influences tensile shear strength, as shown in Fig. 12. Tensile shear strength initially increases gradually with mold temperature, increases rapidly at mold temperatures exceeding 120°C , and becomes constant at mold temperatures exceeding 140°C . This indicates that reaction rate between polymer plating films and PPS polymer becomes constant at temperatures exceeding 140°C . In this case, the surface of fractured magnesium alloy samples is entirely covered with PPS polymer.

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