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Sono-immersion Deposition on Magnesium Alloy

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Abstract

Coating is a viable way to improve the corrosion resistance of magnesium alloys for aerospace and automotive applications. This paper presents the acoustic effect on the copper immersion coating of AZ91 magnesium alloy. Electrochemical impedance spectroscopy and open circuit potential measurements were conducted to characterize the copper immersion-coating processes. The surface morphology changes of the copper immersion coatings obtained with and without sonication were examined using scanning electron microscopy. All experimental results from different techniques employed in this study have clearly demonstrated a significant increase of surface coverage on magnesium alloy. Data analysis indicated that formation of a surface film on the uncoated magnesium area during immersion coating under silent condition restrained magnesium dissolution which, in turn, limited the deposition process. The application of sonication induced asymmetric cavitations at the interface and efficiently destructed or prevented the formation of a surface film. As a result, the anodic reaction (magnesium dissolution) was

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maintained to provide a continuous driving force for cathodic copper reduction and deposition, hence increasing the surface coverage.

Key Words: immersion, sono-immersion, coating, deposition, magnesium, AZ91

1. Introduction

With the increasing awareness of fuel consumption and human ecology, a global commitment has been made to reduce vehicle mass through application of lightweight materials. Magnesium is the lightest structural metal with the highest specific strength and is the eighth most abundant element on the earth. Many researchers and developers have looked to magnesium to provide a solution for vehicular mass reduction for the automotive, aircraft and aerospace industries. However, challenges exist owing to its low corrosion and wear resistance. To achieve the necessary mass reductions, various coating technologies have been applied to enhance the corrosion and wear resistance of magnesium alloys [1]. To date, no deposition technology provides a solution that satisfies a combination of functionality, cost, scalability and environmental friendliness.

Upon completion of a comprehensive review of existing surface finishing technologies [1], it appears that electroless deposition is a good candidate with combined advantages such as excellent uniformity, high corrosion and wear resistances and excellent scalability. However, direct electroless deposition on magnesium alloy generates a concern associated with the bath stability due, in part, to the possible contamination from the high reactivity of Mg substrate. To tackle the issue, it is viable to apply a copper immersion undercoat on the substrate to protect both the unstable magnesium substrate and the subsequent electroless deposition solution. Immersion coating is the deposition of a metallic coating on a substrate by chemical replacement from a solution of a salt of the coating metal. This simple process is advantageous with respect to the reduced cost, increased coating uniformity, simple operation, and excellent scalability. It is particularly promising as an undercoat for subsequent electroless

deposition by providing a stable thin layer with a decreased probability of bath decomposition. For this reason systematic research has been conducted to develop an immersion copper deposition process for magnesium alloy.

Ultrasound is known to cause a multitude of complex phenomena such as bubble oscillation [2] and cavitation [3]. In particular, the asymmetric cavitations in the vicinity of a solid-solution interface [4] have a significant effect on the interfacial processes. Direct exposure of electrochemical processes to intense ultrasound waves therefore appears promising especially in view of the demonstrated impact of sonication on heterogeneous electrochemistry [5]. Although much work needs to be done regarding the fundamental aspects there are already some promising developments leading to the application of sonication in electrochemistry [6-11]. It was reported that the application of sonication to the plating process changes the structure of the deposits and increases their deposition rate, corrosion resistance and the microhardness [7,9,10].

This paper reports our recent progress in the understanding of the sonication effect on the immersion copper deposition process applied to a magnesium surface. This new approach has never been applied, to the best knowledge of the authors. The investigation was conducted using electrochemical impedance and open circuit potential measurements in conjunction with surface topographical analysis.

2. Experimental

2.1. Materials

The substrate used in this study was the AZ91 magnesium alloy (including AZ91D and AZ91E). Its nominal composition is shown in Table 1.

2.2. Immersion processes

Two types of immersion processes were conducted: one was copper immersion coating in electrolytes containing xM HF + $0.67M$ $CuSO_4$; the other was conducted in electrolytes that contain only hydrofluoric acid of various concentrations, referred to as the 'HF etching process' in this paper. In addition, baths used for both processes are distinguished as a 'still bath' and a 'sonicated bath', depending on whether sonication was applied. The frequency of ultrasound applied to the immersion bath was 40kHz. All immersion processes were carried out at room temperature for approximately 10 minutes, unless specified otherwise. The volume of the immersion solution was 100 ml throughout the various experiments.

2.3. Specimen preparation and surface pretreatment

2.3.1. Specimen for immersion processes

For all the immersion processes, including HF etching and copper immersion coating processes, an AZ91D sample of $8 \times 10 \times 1.5$ mm was used. Pretreatment of the samples was conducted using a glass beading process in which the sample was blasted with glass beads for 10 seconds at the pressure of 450 kPa. The stream bombarded the sample in a normal direction from a distance of about 10 cm. The sample was then rinsed in isopropanol for 6 minutes with sonication to remove any particles adhered to the surface.

Finally, alkaline degreasing was performed in a 60g/l NaOH + 10g/l Na₃PO₄ aqueous solution at 75°C for 6 minutes. After alkaline degreasing the sample was thoroughly rinsed in de-ionized water and immediately transferred into electrolytes for HF etching or copper immersion coating.

2.3.2. Specimen for electrochemical characterization

Electrochemical impedance spectroscopy (EIS) and open circuit potential (OCP) measurements were conducted to characterize the HF etching and copper immersion deposition process. AZ91E sample of 10×10×20 mm was used for this purpose. Epoxy resin was employed to seal the sample, leaving 1×1 cm² effective working area. The sample was polished using 400 grit wet emery paper followed by glass beading, isopropanol cleaning, and alkaline degreasing. When thoroughly rinsed in de-ionized water the samples were immediately transferred into the electrolytes for the electrochemical measurements.

2.4. Cell and electrodes

Open circuit potentials were recorded versus time in a cell with two electrodes, i.e. a working electrode and a reference electrode. For the electrochemical impedance experiments a cell fitted with three electrodes, i.e. working electrode, counter electrode (Pt gauze with large surface area of ca. 10 cm²) and reference electrode. The reference electrode used was Ag/AgCl/KCl, 0.21V vs. RHE at 25°C, connected to the electrolyte

through a salt solution bridge of 3M KCl solution. The distance between the reference electrode and the working electrode was maintained at 0.3cm.

The EIS measurements were performed with a bias potential of 0.0 V (vs. OCP) and a 5 mV a.c. perturbation. An EG&G 273A potentiostat was used, coupled with a M5210 lock-in amplifier.

2.5. Scanning electron microscopy (SEM)

An Hitachi S3500N Variable Pressure SEM was employed to examine the surface morphologies of the immersion coating. Copper coating coverage was measured by processing the SEM images with Image – pro Plus software.

3. Results

3.1 OCP-time curves

The changes in potential versus time (OCP –time curves) were recorded during HF etching and copper immersion coating processes.

Figure 1 illustrates the results from HF etching. Results are presented for two bath conditions, i.e. still bath (Figure 1a) and sonicated bath (Figure 1b). In both cases the potential initially shifted positively, due possibly to the formation of a surface film. The OCP reached a plateau after approximately 3 minutes. The plateau potential achieved in the still bath was more noble than the sonicated bath.

OCP – time curves were also collected during copper immersion coating for both the still and sonicated conditions, Figs 2(a) and 2(b), respectively. It is apparent that the time required for the potential to reach a plateau in both conditions was almost identical, and a more noble value of the potential was, again, obtained from the still bath.

In summary, the results from open circuit potential measurements show that the sonication effect on both the HF etching and copper immersion coating processes are significant. More specifically, two important observations can be made in both cases: 1) the OCP reaches a plateau at almost an identical time, regardless of the presence of sonication; 2) the sonicated bath consistently reduces the OCP plateau.

3.2 Electrochemical impedance spectroscopy (EIS)

EIS measurements were conducted to further characterize the copper immersion coating process on the magnesium alloy. Shown in Figures 3 and 4 are the impedance spectra, which are characterized by a capacitive loop in the frequency range studied. A simple, one time constant, equivalent circuit may be applied to represent the capacitive loop, i.e. a solution resistance, R_s , in series with a parallel RC circuit with a resistance, R_p , and a capacitance, C_p . The values of the R_p and C_p were derived by fitting the semicircles using Powersine EIS software. For the HF etching process, the values of R_p and C_p obtained are plotted versus HF concentration in Figure 5. The data show that R_p obtained in the still bath is in the range of 110 to 150 ohm, depending on the HF concentration. In the sonicated bath, however, the R_p value decreased to 20 to 60 ohms. For the copper immersion coating process, the capacitive loops obtained are also significantly affected by the application of sonication (Figure 4). For silent conditions, the resistance, R_p , is

approximately 43 and 50 ohm (Figure 4a) for the 4.4 M and 5.5M HF containing bath respectively. These values decrease to 3 and 25 ohm, respectively, in the presence of sonication (Figure 4b).

3.3 Surface morphology and copper coverage

Scanning electron microscopy was employed to examine the surface morphology of the magnesium alloy treated under the various conditions. Shown in Figure 6 are the secondary electron images obtained after the HF etching process. It is observed that the dissolution of magnesium in the still bath occurred around grain boundaries, which became more pronounced at low HF concentrations (e.g. 2.2M, Figure 6a). In the sonicated bath, however, such a feature is observable over the entire HF concentration range from 2.2M to 5.5M (Figure 6b).

The back scattered electron images of the copper immersion coating are presented in Figure 7. The coating coverage derived from these images is shown in Figure 8. The surface coverage by coatings obtained from sonicated baths is always higher than that from still baths over the entire HF concentration range studied, indicating a significant beneficial effect of sonication. While the surface coverage of coatings from the still bath increases with the decrease of HF concentration, the coverage in a sonicated bath first increases and then decreases after reaching a maximum at the HF concentration of 3.3 M. It was further observed during the experiment that, under silent conditions, a further decrease in HF concentration might result in a higher copper surface coverage. However, the coating was spongy with low adherence. Such a low adherent deposit may easily

separate from the substrate surface. It is readily apparent that sonication promotes the separation at low HF concentrations, thereby reducing the surface coverage, Figure 8.

To obtain more information on the immersion coating process at different stages, surface coverage obtained with and without sonication is plotted versus time, as shown in Figure 9. Back-scattered electron images corresponding to the coating times of 20, 60 and 240 seconds are also presented as inserts. While the surface coverage obtained in the still bath increases initially and then plateaus, the coverage of coating from the sonicated bath increases continually with extension of sonication time. It appears that sonication effect becomes more apparent as immersion coating proceeds.

4. Discussion

The experimental results from the different techniques employed in this study all clearly show the significant effect of sonication on both the HF etching and the copper immersion coating processes.

During HF etching the potential change (Figure 1) indicates that the open circuit potential initially shifted positively before a fairly constant value was reached after 3 minutes. This can be ascribed to the formation of a surface film on the magnesium alloy. It is known that in an F^- containing aqueous solution the following reactions could take place [12-13],

The MgF_2 formed may be followed by a F/OH^- exchange or hydration process, resulting in a more stable surface film containing $\text{Mg}(\text{OH})_n\text{F}_{2-n}$ [13], which could act as a protective film that suppresses anodic dissolution [14]. In a sonicated bath, the initial positive shift of the OCP was similar in the still bath, but the plateau potential attained was more negative. This negative shift in plateau potential under sonication indicates that the surface film formed on the magnesium alloy was possibly partially discontinuous in nature, or more discontinuous than that formed in a still bath.

The effect of sonication on the HF etching process was also clear in the electrochemical impedance spectra. For example, in a 3.3 M HF still bath, the resistance associated with the impedance spectra (Figure 3a) is 120 ohm. After the application of sonication this value decreased to 43 ohm. This reduction in a sonicated bath is consistent with that observed on a lithium surface [15]. With regard to capacitance, the C_p obtained in a still bath ranged between $15\text{--}18 \mu\text{C cm}^{-2}$, but increased to about $25\text{--}40$ with the application of sonication. In both cases, the values are below that anticipated for a double-layer capacitance (around $50 \mu\text{C cm}^{-2}$ [16]). This implies that the impedance spectra obtained on the magnesium alloy can be attributed to both a charge transfer and a film effect, while the associated R_p essentially represents the film resistance as suggested by Baril [16]. This implies that the film formation process might be the rate determining step of the three charge transfer reactions, i.e., film formation, Mg dissolution and Cu reduction. This implication is consistent with, and supported by, the observed reduction of R_p when sonication is applied. Moreover, the Nyquist plots in Figure 3 showed a depressed feature that is more pronounced with the application of sonication. Table 2

gives the depressed angles, ranging from 2.1 to 5.3° and 1.7 to 2.3° in a sonicated and a still bath, respectively. It is generally recognized that the depressed nature associated with the Nyquist spectra is attributable to the existence of pores/voids in the film, i.e., to film discontinuities. Discontinuity was promoted by the application of sonication, which is consistent with the OCP results.

In the field of sono-electrochemistry, ultrasound is known for its capacity to promote interface processes mainly through asymmetric cavitation in the vicinity of a solid–liquid interface, which induces microjets impact and shock wave damage by liberating a high amount of energy, creating intense pressure fields and inducing vigorous local fluid motion [3,4]. As a result, the related phenomena dramatically affecting the electrochemical process at the interface are mass transfer enhancement [17-20] and the erosion and abrasion of the solid surfaces [21-24]. During the etching process in the presence of sonication, asymmetric cavitation disturbs the film formation on the magnesium surface, as evidenced by the erosion on the surface, Figure 6. The effect might also extend to the ‘cleaning’ effect that removes the intermediate species, MgF^+ , away from the electrode surface, thus preventing its conversion, to and subsequent precipitation of, MgF_2 as a protective film. This is consistent with the observations on the prevention of film-reformation previously reported [25,17,23].

The high mass transport and surface erosion induced by the application of sonication plays an important role in copper immersion coating: the obtained surface coverage on the magnesium alloy is low (below 40%) in the still baths, while the value for sonicated bath is much higher (well above 60%, Figure 8). Copper immersion coating is a process involving several reactions taking place simultaneously. This process involves Mg

dissolution as the anodic reaction, and hydrogen evolution and copper deposition as the cathodic reactions:

It is obvious that magnesium dissolution (Eq.3) provides the driving force for the cathodic reactions (Eq.4 & 5). Accordingly, the difference in surface coverage with and without sonication (Figure 8) can be explained. In a still bath, magnesium dissolution takes place violently during the initial stage immediately on the immersion of the sample in the solution, resulting in rapid copper deposition. However, magnesium dissolution is accompanied by the formation of a surface film on uncoated area, which suppresses, or even stops, local magnesium dissolution. As a result, the magnesium surface is covered by either copper deposits (coated area) or a protective film (uncoated area). The immersion coating process gradually stops due to the absence of driving force. In the sonicated bath, however, the formation of the surface film is hindered or prevented by asymmetric cavitations close to the interface, as previously discussed. As a result, the anodic reaction (magnesium dissolution) could be maintained to continuously provide a driving force for the cathodic reduction/deposition of copper.

It is interesting to note that the application of sonication seemed to be less effective in enhancing copper coverage (Figure 9) initially than over an extended period. A comparison of the SEM images indicates that copper deposits obtained after 20 and 60 seconds, with and without sonication, are basically similar in features and coverage. An obvious enhancement in the copper coverage under sonication is observed after approximately a three-minute deposition. It is possible that initially the dissolution of magnesium is a fast process, as indicated by the violent bubbling observed. Under these circumstances, the cathodic reduction of copper may actually be the rate-determining step possibly associated with the first charge transfer ($\text{Cu}^{++} + e = \text{Cu}^+$), assuming a two-step reaction for the copper reduction [26]. At this stage the immersion coating process was controlled by a synergistic mechanism [5], i.e., coupling of the sonication and the associated reaction kinetics. In the synergistic mechanism the application of sonication may play only a minor role. However, as the process proceeded, the uncoated magnesium surface area decreased as the fluoride/hydroxide film formed and thickened in the absence of sonication. Consequently the anodic magnesium dissolution gradually slowed, resulting in a switch in rate determining step from the first charge transfer of the copper reduction to the anodic reaction (Mg dissolution). In the presence of sonication, however, the formation of the surface film on uncoated areas was hindered and prevented. Thus the role of sonication became more obvious at an extended stage than in the initial stage. Interestingly, this is consistent with the OCP measurement results (Figures 1&2), i.e., the time to reach a potential plateau both with and without sonication, is almost identical. This can be attributed to the fact that magnesium dissolution plays a dominant role during the initial stages. The effect of film destruction/prevention by sonication is therefore

insignificant. However, this does not exclude the possibility of a gas bubbling effect due to hydrogen evolution during the initial stage. It was reported that the gas content in a solution plays a major role in cavitation erosion, i.e. as the gas content increases the violence of cavitation events decreases [21]. During copper immersion coating, violent bubbling due to the hydrogen evolution was observed during the initial stage which might limit the sonication effect.

5. Conclusions

- Formation of a fluoride containing film on AZ91 Mg alloy surface was found to affect the Cu immersion coating process. The effect of this film is on the kinetics of chemical/electrochemical reactions occurring during the immersion coating process.
- Sonication was found to be effective in improving the immersion coating process, facilitating the process kinetics by the prevention/removal of fluoride containing film on the substrate surface. This was confirmed by both OCP and EIS measurements and by SEM observations of the deposits.
- The effect of sonication might be attributed to asymmetric cavitation. The resulted local high erosion prevents/removes surface film thereby maintaining available Mg surface for dissolution. The continued supply of electrons generated from this dissolution process rendered a continuous Cu deposition possible, particularly during an extended deposition period of time beyond the initial stage.

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Figure 3. Nyquist plots recorded for the magnesium alloy during HF etching process in xM HF containing electrolytes: (a) still bath and (b) sonicated bath.

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Figure 8. Copper coverage – HF concentration plots of the immersion coating in electrolytes containing $x\text{M HF} + 0.67\text{M CuSO}_4$: (a) still bath and (b) sonicated bath.

Figure 9. Copper coverage – time plots of the immersion coating in a $4.4\text{M HF} + 0.67\text{M CuSO}_4$ containing electrolyte.

Table 1. The nominal chemical composition of the AZ91D and AZ91E magnesium alloy used in the experiments

Table 2. Depressed angles derived from the corresponding Nyquist spectra of Figure 3a (still bath) and 3b (sonicated bath).

Figure 1

Figure 2

Figure 3a

Figure 3b

Figure 4a

Figure 4b

Figure 5

Figure 6a

Figure 6b

Figure 7a

Figure 7b

Figure 8

Figure 9

Table 1

	Al	Zn	Mn	Ni	Cu	Si	Fe	Be	Other Total
AZ91D ¹	8.5-9.5	0.45 - 0.90	0.17 - 0.40	0.001	0.015	0.05	0.004	0.0005-0.003	NS
AZ91E ²	8.3-9.2	0.45 - 0.90	0.15-0.50	0.001	0.015	0.2	0.005		0.03

¹ AZ91D was supplied by Norsk Hydro Canada.

² AZ91E was supplied by Haley Industries Limited, Canada.

Table 2

HF conc./M	Depressed angle / degree	
	Still bath	Sonicated bath
2.2	1.9	5.3
3.3	1.7	4.4
4.4	1.9	2.1
5.5	2.3	2.6

Date		Time		Location	
10/10/2023	10:00	10:15	10:30	10:45	11:00
10/11/2023	10:00	10:15	10:30	10:45	11:00
10/12/2023	10:00	10:15	10:30	10:45	11:00
10/13/2023	10:00	10:15	10:30	10:45	11:00