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Novel copper immersion coating on AZ91D magnesium alloy in an alkaline bath

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Abstract Copper immersion coating of magnesium alloys has, to date, been conducted only in acidic baths. This paper describes a novel alkaline bath for copper immersion coating on AZ91D magnesium alloy. Prior to the coating process, a chemical etching process of the magnesium substrate was optimized using orthogonal experimental methodology. The copper immersion coating was then investigated with regard to the effect of pH and fluoride content in the deposition bath. It was revealed that during the coating process an increase of pH and fluoride content led to a surface film formation on the magnesium substrate. The surface film formation occurred simultaneously with copper reduction rendering a controlled magnesium dissolution, thereby a controlled copper deposition. With optimized conditions of chemical etching and immersion coating processes, uniform copper deposits were achieved.

Key words: Copper immersion coating, alkaline bath, magnesium alloy

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1. INTRODUCTION

Magnesium is known as a difficult to plate metal due to its high reactivity.¹⁻³ A special procedure for its surface coating is therefore required, which includes a chemical etching step to remove the oxide film on magnesium surface, an immersion coating process to form an under layer for protecting the magnesium substrate for the subsequent electroless / electro depositions.⁴⁻⁵ While each step in the procedure is essential, the immersion coating process is critical.

Immersion coating is a simple process involving what is generally referred to as 'metal displacement reactions'.⁶ When a metal (e.g. magnesium substrate) is immersed in a solution containing a second metal ions (e.g. Cu^{++}), magnesium atoms (less noble) dissolve as the anodic reaction and spontaneously replaced by the copper cations from the solution, resulting in a copper deposition on the magnesium surface. The most common immersion coating on magnesium alloy is the zincate process.^{1,3,7-8} To enable the subsequent electro/electroless deposition, however, a copper cyanide strike must be applied after the zincate process,

which has been of concern for a number of reasons.² A copper immersion coating process was therefore developed in our labs⁹⁻¹² which successfully enabled subsequent electroless Ni deposition from an acidic bath. However, challenges still remain, such as the higher than desired level of porosity in the copper deposits.

The present communication focuses on simple copper immersion coating in an alkaline bath. In this study, prior to the copper immersion coating, a chemical etching process of the magnesium alloy substrate was optimized. The coating process was then investigated in terms of pH effect and the role of fluoride content in the alkaline immersion coating bath. Based on the analysis of experimental results the mechanism of copper immersion coating in the alkaline bath is discussed.

2. EXPERIMENTAL

2.1. Pretreatment of magnesium alloy substrate

The magnesium alloy substrates used throughout the experiments were AZ91D. The pretreatment of the substrate was specified elsewhere.⁹ Generally, the substrate was cut into $1.5 \times 10 \times 10$ mm pieces and subsequently glass-beaded for 10 seconds at a pressure of 450 kPa. The substrate was then cleaned in isopropanol for 6 minutes in the presence of sonication, followed by a three minute alkaline degreasing in a solution containing 60g/L NaOH + 10g/L Na₃PO₄ at 75°C. After thoroughly rinsing the substrate in de-ionized water, two parallel processes, i.e. a copper immersion coating and a blank immersion process will be carried out as described below.

2.2. Copper immersion coating and blank immersion process

For the copper immersion coating, the magnesium substrate was further subjected to a chemical etching process in a bath containing 100g/l K₄P₂O₇ + 30g/l Na₂CO₃ and then immediately transferred into an alkaline coating bath for copper deposition. The coating bath contains 100g/L K₄P₂O₇, 30g/L Na₂CO₃, 12.5g/L

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ plus various concentrations of NaF. The surface of the coated samples were then examined by SEM using the back scattered electron (BSE) mode. The resultant BSE images were processed with an Image – pro Plus software (Media Cybernetics Inc.) to obtain copper surface coverage.

With regard to the blank immersion process it is performed by immersing the pretreated substrate into a solution that contains 100g/L $\text{K}_4\text{P}_2\text{O}_7$, 30g/L Na_2CO_3 plus various concentrations of NaF, i.e. the same composition as the copper immersion coating solution, except for the copper sulfate. Investigation of such blank immersion process is expected to benefit in understanding the copper immersion coating.

2.3. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) measurements were performed during the blank immersion process as stated above. The surfaces of magnesium substrate were sealed using epoxy resin, except for a $1 \times 1 \text{ cm}^2$ effective working area to be

exposed to the solutions. The working area was polished using 320 grit wet emery paper, followed by the same pretreatment procedure as specified in Section 2.1, i.e. glass-beading, isopropanol cleaning under sonication, and alkaline degreasing. After thoroughly rinsing in de-ionized water the sample was immediately transferred into the blank immersion solution for EIS measurement.

A cell fitted with three electrodes, i.e. a working electrode, a reference electrode and a counter electrode (Pt gauze with a surface area of $\sim 10 \text{ cm}^2$), was employed for the EIS tests. The reference electrode used was Ag/AgCl/KCl(3M) connected to the electrolyte through a salt solution bridge of 3M KCl. The distance between the reference electrode and the working electrode was maintained at $\sim 0.3 \text{ cm}$. In this paper, all potential values reported are referenced against the Ag/AgCl/KCl (0.21V vs. RHE at 25°C).

An EG&G 273A potentiostat was employed, coupled with a M5210 lock-in amplifier. The frequency range used in this work was set to be between 100 kHz to 1 Hz. For all the EIS tests a bias

potential of 0.0 V (vs. OCP) and a 5 mV AC perturbation were used.

2.4. Chemicals

All the chemicals (AR grade), including NaOH, Na₂CO₃, Na₃PO₄, NaF and CuSO₄ were supplied by Sigma. De-ionized water ($> 15 \text{ M}\Omega \text{ cm}^{-1}$) prepared with Millipore Elix 10 Water Deionization system was used for solution preparations.

3. RESULTS AND DISCUSSION

3.1. Optimization of chemical etching process

It is generally recognized that chemical etching of substrates plays an important role in surface coating. Given the complex effect of different parameters from the etching process it is necessary to consider a systematic approach to study the etching process for the copper immersion coating. For this purpose

orthogonal analysis is known to be an effective tool.¹³⁻¹⁵ In this study the orthogonal design was therefore performed by selecting four factors, at four levels each (Table 1), to evaluate the effect of chemical etching process based on copper surface coverage. The experimental arrangements and the obtained results are shown in Table 2 in which each process parameter is assigned to a column and sixteen parameter combinations (i.e. sixteen treatments) are available. To obtain more reliable results, each treatment was repeated three times to obtain the average surface coverage.

Based on average surface coverage the mean level response of each factor, R_{pl} , is calculated as:

$$R_{pl} = \frac{1}{k} \sum_{i=1}^k \bar{\eta}_i \quad (1)$$

where k ($= 4$) is the number of treatments involving level, l ($l = 1$ to 4), for factor, p ($p = A, B, C$ and D). $\bar{\eta}_i$ is the average coverage corresponding to each treatment.

According to equation (1), the mean level response is calculated and plotted in Figure 1. The mean level response suggests that, within the investigated level ranges, the optimal combination of the chemical etching process to obtain the high surface coverage for the subsequent copper immersion coating is A_2 , B_1 , C_1 and D_1 (Figure 1) i.e.: etching magnesium substrate in 100g/l $K_4P_2O_7$ + 30g/l Na_2CO_3 (A_2), at a temperature of 50°C (B_1), for 10 seconds (C_1), without water rinsing after the chemical etching process (D_1).

The optimized conditions are easily acceptable because both pyrophosphate and carbonate used in the etching solution are also used in the subsequent alkaline copper immersion coating bath. It is also noted that under the optimized condition, rinsing in water after etching process is not necessary. Therefore, the surface state of the magnesium substrate after chemical etching under the optimal conditions directly facilitates the copper immersion coating process. The above conclusion is consistent with Sakata² in terms of the facilitation of chemical etching to the subsequent

coating. The obtained optimal conditions of the chemical etching process are employed in the following studies.

3.2. Optimization of the alkaline copper immersion coating bath

Potential – pH diagrams of copper-water and magnesium-water¹⁶ can be used to thermodynamically determine the theoretical condition of the copper immersion coating. For copper reduction to occur, the potential of magnesium substrate must be in the region where metallic copper is stable, and magnesium dissolves to provide the driving force for copper deposition. According to the potential – pH diagrams¹⁶, there is broad pH region (pH between 2 to 9) in which the theoretical conditions of copper immersion deposition are satisfied. However, a quality coating can not be achieved by a simple immersion of magnesium substrate into a copper ions containing solution within the pH range. It was observed that during the simple immersion coating process, violent reactions of magnesium dissolution, copper reduction with hydrogen evolution took place and the resultant

coating was dark and spongy. The optimization of copper immersion coating bath was therefore carried out in terms of pH effect and the role of fluoride content in the coating bath, as will be discussed below.

3.2.1. The effect of pH on the copper surface coverage.

It is of note that with further increase of pH beyond 9, the thermodynamically stable region of $\text{Mg}(\text{OH})_2$ in the potential-pH diagram of magnesium-water¹⁶ is gradually entered. Accordingly, the dissolution of magnesium may be decreased due to the formation of a stable magnesium hydroxide film¹⁷, thus making it possible to render a controlled magnesium dissolution, and, in turn, a controlled copper reduction.

To investigate the pH effect on magnesium dissolution, a blank immersion process was performed in a bath containing $\text{K}_4\text{P}_2\text{O}_7$ 100g/l + Na_2CO_3 30g/l + NaF 5g/l. Prior to the blank immersion process the magnesium substrate was pretreated by glass-beading, followed by isopropanol cleaning and alkaline degreasing as stated

in Section 2.1. The SEM images before (Figure 2d) and after the blank immersion process (Figure 2a to 2c) are presented. It is interesting to note that the glass beading process resulted in erosion marks¹⁸ on the surface of magnesium alloy substrate, as is clearly observable on the blank sample (Figure 2d). Such erosion marks were lessened but remained on the substrate surface after the subsequent immersion process (Figures 2a to 2c). The remaining erosion marks could be interpreted as an indication for the dissolution of magnesium induced by the immersion process, i.e. the less obvious the erosion marks, the more the magnesium dissolution. As such, a comparison of Figures 2a to 2c clearly indicates that with an increase in pH, the dissolution of magnesium decreases.

To obtain more information during the blank immersion process, EIS measurements were conducted. Shown in Figures 3 are the Nyquist 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 charge transfer resistance, R_{ct} , and a double layer capacitance, C_d (Figure 3, the insert). Figure 3 shows that with increasing pH of the immersion solution, the charge transfer resistance, R_{ct} , measured from the diameter of the Nyquist arc, is significantly increased, reflecting the decrease of magnesium dissolution. This is consistent with the SEM results.

The back scattered electron images of copper immersion coating are presented in Figure 4, showing the effect of pH. The surface coverage derived from these images is shown as an insert. It indicates that with increasing pH, the copper surface coverage first increases then decreases after reaching a maximum point at a pH of 10.3. As is evidenced from the SEM (Figure 2) and EIS (Figure 3) the dissolution of magnesium at the pH of 9.3 is high, which results in a high driving force for the copper reduction. A high copper coverage is therefore expected. However, this is not the case. The observed surface coverage at pH 9.3 is even lower than those at higher pH (e.g. pH 10.3). The analysis of collected data at

pH 9.3 shows that the data widely scattered, as indicated by the standard deviation (the insert, Figure 4). This is because the dissolution of magnesium at pH9.3 is violent, resulting in non-adherent and spongy copper deposits. Such spongy deposits were subsequently partially removed from the substrate surface by violent hydrogen evolution. With increasing pH, a possible film formation on the magnesium surface mediated/limited the magnesium dissolution, which not only prevented magnesium substrate from violent dissolution but also resulted in a uniform coating (Figures 4, pH 10.6). With the further increase in pH, however, the dissolution of magnesium was slowed down and a decrease in copper coverage is observed (Figures 4, pH 10.9 and 11.2), which might be attributed to a reduced driving force due to a reduced dissolution of magnesium.

Based on the above discussion, a pH range of 10.3 – 10.9 (preferably 10.6) should be employed to achieve a uniform copper immersion coating.

3.2.2. The role of fluoride

Shown in Figure 5 is the effect of fluoride concentration on the copper immersion coating. Figure 5a shows that without fluoride in the coating bath, the obtained coating is spongy and a quality coating is not achievable. After addition of fluoride, the observed surface coverage decreases with increasing fluoride content, attributable to a possible formation of fluoride containing surface film.^{19,20} Similar to the pH effect (Section 3.2.1), the effect of fluoride concentration on the dissolution of magnesium is also manifested by SEM images for the magnesium substrate surface processed in the immersion solution (Figure 6) and the change of the charge transfer resistance, R_{ct} , measured from the diameter of the Nyquist arc (Figure 7). It is clear that the dissolution of magnesium in the immersion bath without fluoride is high (Figure 6a). After addition of fluoride, the dissolution of magnesium substrate was mediated / limited by a possible fluoride containing surface film formation. As a result, the copper surface coverage decreases with increasing the fluoride concentration (Figure 5).

Based on the above discussion, a fluoride content of 5g/L to 10g/L should be added to the coating solution to achieve a uniform copper immersion coating.

4. CONCLUSIONS

- The optimization of a chemical etching process for magnesium substrate was performed, resulting in an optimal experimental condition for the subsequent copper immersion coating.
- Both pH and fluoride content in the alkaline coating bath had significant effects on achieving a quality coating. During the coating process, an increase of pH and fluoride content led to a surface film formation on magnesium substrate, which rendered a controlled magnesium dissolution, thereby a controlled copper deposition.

- With the optimal process conditions of chemical etching and the immersion coating, uniform and finely grained copper deposits were achieved.

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Table 2. Experimental arrangements and the results for the orthogonal design for the chemical etching process.

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Figure 2. Secondary electron (SE) images for the magnesium alloy after the immersion process, showing the effect of pH on magnesium dissolution, (a) pH 9.3, (b) pH 10.3, (c) pH 11.2, and (d) blank sample (The immersion process: substrate – pretreatment (see Section 2.1) – immersion process in $\text{K}_4\text{P}_2\text{O}_7$ 100g/l + Na_2CO_3 30g/l + NaF 5g/l at 22°C for 8 minutes).

Figure 3. Nyquist plots recorded for the magnesium alloy during immersion processes in the same experimental condition as stated in the caption of Figure 2, (a) pH 9.3, (b) pH 10.3, and (c) pH 11.2

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Figure 5. Back-scattered electron (BSE) images of the copper immersion coating for magnesium alloy in a bath containing $\text{K}_4\text{P}_2\text{O}_7$ 100g/l + Na_2CO_3 30g/l + NaF + 12.5 g/l $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ at 22°C, pH = 10.6 (The insert is the plot of copper coverage vs. NaF concentration. The coating procedure: substrate – pretreatment (see Section 2.1) – chemical etching in 100g/l $\text{K}_4\text{P}_2\text{O}_7$ + 30g/l Na_3CO_3 10g/l at 50°C for 10 seconds – immersion coating for 15 min).

Figure 6. Secondary electron (SE) images for magnesium alloy after the immersion process, showing the effect of fluoride concentration on magnesium dissolution, (a) 0 g/L, (b) 10g/L, (c) blank sample (The immersion process: substrate – pretreatment (see Section 2.3) – immersion process for 8 minutes in $\text{K}_4\text{P}_2\text{O}_7$ 100g/l + Na_2CO_3 30g/l + NaF, pH = 10.6, at 22°C).

Figure 7. Nyquist plots recorded for the magnesium alloy during immersion process in the same experimental condition as stated in the caption of Figure 6, (a) 0 g/L, (b) 10g/L.

Table 1 Factors and their levels for the optimization of chemical etching process^a of magnesium substrate for the subsequent copper immersion coating^b.

Symbol	Factors	Levels			
	Chemical etching parameter	1	2	3	4
A	Etching bath (EB) ^c	EB ₁	EB ₂	EB ₃	EB ₄
B	Etching temperature / °C	50	60	70	80
C	Etching time / s	10	60	120	240
D	Rinsing time after the etching / s	0	10	20	40

^aGeneral coating procedure: AD91D substrate – glass beading – isopropanol cleaning under sonication for 3 minutes –degreasing in 60g/l NaOH + Na₃PO₄ 10g/l at 75°C for 3min –rinsing – chemical etching process – rinsing – copper immersion coating.

^bThe immersion coating bath contains: K₄P₂O₇ 100g/l + Na₂CO₃ 30g/l + NaF 10g/l + 12.5 g/l CuSO₄.5H₂O (pH = 10.6, temperature: 22°C, coating time: 15 minutes).

^cChemical etching baths (EB) are EB₁: 60g/l NaOH + Na₃PO₄ 10g/l, EB₂: K₄P₂O₇ 100g/l+Na₂CO₃ 30g/l, EB₃: K₄P₂O₇ 100g/l + Na₂CO₃ 30g/l + NaF 5g/l, and EB₄: Na₄P₂O₇ 100g/l + NaNO₃ 50g/l.

Table 2 Experimental arrangements and the results for the orthogonal design for the chemical etching process.

No of treatment	A Etching bath	B EB temp / °C	C Etching time / s	D Rinsing time/s	Coverage ^a %, η_i			Average coverage, $\bar{\eta}_i$
					1	2	3	
1	EB ₁	50	10	0	54	56	55	55
2	EB ₁	60	60	10	43	41	44	43
3	EB ₁	70	120	20	33	35	35	34
4	EB ₁	80	240	40	30	30	32	30
5	EB ₂	50	60	20	43	51	47	47
6	EB ₂	60	10	40	50	51	48	50
7	EB ₂	70	240	0	40	34	40	38
8	EB ₂	80	120	10	42	46	45	44
9	EB ₃	50	120	40	44	42	39	42
10	EB ₃	60	240	20	35	33	38	35
11	EB ₃	70	10	10	33	30	30	31
12	EB ₃	80	60	0	41	44	43	43
13	EB ₄	50	240	10	33	32	32	32
14	EB ₄	60	120	0	32	28	27	29
15	EB ₄	70	60	40	42	40	39	40
16	EB ₄	80	10	20	37	47	45	43
R_{p1}^b	40	44	45	41				
R_{p2}	45	39	43	37				
R_{p3}	38	36	37	40				
R_{p4}	36	40	34	41				

^aCoating coverage was obtained by processing the back-scattered electron images, using Image – pro Plus software (Media Cybernetics Inc.). Three groups of data listed here were obtained from the three-repeated test for each treatment in the orthogonal array.

^b R_{pl} is the mean level response for factor, p at level, l ($l = 1 - 4$, $p = A, B, C$ or D).

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 7