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Optimization and performance analysis of copper immersion coating on AZ91 magnesium alloy

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Abstract Copper immersion coating on AZ91 magnesium alloy from a hydrofluoric acid containing bath was studied, using an orthogonal experimental methodology. Factors such as hydrofluoric acid concentration, sonication time, chemical etching and activation process were considered in the design. The analysis of variance on the orthogonal experimental results was performed, resulting in an optimal condition for achieving a uniform copper coating with high coverage. Hydrofluoric acid was found to be an essential component in the copper immersion coating bath and a possible mechanism was suggested to explain its significance in terms of magnesium film destruction and magnesium dissolution.

Key words Copper immersion coating, magnesium alloy, orthogonal design

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1. INTRODUCTION

Magnesium and its alloys have the highest specific strength of the structural metals. They are regarded as a solution for mass reduction of vehicles such as automobile and aircraft. However, challenges exist due to their low corrosion and wear resistances, although various coating technologies have been applied. Many reports^{1;2;3;4;5} have suggested that magnesium alloys can be electroless or eletro-plated; but satisfactory process sequences have yet to be developed to meet various industrial requirements.

Magnesium is highly reactive. It forms oxide on its surface even more readily than aluminum. Special procedures are therefore required to obtain adherent and corrosion-resistant coating. Generally, the procedure for plating magnesium alloys is similar to that employed for aluminum alloys^{2;6}. A chemical etching process is usually applied to remove the oxide film, followed by an activation step to activate the surface. Immersion zinc coating is then applied to prevent oxide from reforming². However, the zinc immersion pretreatment process has been criticized for the precise control required to ensure adequate adhesion. In many cases non-uniform coverage on the surface is seen with spongy non-adherent zinc deposits on the intermetallic phase of the base alloys. A copper cyanide strike that must follow has also been of concern for a number of reasons⁷.

Our recent research focuses on the exploration of a simple copper immersion coating on AZ91 magnesium alloy in a hydrofluoric acid bath. Challenges encountered during preliminary studies include low surface coverage. Given the complex effect of different parameters, it was necessary to consider a systematic approach to optimize the process. In any experimental setup a systematic analysis of process parameters is essential to find out the significant variables, which have direct impact on the process quality. Orthogonal

experimental design is known to be an effective tool for the purpose and thereby optimizing the process outputs^{8;9;10}. This paper therefore applies orthogonal design for the optimization of copper immersion coating process. The influence of different parameters such as chemical etching and activation processes as well as immersion bath conditions have been analyzed and optimal conditions are established.

2. EXPERIMENTAL

The substrate used in this study is AZ91D magnesium alloy, supplied by Norsk Hydro Canada, with a nominal composition of Al (8.5-9.5%), Zn (0.45-0.9%), Mn (0.17-0.40%), Si (<0.08%), Cu (<0.025%), Ni (<0.001%), Fe (<0.004%) and Be (0.0005-0.003%). The specimens were prepared with dimensions of 10×8×1.5 mm. All chemicals of ACS reagent used in this work were provided by SIGMA. De-ionized water (>15MΩ cm⁻¹) used throughout the experiments was prepared with Millipore Elix 10 Water Deionization System (Millipore Corporation).

Pretreatment of the samples were conducted using glass beading or mechanical polishing. For mechanical polishing, the sample was polished to 400 grits using wet emery papers. During glass-beading process, the sample was blasted with glass beads for 10 seconds, using ECONO-Finish Blast Cabinet (EF-2436, Empire Abrasive Equipment Company). Air pressure applied for the glass beading process was about 450 kPa. The stream hit the sample in a normal direction from a distance of about 10 cm. After glass beading, loosely sticking particles were removed from the blasted surface with compressed air.

Samples were subsequently degreased in an alkaline solution containing 60g/l NaOH + 10g/l Na₃PO₄ at 75°C for 6 mins and thoroughly rinsed in de-ionized water. Rinsed sample was then immediately immersed into a hydrofluoric acid bath for copper immersion coating. Prior to the immersion coating, some samples were subjected to chemical etching and followed by an activation process. The conditions of chemical etching and activation processes are specified in Table 1.

All immersion coating processes were carried out in a hydrofluoric acid bath containing copper sulfate at room temperature for 10 minutes, unless specified otherwise. The volume of the solution placed in the immersion bath was 100 ml. The immersion baths were classified as a 'still bath' and a 'sonicated bath', depending on whether sonication was applied. The sonication system used in this experiment is the Model 9333 ultrasonic bath (Lab-line Instruments Inc.) with a frequency of 40kHz.

A 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, analyzed with Image – pro Plus software (Media Cybernetics Inc.).

3 RESULTS

3.1 Preliminary experimental results

In order to apply copper deposits on magnesium alloy using an immersion coating process a survey experiment was conducted in various immersion baths. The preliminary results revealed that it was difficult for copper to deposit and anchor on the magnesium alloy due to its chemical reactivity and affinity to oxygen. In order to enable the

formation of copper coating, hydrofluoric acid was employed in the immersion-coating bath and was found to be an essential component. Shown in Figure 1 are the back-scattered electron images of copper immersion coatings in the hydrofluoric acid bath. In a 2.2 M HF immersion bath nodular copper deposit was formed on the magnesium surface (Figure 1a). When the immersion coating was performed in a 5.5M HF bath, however, only small amount of copper was deposited (Figure 1b). It is therefore concluded that the copper deposition is directly related to the HF concentration under the investigated range. Moreover, it was observed during our experiments that HF concentration lower than 2M would result in violent magnesium dissolution and spongy non-adherent copper deposits on the magnesium alloy.

Furthermore, back-scattered electron images of the copper coatings from the hydrofluoric acid bath under various conditions were also obtained (Figures 2-4). After analyzing these images the following observations can be made:

(1) Chemical etching, in combination with the subsequent activation process, has a significant effect on the copper immersion coating. Copper coverage on the sample etched by a chromium oxide solution with a subsequent alkaline activation (Figure 2b) is much higher than that etched in an oxalic acid, followed by a fluoride activation (Figure 2a).

(2) Copper coverage on the glass-beaded surface (Figure 3a) is much higher than that on the polished sample (Figure 3b). The images also indicate that the uniformity of the copper coating on the former is much better than on the latter.

(3) A comparison of Figure 4a and 4b indicates that the application of sonication to the immersion coating bath promotes copper growth significantly. The effect of

sonication on the copper immersion coating and its mechanism will be discussed in a separate paper.

In addition, the effect of immersion coating time on the copper coverage was studied, as shown in Figure 5. The copper coverage increases with increasing immersion coating time at the initial stage (within 2 minutes) and then plateaus with an extended coating time.

The preliminary studies of the copper immersion coating addressed multiple effects of different factors. To find the significant variables affecting the immersion coating quality, it is desirable to apply an orthogonal design for optimization of the coating process. From the above discussion the immersion coating time has little influence on the surface coverage beyond 2 min deposition and the glass-beading surface pretreatment is superior to the polishing. As such, the immersion coating time was fixed at 10 minutes and glass beading was conducted on all the samples throughout the orthogonal experiments. Four factors, HF concentration, sonication time, chemical etching and activation processes, were considered in the design.

3.2 Orthogonal experiment results

Based on the preliminary experimental results, four factors, at four levels each, were selected for the orthogonal experiment, as shown in Table 1. The experimental arrangements using an orthogonal array are shown in Table 2. In this table each process parameter was assigned to a column and sixteen parameter combinations are available.

The objective of the orthogonal experiment is to determine the optimal combination of the immersion coating process variable so as to obtain a desired copper immersion

coating on the magnesium alloy. Such a copper coating can act as an intermediate layer to protect the magnesium surface from dissolving and oxidizing during subsequent electroless deposition or electroplating. Our recent studies found that a uniform copper immersion coating with an adequate coverage is essential for achieving the desired electroless deposition on the immersion-coated magnesium surface. The coverage of the copper immersion coating is therefore the most important quality characteristic to be measured. Experiments according to the orthogonal arrangement were conducted. To obtain more reliable results, each treatment in the orthogonal array was repeated three times with the results shown in Table 2.

The mean level response of each factor, R_{pl} , are 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 (parameter, $p = A, B, C$ and D). $\bar{\eta}_i$ is the average coverage corresponding to each treatment.

According to equation (1), the calculated results are listed in Table 2 and plotted in Figure 6. These mean level response curves suggest that, within the investigated level ranges, the optimal combination of the coating process parameter levels to obtain the high coverage is A_1, B_3, C_3 and D_4 (Figure 6). It is noted that further decreasing HF concentration (Factor A) or increasing sonication time (Factor D) may further increase

the coating coverage. However, such conditions would deteriorate the immersion coating quality, as will be discussed in Section 5.

3.3 Analysis of variance

The main purpose of the analysis of variance (ANOVA) is to test the significance of design factors in affecting the quality characteristics. The total sum of square, SS_T , is given by:

$$SS_T = \sum_{i=1}^n \bar{\eta}_i^2 - \frac{1}{n} \left[\sum_{i=1}^n \bar{\eta}_i \right]^2 \quad (2)$$

where n is the total number of treatments, e.g. $n=16$. The sum of squares from the tested factor SS_p , can be calculated as:

$$SS_p = \frac{1}{t} \sum_{l=1}^t \left(\sum_{i=1}^k \bar{\eta}_i \right)^2 - \frac{1}{n} \left[\sum_{i=1}^n \bar{\eta}_i \right]^2 \quad (3)$$

where t ($= 4$) is the number of levels in factor, p .

The remainder of the sum of squares that represents the error term, SS_e , is equal to

$$SS_e = SS_T - SS_A - SS_B - SS_C - SS_D \quad (4)$$

The variances for a factor, V_p , and for the error term, V_e , are calculated by dividing the corresponding sum of squares by the relevant degrees of freedom, D_p and D_e ,

$$V_p = SS_p / D_p, \quad V_e = SS_e / D_e \quad (5)$$

where $D_p = t - 1$ and $D_e = (n - 1) - 4(t - 1)$. Finally, to examine the significance of the factors, values for the F-test are obtained by dividing the variance of a factor by that of the error term,

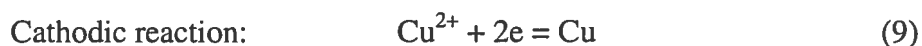
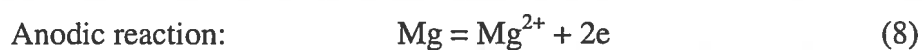
$$F_p = V_p / V_e \quad (6)$$

The results of the analysis of variance based on equations (2) – (6) are shown in Table 3. According to the analysis of variance, the effect of HF concentration on the coating coverage is statistically significant at the confidence level of 0.25.

4. DISCUSSION

Both level response (Figure 6) and the analysis of variance (Table 3) suggest that the effect of HF concentration on the coating coverage is the most significant factor. As has been discussed in Section 3, hydrofluoric acid is an essential component in the immersion bath to enable the formation of copper coating on the magnesium alloy. Within the HF concentration range studied, the mean level response indicates that the lower the HF

concentration, the higher the coverage (Figure 6). Examination of surface morphologies of the copper immersion coatings obtained under different experimental conditions showed that higher coverage was usually accompanied with higher magnesium dissolution. For example, in the immersion bath containing 5.5M hydrofluoric acid, very little material was dissolved from the magnesium surface during the immersion coating process, as indicated by the remaining erosion marks in the uncoated area, which were caused by the glass beading process¹¹ (Figure 1b); correspondingly only small amount of copper was deposited on the magnesium surface. In contrast, in a 2.2M hydrofluoric acid bath, significant magnesium dissolution occurred, as indicated by the rough morphologies in the uncoated area (Figure 1a); the magnesium dissolution led to the formation of clusters of nodular copper deposits on the magnesium surface with a high surface coverage. The dissolution of magnesium as an anodic reaction provides the driving force for the cathodic reaction of copper reduction and deposition:



According to Pourbaix diagram¹², magnesium dissolves readily as Mg^{++} in aqueous solutions with pH below 11. Above pH 11, its dissolvability gradually decreases with the increase of pH due to the formation of a stable magnesium hydroxide film¹³.

In hydrofluoric acid solution, however, pH only varies slightly with HF concentration under the investigated range. The dissolvability of magnesium in hydrofluoric acid is therefore mainly determined by the HF concentration rather than the pH. At low HF concentrations, dissolution of magnesium is significant. As the HF concentration increases, the dissolvability of magnesium decreases and becomes less visible. It was observed during our experiments that, at HF concentrations greater than 5M, very little dissolution of magnesium occurred. This is presumably due to the formation of a relatively insoluble and protective film of magnesium fluoride, MgF_2 , according to the following reaction:



Based on the above discussion, in order to achieve a uniform coating with high surface coverage, the hydrofluoric acid concentration can be adjusted to control the formation of the fluoride film and the dissolution rate of magnesium. On one hand, the formation and growth of the surface film is needed to protect the magnesium from being violently dissolved which, in turn, would create difficulty for the reduction and anchoring of copper; a very concentrated HF bath (e.g. > 5M), on the other hand, will lead to a low dissolution rate in magnesium and hence a very low copper coverage (Figure 1b). However, although higher coating coverage in a low hydrofluoric acid concentration bath (e.g. 2.2M) can be achieved, a spongy non-adherent copper deposit with voids/grooves is

unavoidable (Figure 1a). As such, a concentration range of 3 - 4 M in hydrofluoric acid should be employed to achieve a uniform and adherent copper immersion coating.

The application of sonication to the immersion-coating bath is also an important factor. The back-scattered electron images (Figures 4 a and b) showed that copper growth was significantly promoted by applying sonication to the immersion-coating bath. According to the level response it seems that the effect of sonication on the coating coverage is relatively low at the short times from 0.5 to 2 minutes (Figure 6). However, there was an apparent increase in coating coverage when the sonication time was increased to 10 minutes. In this study, the degreasing process was performed in the alkaline solution, which possibly caused the formation of magnesium hydroxide film on the sample surface¹². During the subsequent immersion coating, an electrochemical process including the hydroxide film destruction, transformation, accompanied with magnesium dissolution could occur. Such a process presumably predominated the immersion coating process at the initial stage, as indicated in the coverage – time curve obtained in a still bath (Figure 5). The curve shows that the coating coverage increases with increasing coating time initially and then reaches the plateau, possibly due to the formation and subsequent thickening of the hydroxide-fluoride film¹⁴ on the magnesium surface. In the sonicated bath, however, the sonication might have produced jets or cavitations, which continually attack the magnesium surface film, leading to continued magnesium dissolution and, in turn, copper deposition. The copper coverage was therefore increased with increasing immersion coating time in the sonicated bath, as indicated from the mean level response curve (Figure 6). However, it was noticed during

our experiment that prolonged sonication to the immersion bath would result in large voids. Thus, the sonication time should not exceed 10 minutes.

For the other two factors investigated, the optimal conditions for obtaining better coverage are obvious, i.e., B₃ for etching bath (EB₃) and C₃ for activation bath (AB₃). From the above discussions, the optimal experiment conditions for obtaining a uniform copper immersion coating with an adequate coverage can be identified as: A₂, B₃, C₃ and D₄, i.e. the sample is chemically etched using the chromium oxide solution (B₃), followed by the alkaline activation (C₃) and then the copper immersion coating is performed in the 3.3M hydrofluoric acid bath (A₂) with a sonication time of 10 minutes (D₄) from the beginning of the immersion coating process.

According to the above optimal combination of factor levels (A₂B₃C₃D₄), immersion coating on the magnesium alloy was conducted. Shown in Figure 7 is the back-scattered electron image. It is apparent that the coating coverage (Figure 7) is much higher than those obtained from experiments prior to the optimization using the orthogonal design, for example, Figure 1.

It should be pointed out that the present study only investigated the main effects of the four factors while their interactions have not been considered. The analysis of variance shown in Table 3 indicates that the significance levels (F-values) for the tested factors are low; even for the most significant factor (HF concentration) it is significant only at a confidence level of 0.25. However, experimentally, it has been observed that the coating coverage did show very significant changes as the factor levels changed. For example, a comparison of copper coatings obtained from the sonicated bath (Figure 1a)

and the still bath (Figure 1b) clearly indicated that sonication significantly promoted the copper deposition. However, such a very significant effect was not fully reflected from the analysis of variance. The low significant contribution of the sonication factor from the analysis of variance might be attributed to interactions among the experiment factors. Further studies are required to clarify these interaction effects using a different experiment array.

5. CONCLUSIONS

Optimization of the copper immersion coating on magnesium alloy using orthogonal methodology was performed. After analyzing the effect of the tested parameters on the copper immersion coatings, an optimal experiment condition was identified as: A₂, B₃, C₃ D₄, i.e. the sample is chemically etched using chromium oxide solution (B₃), followed by an alkaline activation (C₃). The copper immersion coating is performed in a bath containing 3.3M hydrofluoric acid (A₂) with sonication for 10 minutes (D₄) from the beginning of the immersion coating process. The coating coverage obtained under the optimal experimental conditions was significantly increased, as compared to those obtained from experiments prior to the optimization. Furthermore, the hydrofluoric acid concentration in the immersion bath was identified as possibly the most significant factor. A possible mechanism was suggested to explain the significance of hydrofluoric acid in terms of magnesium film destruction and magnesium dissolution.

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Figure 1. Back-scattered electron images of the copper immersion coatings on the AZ 91 magnesium alloy in a still bath containing: (a) 2.2M HF +0.67 CuSO₄ and (b) 5.5M HF +0.67 CuSO₄. (The coating procedure: substrate - glass beading - degreasing in 60g/l NaOH + Na₃PO₄ 10g/l at 75°C for 6min - immersion coating).

Figure 2. Back-scattered electron images of the copper immersion coatings in a still bath containing 4.4M HF + 0.67M CuSO₄ on the AZ 91 magnesium alloy with different chemical etching process: (a) EB₃ + AB₃ and (b) EB₄ + AB₂ (see Table 1 for the chemical etching bath conditions). (The coating procedure: substrate – glass beading - degreasing in 60g/l NaOH + Na₃PO₄ 10g/l at 75°C for 6min - chemical etching - immersion coating).

Figure 3. Back-scattered electron images of the copper immersion coatings in a still bath containing 4.4M HF + 0.67M CuSO₄ on the AZ 91 magnesium alloy with different pretreatment: (a) glass beading, (b) mechanical polishing. (The coating procedure: substrate - pretreatment - degreasing in 60g/l NaOH + Na₃PO₄ 10g/l at 75°C for 6min - immersion coating).

Figure 4. Back-scattered electron images of the copper immersion coatings on the AZ 91 magnesium alloy in a bath containing 4.4M HF +0.67 CuSO₄): (a) still bath and (b) sonicated bath. (The coating procedure: substrate - glass beading - degreasing in 60g/l NaOH + Na₃PO₄ 10g/l at 75°C for 6min - immersion coating).

Figure 5. Coverage- time curve of the copper immersion coatings on AZ 91 magnesium alloy in a still bath containing 4.4M HF +0.67 CuSO₄. (The coating procedure: substrate - glass beading - degreasing in 60g/l NaOH + Na₃PO₄ 10g/l at 75°C for 6min - immersion coating).

Figure 6. Mean level response of the factors for the average coverage of the copper coatings

Figure 7 Back-scattered electron images of the copper immersion coatings obtained under the optimal conditions (A₂B₃C₃D₄).

Table 1 Coating process factors and their levels

Table 2 Experimental arrangements using a L16 orthogonal array

Table 3 Results of the analysis of variance

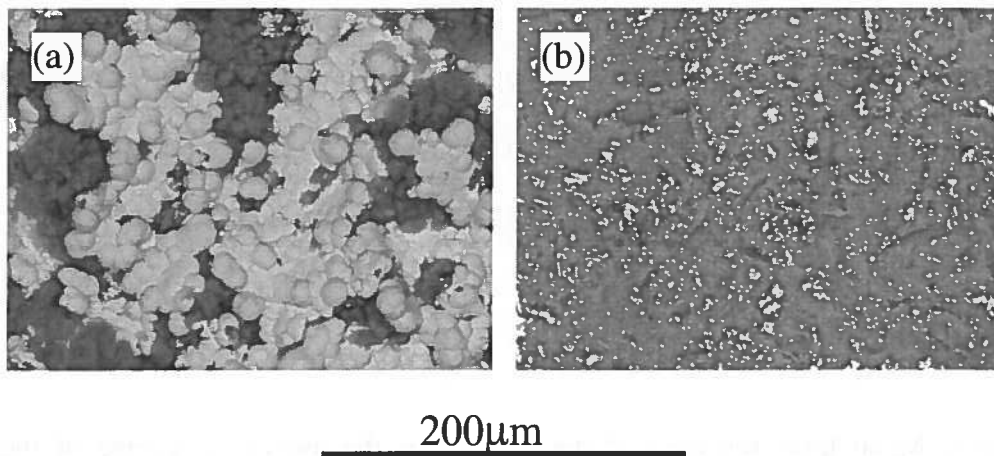


Figure 1

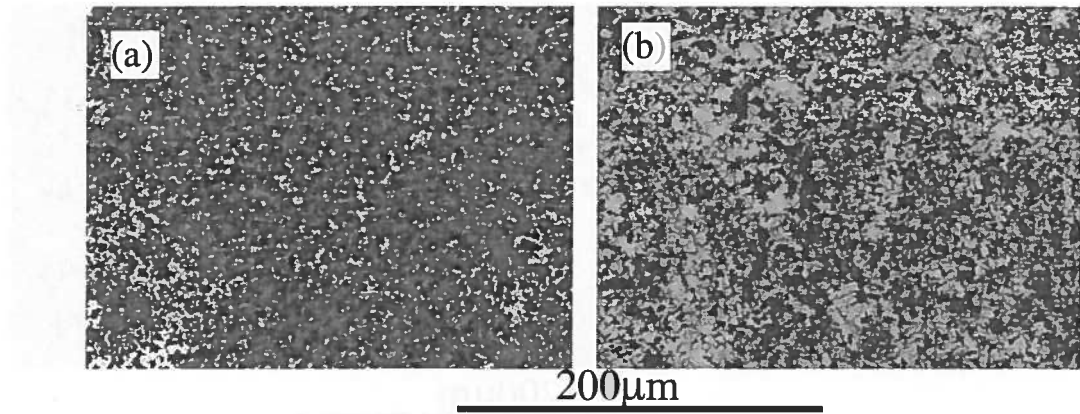


Figure 2

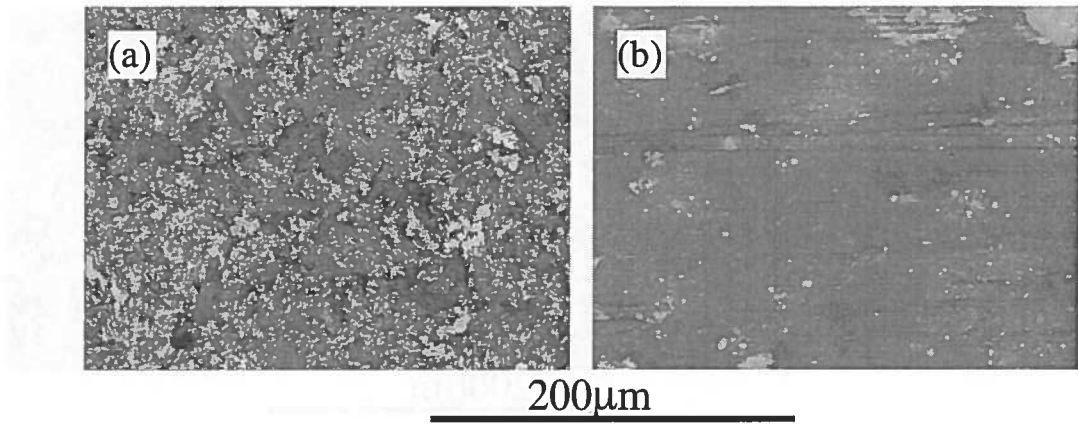


Figure 3

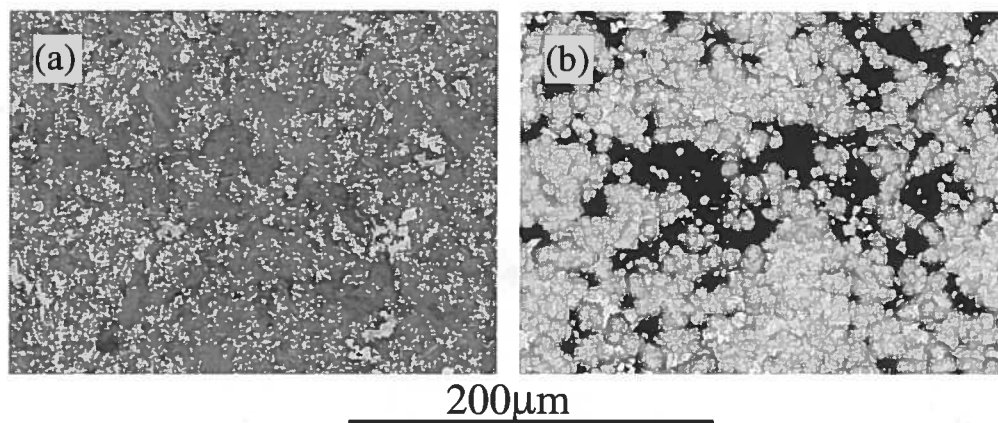


Figure 4

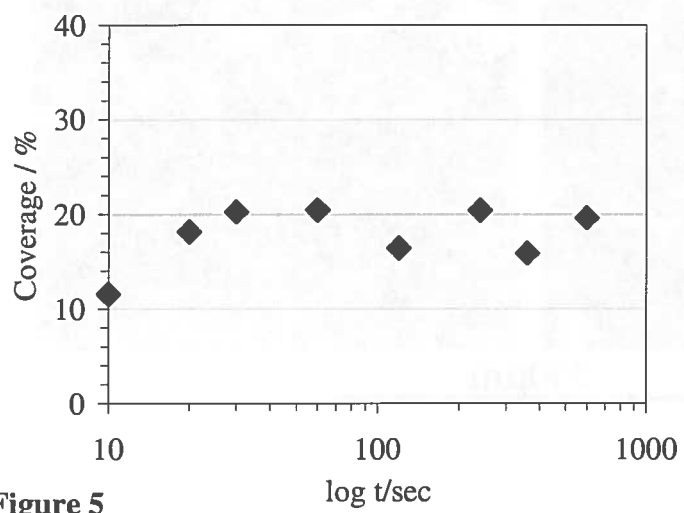
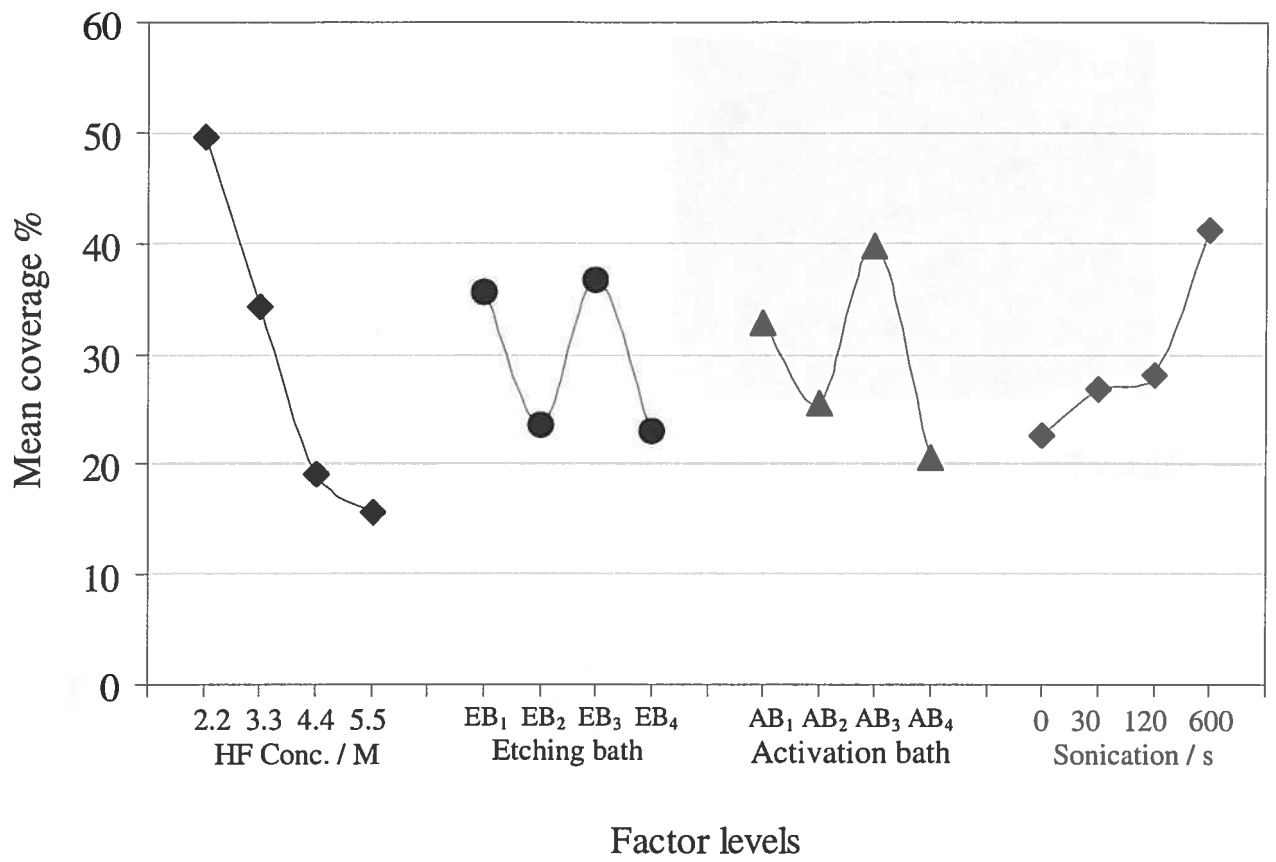


Figure 5

**Figure 6**

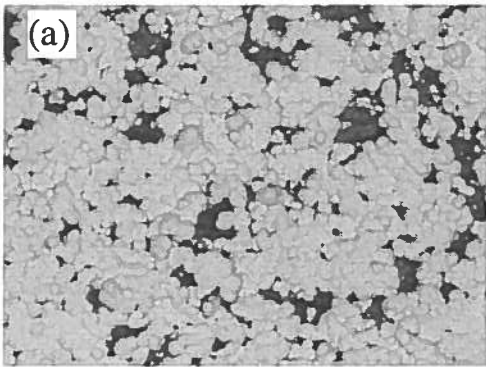


Figure 7

Table 1 Coating process^a parameters and their levels

Symbol	Factors		Levels			
	Coating parameter	Unit	1	2	3	4
A	HF concentration ^b	Molar	2.2	3.3	4.4	5.5
B	Etching bath ^c		EB ₁	EB ₂	EB ₃	EB ₄
C	Activation bath ^d		AB ₁	AB ₂	AB ₃	AB ₄
D	Sonication time ^e	Minute	0	0.5	2	10

^aGeneral coating procedure: Substrate – glass beading - degreasing in 60g/l Na OH + Na₃PO₄ 10g/l at 75°C for 6min - chemical etching – activation - immersion coating (room temperature, 10 minutes)

^bHF concentration is the hydrofluoric acid concentration in the immersion coating bath (0.67M CuSO₄ + xM HF: x = 2.2, 3.3, 4.4, 5.5 M).

^cEtching baths (EB) were chosen as: EB₁ - without etching, EB₂ – H₃PO₄ (85%) 380ml/l + H₂SO₄ (98%) 16ml/l, EB₃ - CrO₃ 180g/l + Fe(NO₃)₃·9H₂O 40g/l + KF 3.5g/l and EB₄ - Oxalic acid (C₂H₂O₄) 10g/l + wetting agent (62A from Entrone-Ont Inc, New Haven CT06508). The etching process was performed at room temperature for 30s.

^dActivation baths (AB) were chosen as: AB₁ - without, AB₂ - 100 g/l NH₄HF₂ + 200 ml/l H₃PO₄ (75%), AB₃ - K₄P₂O₇ 100g/l+Na₂CO₃ 30g/l+NaF 5g/l and AB₄ – 340ml/l HF (38% hydrofluoric acid). The activation process was performed at room temperature for 30s.

^eSonication was applied to the immersion bath, just before the sample was put into the bath for copper coating, and then stopped at the predetermined time (Factor D) in Table 1, leaving the immersion coating process to continue until a total of 10 minutes had elapsed.

Table 2 Orthogonal experimental arrangement and results

No of treatment	A HF conc./ M	B Etching bath	C Activation bath	D Sonication/min	Coverage ^a %, η_i			Average coverage, $\bar{\eta}_i$
					1	2	3	
1	2.2	EB ₂	AB ₁	0.0	47	29	35	37
2	2.2	EB ₃	AB ₂	0.5	40	34	55	43
3	2.2	EB ₄	AB ₃	2.0	61	58	54	58
4	2.2	EB ₁	AB ₄	10	65	71	48	61
5	3.3	EB ₂	AB ₂	2.0	22	30	24	26
6	3.3	EB ₃	AB ₁	10	60	65	61	62
7	3.3	EB ₄	AB ₄	0.0	6	5	4	5
8	3.3	EB ₁	AB ₃	0.5	40	37	57	45
9	4.4	EB ₂	AB ₃	10	23	30	31	28
10	4.4	EB ₃	AB ₄	2.0	14	12	13	13
11	4.4	EB ₄	AB ₁	0.5	18	18	11	16
12	4.4	EB ₁	AB ₂	0.0	20	20	20	20
13	5.5	EB ₂	AB ₄	0.5	4	4	3	4
14	5.5	EB ₃	AB ₃	0.0	28	36	23	29
15	5.5	EB ₄	AB ₂	10	12	18	11	14
16	5.5	EB ₁	AB ₁	2.0	13	20	16	16
R_{p1} ^b	50	36	33	23				
R_{p2}	34	24	25	27				
R_{p3}	19	37	40	28				
R_{p4}	14	23	21	41				
X ^c	36	14	19	18				

^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).

^c X is the extreme level difference ($X = R_{max} - R_{min}$)

Table 3 Result of the analysis of variance

Symbol	Coating Parameter	df	SS	V_p	F_p
A	HF concentration	3	2911	970	7.22
B	Etching bath	3	665	222	1.65
C	Activation bath	3	845	282	2.09
D	Sonication time	3	778	259	1.93
Error		3	403	134	$F_{0.25}(3,3) = 2.36$
Total		15	5603		

Note: df is the degree of freedom; SS is the sum of squares; $V_p (= SS_p/df.)$ is the variance of the parameter tested and $F_p = V_p/V_e$, V_e is the variance of the error term.

Table 3 Results of the analysis of variance

Source	df	MS	F	Significance
Between groups	4	10.2	1.8	0.13
Within groups	100	5.7		
Total	104			

MS = Mean Square; df = degrees of freedom; F = F-ratio; Significance = probability of Type I error (alpha) = 0.05