# Surface Analysis of Zinc Alloy Immersion Films on Aluminum

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Composition profiles of displacement films obtained on aluminum in modified zincate solutions showed that an initial zinc deposit was followed by the deposition of copper by an exchange reaction with zinc atoms. Although the solutions contained a large concentration of nickel ions, the displacement film contained less than 3 atomic percent nickel. During nickel electroplating, zincrich regions of the film were partly dissolved.

luminum is considered a difficult-to-plate metal substrate.<sup>112</sup> Plating after simply cleaning and pickling it is rarely successful because electroplated coatings tend to be poorly adherent to aluminum and especially to its alloys. Attempts to improve surface preparation have included anodizing in phosphoric acid and immersing in simple stannate or zincate solutions, but these processes have been limited in success and often fail to provide the desired degree of adhesion. More recently adhesion has been improved by using modified alloy zincate (MAZ) pretreatments. This report deals with the analysis of displacement films that grow during immersion of aluminum in MAZ solutions, based on a study of the MAZ pretreatment process.\*

Our MAZ solutions contained copper, nickel and iron,<sup>3</sup> which codeposit with zinc in varying degrees, forming a thin (<1  $\mu$ m) metallic layer suitable for the application of electroplated metals. Lashmore<sup>4</sup>observed that the displacement film formed in a zincate solution containing iron ions also contained a small amount of iron.

Previous reports<sup>56</sup> discussed morphological aspects and

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Fig. 1—Copper and zinc contents es a function of film thickness on aluminum. Single dip immersion time varied from 5 to 60 sec.

the results of metal distribution studies in single and double MAZ immersion films. Composition-depth profiles 'during film growth and after electrodeposition of a thin nickel layer are discussed in this paper. The results enabled assessments of the roles of the different metals in the solution and the films.

## **Experimental Procedure**

Commercial, wrought alloy sheet containing 99 percent aluminum and usually, about 1 mm thick was selected for this study. Surfaces were prepared as recommended by the supplier <sup>7</sup>with modifications.<sup>58</sup> MAZ immersion time was varied from 5 to 90 sec on different samples. Single-dip samples and others given a double-dip treatment with an intermediate nitric acid dip were examined. Surfaces were analyzed, using Auger electron spectrometry (AES). A depth profile analysis, calibrated against standard alloys, was performed after argon sputtering. Solutions were analyzed by using atomic absorption spectrometry (AAS). Growth kinetics of the films were followed by weight change measurements. At least six replicates were made for each time sequence.

Scanning electron microscopy (SEM) was adopted for the observation of surface morphology at different stages of film growth. The SEM images were further examined to make quantitative measurements of surface coverage.

# Results

Figures 1 and 2 are depth profiles of single and double dip films applied in 5 to 90 sec. The diagrams show the atomic percentages of zinc and copper. Aluminum was omitted for the sake of clarity and accounts for the balance of the film composition. However, elements with a concentration below 2 percent were ignored in these plots.



Fig. 2—Copper end zinc contents es e function of the thickness of Immersion films obtained during the second of double-dipped aluminum samples.

A 40-nm-thick film containing about 85 percent zinc and a small amount of copper was formed during a 5-sec immersion. In another experiment, up to 22.5 atomic percent oxygen was detected at about 33 nm from the aluminum substrate interface. Film thickness increased considerably to 130 nm when the immersion time was increased to 15 sec. About 5 percent copper was detected at about 70 nm from the aluminum interface. The aluminum content of nearly 40 percent indicates uncovered aluminum areas associated with the rough aluminum surface and signifies that the film nucleates and grows preferentially at discrete sites.

Film thickness increased to 250 nm after 30 sec of immersion but the rate of film growth had obviously declined. After 60 sec of immersion, film thickness was only about 225 nm, indicating zinc dissolution during the final 30 sec of immersion. The copper content exceeded the zinc content in the 25-nm-thick layer next to the aluminum interface, but zinc dominated in thicker layers. At 50 nm from the aluminum surface, the copper content reached a maximum of about 25 percent and the aluminum content declined to less than 40 percent. Increases in the zinc and decreases in the aluminum contents continued at levels even farther from the substrate.

The thickness of a 90-sec film was only about 210 nm, indicating further dissolution of the film after 60 sec. There was a significant increase in copper throughout the film, especially at and above 70 nm from the aluminum interface.

In the double dip immersion process, which gives better results than a single dip,<sup>79</sup> the initial 60-sec film was etched during an intermediate 30-sec dip in a solution containing 50-volume percent nitric acid and 2-volume percent hydrofluoric acid. Figure 2 shows depth profiles for double dip films labeled in accordance with the immersion time in the second dip after the nitric acid etch. After acid etching, which equates to zero immersion time in the second dip, there was a 60-nm-thick film left on the surface. This layer, which was discontinuous, contained about 50 percent copper and only 7.5 percent zinc.

After 5 sec in the second dip, aluminum was the major element, indicating that the film was still discontinuous. Moreover, the copper content was still greater than the zinc and was equal to 32.5 percent. Zinc was confined to the outer portion. An appreciable amount of oxygen was concentrated at or near the substrate surface.

The depth profiles of films formed during a 15-sec or longer time period were similar in shape to single-dip profiles. The thickness of films formed in 15, 30 or 60 sec was in the range of 180 to 200 nm. The maximum copper content in the 15- or 30-sec films was about 15 or 20 percent, but surged to 32 percent in a 60-sec film and to nearly 40 percent in a 90-sec film that was only 140 nm thick—clear evidence of film dissolution after 60 sec of immersion.

Figure 3 shows weight gains for samples immersed in MAZ solutions. The gains for single- and double-dip samples are similar, indicating the same sequence of nucleation, growth and stabilization. However, the double-dip samples showed less spread in the data than the single-dip specimens.

Figures 4 and 5 show SEM photographs of single- and double-dip films, respectively. Although the immersion time in both cases was 40 see, the double-dip film is better developed and shows a greater degree of surface coverage. A quantitative, computer-aided image analysis of a



Fig. 3—Weight changes with time of immersion of single and double-dipped aluminum samples. The vertical bars a how the ranges obtained in the weight change data.



Fig. 4—SEM photograph of a 40-sec single immersion film.



Fig. 5—SEM photograph of a double-dipped film after 40 sec in the second din



Fig. 6—Surface coverage determined by image analysis as a function of single-dip immersion time.

Sample	Metal, percent of total				
	Cu	Zn	Ni	Fe	AI
MAZ solution	10.1	29.6	56.1	3.9	_
Used MAZ solution	6.8	26.6	52.3	3.0	10.3
First immersion film	4.9	92.6	<2	<1	_
Second immersion film	12.4	84 1	<3	<1	_

Table 1							
Metal Content of	Solutions	and	Zinc-Rich	Films*			

'Metal contents determined by atomic absorption spectrometry

sequence of similar SEM photographs taken to study the evolution of film growth showed the surface coverage data in Figs. 6 and 7 for single- and double-dipped samples, respectively. Surface coverage was consistently greater with the double-dip films, which also showed less spread in coverage for samples immersed for a given time.

The metal concentrations, determined by AAS, in fresh and used MAZ solutions are summarized in Table 1, which also shows the proportions of codeposited metals in singleand double-dip films. Although the nickel concentration in the MAZ solution was much higher than the zinc or copper concentrations, less than 2 percent nickel showed up in the single dip film. Zinc was enriched in the film, relative to the proportion in solution. The double-dipped film had a much higher copper content than the single-dipped film. The aluminum concentration in solution increased as the solution was used. Copper, nickel and zinc decreased, but copper decreased more than the others.

Figure 8 shows AES analytical data for double-dipped samples electroplated for 3 see with nickel at current densities of 2 and 5 A/dm<sup>2</sup>. The thickness of the MAZ film nickel plated at 2 A/dm<sup>2</sup>was about 40 nm less than the other. Nickel plating at 5 A/dm<sup>2</sup>produced a visible nickel layer, but deposition at 2 A/dm<sup>2</sup>did not. The amount of nickel detected throughout the MAZ film under the visible nickel was greater than the amount in films not plated with nickel, indicative of porosity.

Analysis of the nickel sulfate solutions showed that more zinc dissolved than copper during electroplating. After a 35-cm<sup>2</sup>, zincated aluminum panel was nickel plated in the 200-L sulfate bath, which initially contained 92 g/L of zinc and 15 g/L of copper, analysis of a 15-mL sample showed increases in the zinc and copper concentrations to 149 and 20 mg/L, respectively. The Cu:Zn ratio in the MAZ film plated with nickel was 0.17 by comparison with a Cu:Zn ratio of 0.14 in the film on a sample that was not nickel plated.

# Discussion

Although previous investigators<sup>10-13</sup> reported 81 to 86 percent zinc, 8 to 16 percent copper and 2 to 6 percent nickel in MAZ films, no data were given on variations in composition within the films. AES proved to be a suitable technique for determining composition changes as ion beam etching gradually removed successive layers of the film. The area of bare aluminum increased with the removal of successive layers and the zinc content decreased. The copper contents, which peaked at 50 to 90 nm from the aluminum interface depending on the immersion time, also decreased when ion beam etching was continued below this level.



Fig. 7—Surface coverage determined by Image analysis as a function of the thickness of immersion films obtained in the second of double-dipped samples.



Fig. 8—Aluminum, copper and zinc contents as a function of immersion time in the second of double-dipped aluminum samples after electroplating for 3 sec at 2 and 5 A/dm<sup>2</sup>.

Nucleation and growth starts with isolated islands of zinc. Little or no copper is deposited during immersion for 5 or 15 see, but the copper content of the film proved to be greater than the zinc content after a 30-sec treatment. However, zinc was the main element in thicker films. Nevertheless, films as thick as 200 nm remained discontinuous. The mechanism of MAZ film formation is far from simple. Not only is there a displacement reaction between the aluminum and zinc, promoting film nucleation and growth, but there also appears to be a displacement reaction within the film whereby copper displaces zinc. The initial zinc layer evolves to a state where copper dominates. This may involve some form of ion exchange reaction. Solid state diffusion is considered unlikely because the temperature of the environment remains at room temperature. Copper was never found alone at the aluminum interface. Zinc is required before copper can start displacing zinc. When the solution adjacent to the film surface becomes depleted in copper, zinc deposition continues as the main reaction.

Some aluminum was found in all MAZ films. Possibly aluminum ions released during the exchange with zinc ions become entrapped by the large flux of zinc and copper ions reaching the aluminum surface. Or, zinc aluminate generated by the reaction of aluminum and hydroxyl ions may be reaching a saturation level in the zone near the aluminum and precipitating. This reaction would explain the oxygen content in the film.

MAZ films are more compact than unalloyed zinc deposited by displacement on aluminum. Double-dipped MAZ films grow faster and become more compact than single-dipped films. Copper has a greater role in the double-dipped films.

#### Conclusions

MAZ immersion films contain copper, nickel and iron in addition to zinc but their proportions in films do not replicate proportions in the MAZ solutions. Composition profiles of immersion films show a heterogeneous distribution of the metals at different growth stages. Initially only zinc is deposited. Later, copper becomes the dominant metal in the film, but zinc again becomes the major element in thicker films. Some aluminum, usually associated with oxygen, appeared frequently in the outer zone of the relatively thick films. Nickel and iron never exceed 2 or 3 percent of the total metal content.

The acid treatment between the dips in a double-dipped sample removes much of the film formed during the first dip. However, a thin layer with a high copper content remains. This layer promotes the nucleation of closely spaced crystallite and increases the film growth rate. Profile changes occur in the film when it is overplated with nickel. Zones in the film where zinc is concentrated are dissolved during the electroplating process and film thickness is reduced.

#### Acknowledgments

The authors acknowledge the support and facilities provided by Professors I.A. Menzies, Loughborough University, and M. Costa, Porto University. Financial support was provided by NATO in the "double jump" program, the British Council, JNICT and the Portuguese Ministry of Industry. Chemicals were supplied by W. Canning Materials Company, Birmingham, UK. Dr. D. Hall carried out surface analyses. Valuable discussions with Dr. E. Wyszynski were most stimulating.

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