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**The Influence of Surface Microchemistry in Protective Film Formation on Multi
Phase Magnesium Alloys**

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Abstract:

The high strength:weight ratio of magnesium alloys make them an ideal metal for automotive and aerospace applications where weight reduction is of significant concern. Unfortunately, magnesium alloys are highly susceptible to corrosion particularly in salt-spray conditions. This has limited their use in the automotive and aerospace industries, where exposure to harsh service conditions is unavoidable. The simplest way to avoid corrosion is to coat the magnesium-based substrate by a process such as electroless plating, which is a low-cost, non line of sight process.

Magnesium is classified as a difficult to plate metal due to its high reactivity. This means that in the presence of air magnesium very quickly forms a passive oxide layer that must be removed prior to plating. Furthermore, high aluminium content alloys are especially difficult to plate due to the formation of intermetallic species at the grain boundaries, resulting in a non-uniform surface potential across the substrate and thereby further complicating the plating process.

The objective of this study is to understand how the magnesium alloy microstructure influences the surface chemistry of the alloy during both pretreatment and immersion copper coating of the substrate.

A combination of scanning electron microscopy, energy dispersive spectroscopy and scanning auger microscopy have been used to study the surface chemistry at the various stages of the coating process. Our results indicate that the surface chemistry of the alloy is different on the aluminum rich β phase of the material compared to the magnesium matrix which leads to preferential deposition of the metal on the aluminum rich phase of the alloy.

Keywords: Magnesium Alloys, Electroless Plating, Fluoride, Copper, Metallization

1 - Introduction

Magnesium and its alloys have excellent physical and mechanical properties for a number of applications. In particular its high strength:weight ratio makes it an ideal metal for automotive and aerospace application, where weight reduction is ^aof significant concern ←

[1]. Unfortunately, magnesium and its alloys are highly susceptible to corrosion, particularly in salt-spray conditions. This has limited its use in the automotive and aerospace industries, where exposure to harsh service conditions is unavoidable. The simplest way to avoid corrosion is to coat the magnesium-based substrate by a process such as electroless plating, which is a low-cost, non line of sight coating process.

However, magnesium is prone to galvanic corrosion because most other metals have a more noble electrochemical potential. This means than any metallic coating applied must be pore-free or accelerated corrosion will occur. Another challenge in the plating of magnesium alloys is that the deposition process depends on the type of alloy being coated. High aluminum content alloys are especially difficult to plate due to the formation of intermetallic ($Mg_{17}Al_{12}$) species at the grain boundaries, resulting in a non-uniform surface potential across the substrate and thereby further complicating the plating process [1].

Magnesium is classified as a difficult to plate metal due to its high reactivity. This means that in the presence of air magnesium very quickly forms a passive oxide layer that must be removed prior to plating [1]. This rapid oxidation necessitates an appropriate pretreatment of the surface to introduce a surface layer that prevents oxidation but which can be easily removed during the plating process [1]. Typically fluoride activation is employed to replace the oxide layer with a magnesium fluoride

layer and to provide an equipotential surface for subsequent plating [2-5]. Despite this pretreatment step, it has been shown that non-uniform deposition of the metallic films occurs. In general, it has been observed that preferential nucleation and growth of the electroless metal films occurs on the aluminum rich β phase of the material [3,6-8]. The metal initially deposits on the β phase and then extends to the eutectic α and finally the primary α phase [3,8]. It has been postulated that the aluminum rich β phase of the material acts as micro-cathodic sites while the α phase behaves as micro-anodic sites [3, 7-8]. In essence the complex microstructure of the alloy results in an internal galvanic couple between the two phases of the material. It has been shown that both fluoride activation and the presence of fluoride in the plating bath have a significant influence on the deposition rate of the metal [2-4, 9]. It has also been postulated that the formation of a more stable magnesium fluoride layer on the α phase of the material induces cathodic behaviour in these regions[7].

The main objective for this research is to gain an improved understanding of how the magnesium alloy microstructure influences aqueous coating deposition mechanisms. In particular, we studied the local surface chemistry of the alloy in the fluoride activation bath that is commonly used to prepare the surface for electroless plating. The surface chemistry of the acid activation with respect to the individual alloy phases has not been previously studied. We also examined the influence of the microstructure on the deposition of copper films from an acid fluoride bath onto a magnesium AZ91 substrate.

2. Experimental

2.1. Sample Preparation

The die-cast magnesium alloy AZ91D test plates used throughout this study were supplied by Lunt Manufacturing. The nominal composition of the alloy is shown in Table 1. All other chemicals were purchased from Sigma Aldrich.

The test plates were cut into 2 cm x 1 cm coupons and polished to a 1 micron mirror finish. The surface was first ground with 320 grit SiC paper followed by sequential polishing with 9 micron, 3 micron and finally 1 micron diamond suspension in oil. The polished specimens were degreased by sonicating in acetone then methanol for 20 minutes each with a final deionized water rinse.

2.2. Acid Activation

Acid activation was performed by immersing the polished, degreased samples in a room temperature aqueous solution of 100 g/L NH_4HF_2 and 200 ml/L H_3PO_4 for 60 seconds followed by rinsing in deionized water.

2.3. Copper Immersion Coating

Following acid activation, the samples were immediately immersed in a solution containing 20g/L $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 125 ml/L HF (48% w/w). The temperature of the bath was maintained at 10-13 °C and sonication was employed during the deposition process. It has been previously shown that both sonication of the bath during deposition and lower bath temperature result in improved copper coverage. [4, 9-10].

2.4. Surface Characterization

A combination of surface analytical techniques including X-ray photoelectron spectroscopy (XPS), Scanning Electron Microscopy (SEM), Energy dispersive

spectroscopy (EDS) and Scanning Auger Microscopy (SAM) were used to characterize the surface chemistry of the magnesium substrates at each stage of the coating process.

X-ray photoelectron spectroscopy studies were performed on an SSL SSX-100 XPS spectrometer using a monochromatized Al K α X-ray source and hemispherical analyzer at a take off angle of 90°. Elemental analysis was conducted with a 600 μ m spot size and 129 eV pass energy while high resolution spectra had a spot size of 300 μ m and a pass energy of 54 eV. An electron flood gun was used for charge compensation (1V, 0.05 μ A). The binding energies were corrected for charging using the C 1s binding energy peak for C-H in adventitious carbon at 285.0 eV as a reference [11].

Scanning electron microscopy images and EDS spectra were obtained with a Zeiss EVO 50 SEM/EDS spectrometer. Prior to analysis the samples were sputter coated with a thin film of carbon to render them conductive. The vacuum in the chamber was 1.14×10^{-6} mbar. The beam current of the electron gun was set at 1.0 nA with a working distance of 8.5-9 mm. The collection time for the EDS was set for 45 seconds.

Scanning Auger microscopy was performed on a PHI P660 scanning auger microprobe system. The vacuum in the analysis chamber was $< 7 \times 10^{-9}$ torr. The electron beam accelerating voltage was set to 10 kV and the samples were tilted 30° from normal beam incidence towards the Ar⁺ sputter gun which was operated at 3kV with a raster area of 0.75 x 0.75 mm. The kinetic energy scale was calibrated with a NIST traceable copper standard (SRM 885); the E*dN(E)/dE peak for Cu LMM was 917.5 ± 1 eV. The image magnification scale was calibrated with a NIST traceable standard (MRS3-XYZ) at 10kV from 5000X-10000X magnification.

3. Results and Discussion

3.1. *The surface chemistry of the as-polished alloys*

Bulk magnesium alloy AZ91 has a two phase microstructure that consists of a magnesium rich matrix (α phase) and an aluminum rich intermetallic species, $Mg_{17}Al_{12}$, (β phase) that is precipitated along the grain boundaries [12]. Figure 1 shows an SEM image of the polished magnesium surface and the corresponding elemental maps showing the distribution of magnesium and aluminum at the alloy surface. Scanning auger microscopy is a surface sensitive technique that probes the first 3-5 nm of the sample surface, therefore, the elemental maps are a true representation of the surface chemistry of the material with no contribution from the bulk of the material. The SEM image in figure 1 shows a uniform surface morphology of the polished alloy. Polishing grooves are visible but the microstructure of the alloy is not apparent. The scanning auger maps in figure 1 clearly show the presence of both aluminum and magnesium at the alloy surface. It is also evident from the aluminum map that the aluminum rich β phase is present as an interconnected network on the surface of the alloy. Furthermore, it is clear from the changes in intensity that the amount of aluminum is greater in the center of the β phase particles and gradually decreases as we move away from the center of the particle in agreement with previous SEM studies [3]. This confirms that the gradual decrease in aluminum concentration from the center of the β phase out to the eutectic α phase is the same at the surface as in the bulk. The dark areas in the magnesium element map correlate with the high aluminum content regions seen in the aluminum map. This indicates that in comparison to the α phase of the material, the β phase has less surface

magnesium. This uneven distribution of aluminum and magnesium results in a non-equipotential surface and therefore galvanic coupling between the two phases can occur.

3.2. The global surface chemistry of magnesium alloy AZ91 after acid activation

Activation of magnesium in an acid fluoride bath is used to remove the native oxide layer and replace it with a protective fluoride film [2-5] that acts as a barrier to oxidation and helps prevent corrosion of the substrate in the plating bath.

Upon immersion in the acid activation bath, anodic dissolution of magnesium coupled with reduction of hydrogen was immediately observed as evidenced by hydrogen gas evolution. As the treatment time increased, the bubbling gradually slowed until the reaction ceased. This is indicative of passive film formation on the surface of the alloy in the acid fluoride bath. The acid activation time had a significant effect on subsequent copper plating. If the acid activation time was too short, non-adherent copper films were produced. If the acid activation time was too long, very little copper deposition occurred.

The influence of acid activation time on the wettability of the substrates has been investigated by contact angle goniometry with water as a probe liquid. These results are shown in figure 2. The contact angle of the substrate decreases linearly and approaches zero after 60 seconds in the acid activation bath. This indicates that the wettability of the substrate is improved by the fluoride treatment. However, after 60 seconds, the contact angle increases and the surface becomes less wettable. This result correlates well with our observation that the acid activation time has a significant influence on subsequent copper plating.

In general, two factors influence the static contact angle of a surface. These include the presence of hydrophilic/hydrophobic functional groups at the surface and surface roughness. Heterogeneous surfaces tend to have lower contact angles than homogeneous surfaces [13]. This is likely the reason that our contact angle initially decreases and then increases with acid activation time. In the initial stages of surface activation a non-uniform fluoride film is formed resulting in a lower contact angle. As the acid activation time increased the passive fluoride film became more uniform, the surface roughness decreased and the contact angle went up. Previous studies on the influence of fluoride concentration have demonstrated that the fluoride films do become more compact as the fluoride concentration in the bath increases [4]. It is a logical conclusion that increasing the immersion time would have the same effect. In order to better understand this phenomenon, the changes in surface chemistry of the alloy after acid activation have been characterized by XPS.

The analysis area was 600 x 600 μm , therefore, our XPS results give us an average surface chemistry over all phases of the material. Figure 3 shows XPS ratios as a function of acid activation time. A decrease in Mg/Al ratio in the early stages of immersion indicates that there is initial etching of surface magnesium. The corresponding increase in F/Mg ratio indicates the formation of a fluoride film on the surface. The O/Al, O/Mg and O/F ratios also decrease indicating the removal of the oxide layer.

It has been previously proposed that the fluoride layer formed may be a fluoride substituted magnesium hydroxide layer of the form $\text{Mg}(\text{OH})_{2-x}\text{F}_x$ [14] or a mixture of MgF_2 and $\text{Mg}(\text{OH})_2$. It is well established that the native oxide layer on magnesium

alloys is a mixed oxide/hydroxide/carbonate layer with magnesium hydroxide being the favoured product in atmospheres containing water [15,16]. Two mechanisms for the formation of a fluoride substituted magnesium hydroxide layer have been proposed [14]. The first is a two step mechanism with anodic dissolution of the metal followed by a precipitation reaction with hydroxyl ions and fluoride ions in solution according to the following reactions.

The second possible mechanism involves dissolution of the $\text{Mg}(\text{OH})_2$ layer followed by exchange or substitution of fluoride ions for hydroxyl ions in the magnesium hydroxide structure [14].

It is also possible that magnesium fluoride forms directly by anodic dissolution of either the magnesium metal or magnesium hydroxide film followed by reaction of magnesium ions with fluoride ions in solution according to the following reactions.

Our XPS results cannot definitively differentiate between a fluoride substituted magnesium hydroxide and a mixed magnesium hydroxide/magnesium fluoride layer. However, high resolution XPS spectra (Table 2) indicate that there is an increase to higher binding energy for both the Mg 2p and Al 2p peaks. The binding energy shift

between $\text{Mg}(\text{OH})_2$ and MgF_2 has been previously reported to be about 1.5 eV . The 0.7 eV increase in the Mg 2p binding energy is midway between the two compounds and is consistent with the formation of $\text{Mg}(\text{OH})_{2-x}\text{F}_x$ at the surface [14]. The increase in binding energy of the Al 2p peak may indicate the presence of a mixed $\text{AlF}_3/\text{Al}(\text{OH})_3$ layer [17, 18].

3.3. The local surface chemistry of magnesium alloy AZ91 after acid activation

Our results have demonstrated that acid activation results in the formation of magnesium oxy fluoride species and aluminum fluoride at the sample surface. These results are for the overall surface and don't give information about the surface chemistry on the individual phases of the magnesium alloy. However, it is important to understand the local chemistry of the alloy during acid activation in order to better understand the influence of the alloy microstructure on the surface chemistry during coating deposition. EDS spectra obtained after acid activation on the aluminum rich β phase and the magnesium matrix (α phase) are shown in figure 4. These spectra clearly reveal that the concentration of fluoride is higher near the β -phase of the material.

Scanning auger microscopy maps were collected for the magnesium substrates after acid activation. In contrast to the as-polished sample (figure 1), the SED image for the sample after acid activation (figure 5) clearly shows both phases of the material. This reveals that acid activation results in preferential etching of the α phase, at least in the early stages. This is consistent with our XPS results which indicated a decrease in the Mg/Al ratio as a function of acid activation time.

The magnesium and aluminum scanning auger microscopy maps of the sample surface support this assertion. The higher areas in the SED image are aluminum rich while the lower areas are magnesium rich. The Auger maps for oxygen and fluorine also show significant variations in fluoride and oxygen concentrations on the different phases of the material. These element maps reveal that the concentration of both O and F is greater on the aluminum rich β phase of the alloy.

Corrosion studies on the AZ91 alloy have shown that the β phase of the material is electrochemically more noble than the α phase [19]. This results in internal galvanic corrosion that initiates at the grain boundaries [12]. It has also been previously proposed that the aluminum content in the matrix phase of the alloy is low enough that the formation of aluminum oxide is negligible whereas on the β phase of the material $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ readily forms [7]. The presence of aluminum oxide on the β phase decreases its stability and makes the surface more active [7]. During the acid activation a thin protective $\text{MgF}_2/\text{Mg}(\text{OH})_{2-x}\text{F}_x$ film is rapidly formed on the α phase of the material due to anodic dissolution of magnesium. The film that forms on the α phase is thin, as evidenced by both the low concentrations observed in both the EDS and SAM spectra. This indicates that once the fluoride film was formed the reaction ceased on these regions. Our SAM images clearly demonstrate an increased concentration of corrosion/etching products on the aluminum rich phase of the material. This is because, on the β phase of the material the surface does not passivate due to the presence of aluminum and the formation of a non-protective film of soluble aluminum fluoride and aluminum hydroxide [7]. This results in continued etching of the surface by the acid fluoride solution on the β phase of the material and consequently a higher fluoride/oxide

concentration in these regions as we observed by scanning auger microscopy. The shift to higher binding energy of the Al 3p peak in our XPS experiment also showed that acid activation resulted in a probable mixture of aluminum fluoride and aluminum hydroxide at the sample surface.

3.4. *Surface Microstructure of Copper Deposits on Magnesium Alloy AZ91*

In order to examine the influence of the alloy microstructure on the mechanism of copper deposition, SEM and SAM studies of the local morphology and surface chemistry of the AZ91 alloy during the deposition of an immersion copper coating have been performed. Figure 6 shows backscattered SEM images of the as polished alloy (6a) as well as the copper deposits in the initial (6b) and final (6c) stages of copper deposition. The bright features in the SEM image of the as-polished alloy are the high aluminum content phase of the alloy while the darker areas are the magnesium rich matrix. In the early stages of copper deposition (6b) small copper clusters have nucleated on the β phase of the alloy. At higher plating times the existing nuclei continue to grow until the aluminum rich phase is completely covered. Under our experimental conditions no copper deposition occurs on the α phase of the material even at longer plating times. This is due to the high fluoride concentration in the copper bath. It has been previously proposed that the rate determining step for copper immersion coating in an acid fluoride bath is the anodic dissolution of magnesium. Our studies on the surface chemistry of the acid activation process have clearly demonstrated that a passive film is formed on the magnesium matrix of the alloy. In a copper immersion bath with high concentrations of fluoride this passive film is stable and anodic dissolution cannot occur in these regions, effectively inhibiting copper deposition.

However, on the aluminum rich regions of the alloy, continued etching of the substrate occurs due to the formation of soluble aluminum fluoride/aluminum hydroxide products. In order to confirm this assumption, an Auger linescan across the surface of a copper coated β phase grain has been taken (Figure 7). The yellow line shows the distribution of copper on the surface and again we observe that copper is deposited on the β phase of the alloy. The pink line shows the distribution of fluoride on the surface. It is interesting to note that there is a marked increase in fluoride concentration at the edges of the copper coated β phase..

Preferential nucleation of electroless nickel on the β phase of AZ91 has been previously attributed to galvanic coupling between the two phases of the alloy [3, 6-8]. Luan et al. [4, 10] have reported that anodic dissolution during Cu plating occurs at imperfections in the fluoride film, resulting in deposition of Cu. Our results indicate that Cu deposition preferentially occurs on the more noble β phase of the material. It is likely that the stability of the F/OH layer is lower at the grain boundaries resulting in anodic dissolution of Mg in these regions followed by deposition of Cu on the more noble β phase.

4. Conclusions

The microstructure of magnesium alloys has been shown to have a significant impact on the deposition mechanism of an aqueous copper coating, with preferential nucleation on the aluminum rich phase of the material. Our results suggest that this preferential nucleation is mainly due to differences in the stability of the fluoride film on the matrix phase and β phase of the material. On the matrix phase a passive magnesium

fluoride film is formed which inhibits copper deposition. On the aluminum rich β phase of the alloy, unstable aluminum fluoride is formed resulting in anodic dissolution in these regions coupled with reduction of copper.

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6. Figures

Figure 1. Auger maps (20 μm x 20 μm) for selected elements from a polished magnesium AZ91 sample. In these images, aluminum is represented by red and magnesium is green.

Figure 2. Surface wettability as a function of immersion time in the acid activation bath.

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Figure 3. XPS atomic ratios as a function of immersion time in the acid activation bath.

Figure 4. EDS spectra on the two microstructural components of Magnesium AZ91 after acid activation.

Figure 5. Overlay images of Auger maps (20 μ m x 20 μ m) for selected elements from Sample #2. In these overlay images, aluminium represented by red, magnesium in yellow, fluorine in blue and oxygen in pink.

 

Figure 6. SEM images (25 μm x 25 μm) of (a) Mg Alloy AZ91, (b) initial stage of Cu deposition and (c) final stages of Cu deposition

Figure 6. AES linescan across a copper structure after sputtering (15 minutes, Ar^+)

7. Tables

%Al	%Zn	%Mn	%Ni	%Cu	%Si	%Fe	%Be	%Mg
8.5-9.5	0.45-0.90	0.17-0.40	0.001	0.015	0.05	0.004	0.0005	Balance

Table 1. Nominal chemical composition of AZ91D

Peak	Binding Energy	
	Before Acid Activation (eV)	After Acid Activation (eV)
Mg 2p	50.5	51.2
Al 2p	74.6	75.5

Table 1. XPS Binding Energies Before and After Acid Activation