The Effect of Electrolyte on the Anodized Finish Of a Magnesium Alloy

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Anodization was studied as a finishing technique for decorative, durable and corrosion-resistant coatings on magnesium. The influence of solution electrolytes on the process of anodization and the resulting porous surface film was also investigated. Certain electrolytes, including aluminate and tetraborate, contribute to film thickness and structure, while other electrolytes, such as fluoride and phosphate, contribute to film color, opacity, and uniformity of finish. Control of the sparking process, inherent in magnesium anodization, is also affected by bath components that do not otherwise contribute to the magnesium anodized coating. Polarization resistances of fluoride or phosphate anodized alloys show a ten-fold increase in protection vs. a non-anodized surface.

Worldwide use of magnesium alloys is increasing for a number of products where weight is an important criterion. The density of magnesium is approximately two-thirds that of aluminum and the strength is comparable. The automotive industry has recognized these facts, and the use of magnesium alloys, such as AZ91, in automobile parts is expected to continue to increase over the next decade¹ as a result of demands of the CAFE (Corporate Average Fuel Economy) legislation. In applications where surface finish is important for decorative or durability reasons, magnesium alloys have some disadvantages compared to alloys of steel or aluminum. Aluminum and ferrous alloys, such as stainless steel, produce a passive layer on exposure to moist air. Anodization, the electrochemical process that produces a well-structured oxide layer on aluminum, is both well known and widely employed to provide a corrosion-resistant and durable coating on aluminum products. Magnesium alloys do not form a significant passive coating naturally, and the formation of a passive layer by anodization is neither as straightforward nor as well-studied as that for anodization of aluminum.

The process of anodization of magnesium involves quite high potential and current operations and occurs by a sparking process. The formation of a coating is dependent upon a number of factors, including the solution electrolytes.²⁻⁴ This investigation covered the effects of electrolytes on the anodization process and the resulting films formed on magnesium alloy.

The Anodization Process

Anodization of aluminum occurs during the application of a current to an aluminum anode in an acidic bath. The oxidation reaction takes place over the entire surface of the anode; film thickness is dependent upon time at the raised potential and current flow, to a steady state limit, at which dissolution of the film into the acidic solution matches its growth rate. The anodic film produced is regular in structure and consists of a barrier layer adjacent to the metal surface, as well as a layer containing uniform parallel pores normal to the surface. The mechanism of the anodization of magnesium is significantly different from that for aluminum in that it occurs in alkaline solutions and by way of a sparking process. At potentials over a given voltage, usually near 50V DC, sparks form on the surface of the magnesium anode. These sparks move over the

surface and, where they travel, a film is produced. The film is produced in a chemical reaction between the magnesium alloy, oxygen, the electrolytes and other components of the anodizing bath.

Because of the temperatures reached in a spark, there is a significant number of excited species available to contribute to the chemical and electrochemical reactions. The phases involved include liquids, dissolved species, gases from electrolysis and boiling, and the solid electrode. Physical processes, such as fusion, can also occur at this temperature. The process is, therefore, very complex, and the variables that contribute to the film formation are somewhat difficult to isolate. In this study, most variables were held constant, while the type of electrolyte was varied.

Experimental Procedure

All magnesium anodes were diecast from alloy AZ91, containing 90 percent Mg, 9 percent Al, and 1 percent Zn by weight. The anodes were approximately 20 cm² in area. The counter electrode was a stainless steel flat hoop, 20 cm in diameter, wide enough to provide an even current distribution at the anode. The foundation of the electrolyte solution in each case was 3 M sodium hydroxide. Additional electrolytes were added to this solution at 0.15 M except for disodium hydrogen phosphate, which had limited solubility at this pH and was studied at 0.05 M. All reagents used were analytical grade and included: Sodium aluminate, sodium fluoride, sodium iodide, disodium hydrogen phosphate, sodium citrate, and sodium tetraborate. The electrolyte bath of 6 L was surrounded by a water bath of 45 L at 22 °C. These volumes were found sufficient to prevent temperature changes greater than 1 °C of the electrolyte over the 15 min in which the anodization was carried out. Rapid stirring of the electrolyte bath also aided heat removal from the surface of the electrode.

Sample Preparation

Each anode was pretreated before anodization by abrasion of the surface with 600-grit paper, followed by a hot alkaline cleaner, a hot chromic acid cleaner, and rinses in distilled water.



Fig. 1—SEM photomicrograph of the porous surface of magnesium anodized in 3 M sodium hydroxide solution containing 0.15 M sodium fluoride.



Fig. 2—The effect of electrolyte on the surface roughness of anodized magnesium.

Anodization

Anodization was conducted by slowly increasing the potential of the magnesium anode until sparks began to form on the surface (generally around 50V DC). The potential was adjusted to maintain constant sparking for 15 min, up to a maximum potential of 90 V. If 90 V was reached before 15 min, the potential was left at 90 V for the remainder of the experiment.

Observations of the Anodizing Process

Electrolysis

During the initial voltage ramp, before any sparking occurred on the anode, some electrolysis of water was always noted. The extent of this electrolysis varied widely among the different electrolyte mixtures. Bubble formation was often initially vigorous, but decreased with time as if the magnesium anode was somewhat passivated before sparking occurred. In a 3 M NaOH solution, extensive electrolysis occurred and continued during spark anodization. Addition of fluoride, aluminate, phosphate or tetraborate to the electrolyte solution reduced the electrolysis significantly from the level noted for 3M NaOH.

Spark Formation

The formation of sparks on the surface of the magnesium anode did not occur in any electrolyte until the potential reached 50V. Initially the sparks were very small and were extinguished very quickly. As the potential was increased, the sparks became larger and began to move over the surface of the anode. By stepping the potential during anodization, the anode would activate and passivate as the film was grown, so the current fluctuated at any given potential. As the anode remained at a particular potential, the rate of formation of sparks would diminish. If the potential was then increased slightly, the sparks would start to form again and move about the surface. Moving waves of sparks sometimes occurred when a front several centimeters wide, consisting of a number of sparks, would move slowly over the surface. If a spark

Table 1
Visual Characteristics of the Anodized Surfaces

Electrolyte Hydroxide Aluminate [•] Tetraborate [•] Fluoride [•]	Conc. 3M 0.15M 0.15M 0.15M	Color transparent light gray white gray	Texture even patchy patchy even	
Phosphate	0.05M	gray	even	
* added to 3 M sodium hydroxide solution				

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Fig. 3—Optical photomicrograph of a cross-section of magnesium anodized in 3 M sodium hydroxide solution containing 0.15 M sodium aluminate. 500X.

formed at a sharp edge or what were presumed to be point defects on the surface and did not move, the spark would grow over time and draw a significant portion of the current. At these fixed spark locations there was inevitably a large pit burned into the anode.

The behavior of the sparks did change with the electrolyte solution composition and concentration. The potential required to maintain continuous sparking varied among the electrolytes. The speed at which the sparks formed and traveled was very dependent on the solution formulation, as was the tendency to form fixed sparks that led to pitting. In the wake of the moving sparks, a change in color of the surface marked formation of an anodized layer. The sparks moved to cover the entire surface of the anode by the time the process was completed. One electrolyte, sodium citrate, seemed to influence the sparking process; in this instance, the sparking seemed to occur in a more controlled manner. When added into a bath containing other electrolytes, sodium citrate acted to produce many small sparks that moved over the surface and did not form fixed sparks.

Physical Characterization

Visual Inspection

A visual examination of the surface of the anodized electrodes was conducted (Fig. 1, Table 1). The anodized coatings ranged from nearly transparent, colorless films to opaque gray. Some coatings were very smooth; others were patchy, although all were porous on a microscopic scale. In the more translucent coatings, non-uniformities in color on the surface because of poor surface pretreatment were visible. Properly abraded and cleaned surfaces generally gave uniformly colored coatings. Anodization in sodium hydroxide, with no other additional electrolyte, produced a nearly transparent coating. Fluoride and phosphate additions to the electrolyte resulted in the smoothest and most uniformly opaque coatings, gray in color. Aluminate and tetraborate additions produced whiter, but patchier, coatings. Pitting was evident on those anodes that had fixed sparks occur during anodization. The large extent of pitting that occurred during anodization in sodium iodide did not permit that experiment to be taken to completion.

Surface Roughness Measurement

Surface roughness measurements were conducted on representative anodized samples, using a diamond stylus technique. The results are shown in Fig. 2. The order of increasing roughness for samples was aluminate < phosphate < fluoride

Table 2 Anodized Film Thickness

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* added to 3 M sodium hydroxide solution

< hydroxide << tetraborate, although there was considerable overlap in measurements among the first four samples. Local defects were noted on several of the samples that did not contribute to the roughness measurement value significantly, but did address sample uniformity.

Thickness Measurement

Coating thickness measurements were conducted on crosssectioned, mounted samples using optical photomicrographs and a calibration gauge. Photos of a representative sample are shown in Fig. 3. The thickness values are listed in Table 2. From these results, it is obvious that only some electrolytes contribute to layers of significant thickness. Aluminate and tetraborate produced measurable layers under these conditions, although the thickness of the tetraborate layer varied greatly over the surface of the anode. Other electrolytes, such as phosphate and fluoride, did not produce a layer of sufficient thickness to be measured optically, although all evidence pointed to a surface film of some type.

Chemical Characterization

X-ray Photoelectron Spectroscopy (XPS)

XPS is a chemical analysis technique that gives semi-quantitative information about the composition of the outer 10 nm of a surface. The results for XPS analysis of several of the anodized samples are given in Table 3. The large amount of surface carbon is common for samples that have not undergone any sputter cleaning; however, this does not rule out the possibility of incorporation of organic species contamination in the film during the spark process. The outermost layer of the phosphate anodized sample showed no phosphorus, nor did the tetraborate sample contain any boron. Visually, there were changes in the coating because of the presence of these electrolytes; however, any phosphorus or boron incorporated in the film might not be located at the surface, but remain concentrated at the interface between the metal and the anodized layer. Fluoride was found in the fluoride-anodized surface, but in relatively small amounts. Aluminate showed up in abundant concentration, corresponding to the significant layer noted in thickness measurements. Although the alloy provided a constant concentration of aluminum in each sample (9%), the amount of aluminum in the anodized coating was not consistent. No aluminum was found in the fluoride, phosphate, or borate coatings.

Electrochemical Characterization

Electrochemical Impedance Spectroscopy (EIS)^{5,6} Electrodes used for EIS were produced by hot-mounting flat one-cm² (0.15 in²) anodized sections in phenolic resin. Electrical connections were made from the back of the mounts using screws into tapped holes and copper-filled epoxy. Impedance measurements were carried out using a potentiostat and a frequency response analyzer. Experiments were carried out in 0.1 M sodium perchlorate at the open circuit potential

Table 3 XPS Analysis of the Anodized Films

Electrolyte	Composition in Atomic Percent
Hydroxide	C - 16.4, O - 39.7, Mg - 36.7, Al - 7.2
Aluminate	C - 12.3, O - 41.3, Mg - 29.0, Al - 17.4
Tetraborate	C - 28.3, O - 37.4, Mg - 34.3, B - < 0.1
Fluoride	C - 40.0, O - 31.0, Mg - 27.5, F - 1.5
Phosphate	C - 20.6, O - 39.4, Mg - 40.0, P - < 0.1

of the electrodes, generally near -1.5 V vs. SCE after equilibration for one hr and a frequency range of 10⁵ Hz to 0.5 mHz. Potential drift reduced the accuracy of low-frequency measurements; however, reasonable results were obtained for magnesium anodized in 3 M NaOH, 0.15 M sodium fluoride, and 0.05 M disodium hydrogen phosphate. Impedance data were also obtained for a magnesium electrode not anodized. Using software for equivalent circuits, estimates were made of the capacitance and polarization resistance of the electrodes. The data are listed in Table 4.

The EIS data of the anodized samples could be fitted to a simple Randles circuit with reasonable accuracy.⁵ The data corresponded well to a planar capacitor as the sole frequency-dependent component (based on information in the shape of the Bode and Nyquist plots, Fig. 4). This was despite the fact that microscopic examination showed that the surface film on all the anodized samples was porous. The EIS response was probably not influenced by film porosity inasmuch as the pores were of large diameter compared to the thickness of the film.

The EIS data also provided information on the corrosion resistance of the anodized films. In the case of the samples



Fig. 4—(a) Nyquist and (b) Bode plots for electro-chemical impedance data generated for a non-anodized magnesium electrode in 0.1 M sodium perchlorate solution at -1.5 V vs. SCE.

Table 4 Impedance Spectroscopy Data for Anodized Films

Electrolyte	Capacitance µF/cm ²	Resistance Ω-cm ²
Non-anodized	42	6600
Hydroxide	3.5	2400
Fluoride	0.7	90,000
Phosphate	9.5	29,000

anodized in sodium fluoride and phosphate electrolytes, the corrosion resistance was markedly improved, compared to the non-anodized material as measured by the polarization resistance. A value for polarization resistance of 90 k Ω -cm² for the sodium fluoride-anodized film corresponds to only microamperes of corrosion current, given normal assumptions concerning the electrical behavior of the electrode.⁷

The capacitance value measured for the non-anodized magnesium electrode was $42 \,\mu\text{F/cm}^2$, which falls in the range of normal metal solution interfaces⁴ from 10 to 100 µF per cm². The capacitances measured for the anodized surfaces were significantly below this value, in a range from 0.65 to 9.5 μ F/cm². It is possible that the decrease in capacitance is simply an area effect, where some percentage of the magnesium surface remains uncovered by a passivating film. Then, the decrease in capacitance would be inversely related to an increase in the polarization resistance, compared to the nonanodized surface. If the area normalization of the data in Table 4 is ignored, there is a good relationship between the area and values of capacitance and resistance shown for the case of phosphate. An area of 0.23 cm² would account for the decrease in capacitance to 9.5 µF and this area would correspond to a polarization resistance of approximately 29 k Ω . In the cases of hydroxide- and fluoride-anodized films, however, such an area relationship does not seem applicable. In this instance, it seems more likely that the decreased capacitance is associated with film formation at the base of the pores, where the polarization resistance is likely to be at a minimum. Accordingly, these sites would probably dominate the frequency response measured in the EIS data. The decreased values of capacitance may contain both an area effect and a contribution from the change in dielectric properties and thickness of the film, compared to the metal/ solution interface.

Summary

Different anodized films were produced on magnesium, using various electrolyte mixtures. The influence of each electrolyte on the high-voltage anodization process was different; the sparking process was different, the potential/ current behavior changed, and the film formed was different. Aluminate was incorporated into the coating as a significant component, producing a coating µm in thickness. The coating had low surface roughness, but was visually non-uniform. The form of the aluminum on the surface was likely to be as magnesium aluminate, combined with magnesium oxide and hydroxide. In contrast, anodization in sodium fluoride resulted in improved surface texture, opacity, and color, but did not add significantly to the thickness. The impedance measurement showed the coating to be quite protective of the metal surface. The fluoride, as magnesium fluoride, appeared to be forming at the interface between the metal surface and the anodized coating, which was predominantly magnesium oxide and hydroxide. Phosphate behaved in a manner similar to fluoride by incorporating at the interface of the metal/coating, but did not provide the protective nature of the fluoride layer with respect to impedance spectroscopy. Citrate in the electrolyte mixture produced a more controlled sparking process, and prevented pit formation, which occurred under localized sparks. Iodide was a damaging electrolyte and led to uncontrolled pitting. Tetraborate contributed both to coating thickness and color, and lowered sparking voltage.

The coatings were all porous under the SEM, though the porosity was irregular. Electrochemical analysis, using impedance spectroscopy, suggested that the electrical properties of the anodized films were affected by both the extent of the coverage and the barrier characteristics of the film at the bottoms of the pores. The evidence pointed to a very mixed composition of magnesium compounds in the anodized layer under most circumstances. The mechanism of film formation during the sparking process remains unclear because of the energetic and vigorous nature of the reactions involved. The difficulty in separating chemical reactions between heated species and electrochemical processes between excited species and electrons within the spark will continue to be the largest challenge to predicting the effects of anodizing conditions.

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