A New Pretreatment Cycle for Plating Magnesium Alloys

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There are two ways to process magnesium for electroplating: (1) zincate and alkaline copper plate and (2) fluoride activation and electroless nickel plate. This paper will discuss a new pretreatment that is hexavalent chromium-free and also features an ELV-compliant electroless nickel process. The electroless nickel pretreatment cycle for magnesium was first developed in the late 1950s and early 1960s and is typically referred to as the Dow® process. The Dow® process characteristically consisted of a hexavalent chromium/nitric acid etch and a hydrofluoric acid activation step before direct electroless nickel plating could commence. The new pretreatment cycle is hexavalent chromium and hydrofluoric acid-free. This pretreatment cycle consists of an alkaline etch used in conjunction with an acid fluoride activation. This paper will discuss the differences between the old chromic acid etch as compared to the new alkaline etch. In addition this paper will also discuss the differences between the non-ELV electroless nickel process versus the new ELV-compliant electroless nickel. I will show that the non-chromic acid etch is a significant improvement over the standard chromic/nitric acid etch in terms of both corrosion resistance and adhesion.

Keywords: *Plating on magnesium, hexavalent chromium replacement, electroless nickel, ELV compliance*

Introduction

End of Life Vehicle (ELV) regulations should not only mean the elimination or reduction of hazardous materials such as Cd, Hg, Pb and Cr (VI) in the final coating, but also in the use of these chemicals in the processing of the parts. The standard practice to process magnesium castings before electroless nickel plating was to use a hexavalent chromium etch to remove oxide from the surface and to roughen the surface for subsequent electroless nickel deposition. This etching cleaned the surface of oxides plus micro-roughened the surface for the electroless nickel to anchor on the surface.

Recently there has been more work done on the direct plating of magnesium alloys with electroless nickel.[1,2] The original work was done in the late 1950s and early 1960s.[3] From these works can be found the classical electroless nickel formula of nickel carbonate, citric acid and fluoride. Missing from this formula are the stabilizer and accelerator that are formulated in today's electroless nickel chemistry. The new ELV electroless nickel described in this paper is only stabilized with organic compounds and uses no metal stabilizers.

The most important process step is the etch. Proper etching of the surface will ensure excellent adhesion of the electroless nickel. In addition, the etch provides an excellent surface for the activation to occur. With the new alkaline etch, there are no concerns about contaminating the activator or electroless nickel with hexavalent chromium. Also the etch rate of the alkaline etch is less than that of the standard chromic/nitric acid etch, making the process more adaptable for an automatic line. The typical time in the chromic/nitric acid etch was between 30 and 60 seconds, whereas the alkaline etch time is between 2 and 4 min.

The electroless nickel used in this process is designed more as a pretreatment step for further processing and not for extended corrosion protection. The operating parameters of the special electroless nickel for plating on magnesium limit the phosphorus content of the deposit and therefore limit the corrosion protection from the electroless nickel. The typical phosphorus content from this electroless nickel solution ranges from 3 to 7 wt%. With the proper design of other electroplated or electroless plated coatings one can obtain hundreds of hours of salt spray on good quality castings.

Magnesium is the eighth most abundant element in the earth's crust and the third most abundant element in seawater. In addition, magnesium is the world's most readily available metal. The ocean is an enormous reservoir of magnesium, whereas other engineering metals face the eventual exhaustion of their most economical ore bodies or political instability where they are mined may limit their supply. Therefore, it may be expected that magnesium could become increasingly more important in the future as costs of production of other structural metals increases.

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Processing magnesium

The usual steps of cleaning, chemical treatment, anodizing, electroplating and painting are used to finish magnesium parts. As with other metals, cleaning is a very important step in the surface treatment of magnesium, since the effectiveness of subsequent coating processes depends to a marked extent upon removal of all surface contamination. Most magnesium alloys, unlike aluminum or zinc, are unaffected by strong alkaline cleaners. Most high alkaline steel cleaners will work on cleaning magnesium alloys whereas the low alkaline aluminum cleaners would not be recommended. Figure 1 shows the potential-pH plot of magnesium in water. This diagram shows that with a pH of less than 9, the protective hydroxide layer is unstable and the magnesium is attacked. With high pH, the magnesium hydroxide film, $Mg(OH)_2$, on the surface prevents attack.

After cleaning, the parts are etched or pickled in a chromic/nitric acid solution to remove any oxide layer or certain chemical coatings not fully removed by alkaline cleaning. In this work we compared the chromic/nitric acid etch to the new alkaline etch. The main difference between the two etches, besides pH, is the time needed to etch the surface. The chromic/nitric etch removes approximately ten times more material than the alkaline etch. For the chromic/nitric etch, a three-level four-factor design was used to evaluate the amount of material removed from a 2.0 in^2 magnesium coupon. Table 1 shows the design matrix. From this work, the main factors that effected the etch rate were time and nitric concentration. In addition, there was one main interaction between time and nitric acid. Table 2 shows the analysis of variance (ANOVA) of the design. Figure 2 shows the effects of the main factors on etch rate in the chromic/nitric acid etch.

To evaluate the alkaline etch, only a two-level two-factor design was used, as outlined in Table 3. From this work, Additive A had the largest effect on the etch rate. The time and temperature were held constant in this study. The standard time for the alkaline etch was 3.0 min and the temperature was in the range of 65 to 75°C (150 to 167°F). Figure 3 shows the results of the alkaline etch study. This work shows that the chrome/nitric etch was more aggressive than the alkaline etch with about ten times the removal rate. Measuring the rates by linear polarization, the chromic/nitric etch rate was about four times higher than that of the alkaline etch. Table 4 shows the results.

A primary consideration in this study was the surface appearance after etching. Figures 4 and 5 show the surface of etched panels in the chromic/nitric and new alkaline etches, respectively. This work shows that the alkaline etch produced an excellent micro-roughened topography for further processing. The chromic/nitric etch also produced a micro-roughened topography, but one which can trap solution which will ultimately be carried over to the activator solution and on to the electroless nickel. The alkaline etch will also be carried over but would be neutralized in the activator solution. Further, this material is not as detrimental to the electroless nickel solution as is hexavalent chromium.

Table 1
Chromic/nitric acid etch matrix

Factor	Name	Units	Low Actual	High Actual
A	Time	sec	20	120
B	Temp	°F	68	77
C	CrO_3	g/L	125	175
D	HNO_3	Vol %	8	12

Table 2
ANOVA for the chromic/nitric acid etch

ANOVA for Response Surface Reduced 2FI Model

Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	0.024	8	3.02E-03	22.14	< 0.0001
A - Time	0.017	1	0.017	121.26	< 0.0001
B - Temp	1.01E-03	1	1.01E-03	7.39	0.0159
C - CrO_3	1.01E-03	1	1.01E-03	7.42	0.0157
D - HNO_3	8.40E-03	1	8.40E-03	61.67	< 0.0001
AB	4.88E-04	1	4.88E-04	3.58	0.0779
AC	4.85E-04	1	4.85E-04	3.56	0.0788
AD	4.36E-03	1	4.36E-03	32	< 0.0001
CD	5.37E-04	1	5.37E-04	3.94	0.0657
Residual	2.04E-03	15	1.36E-04		
Lack of fit	1.65E-03	11	1.50E-04	1.52	0.3673
Pure error	3.95E-04	4	9.89E-05		

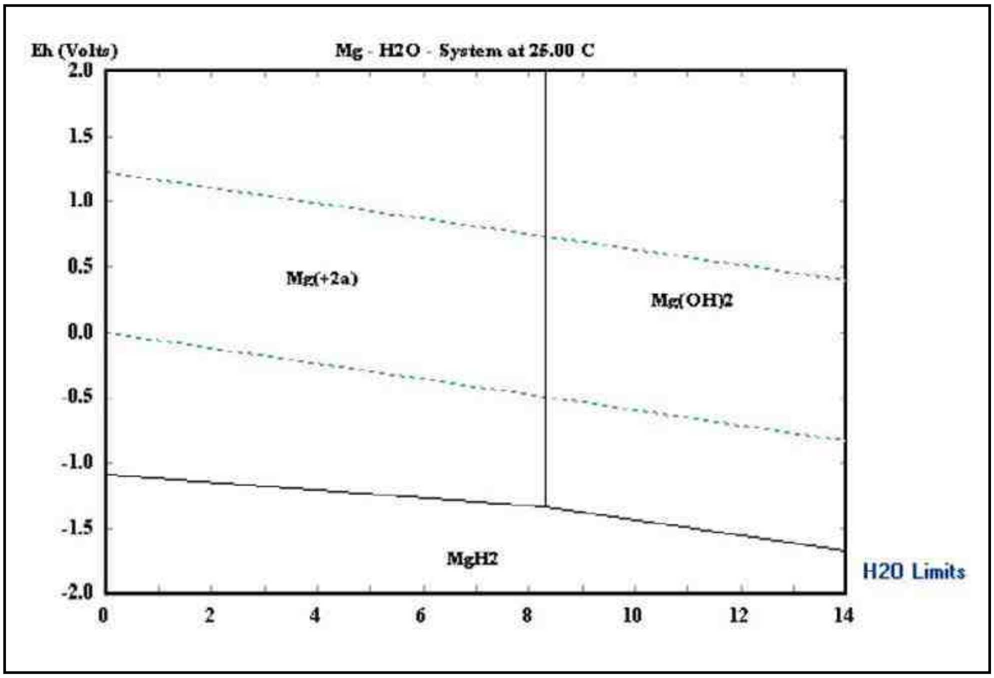

Figure 1—*Potential-pH diagram of magnesium in water.*

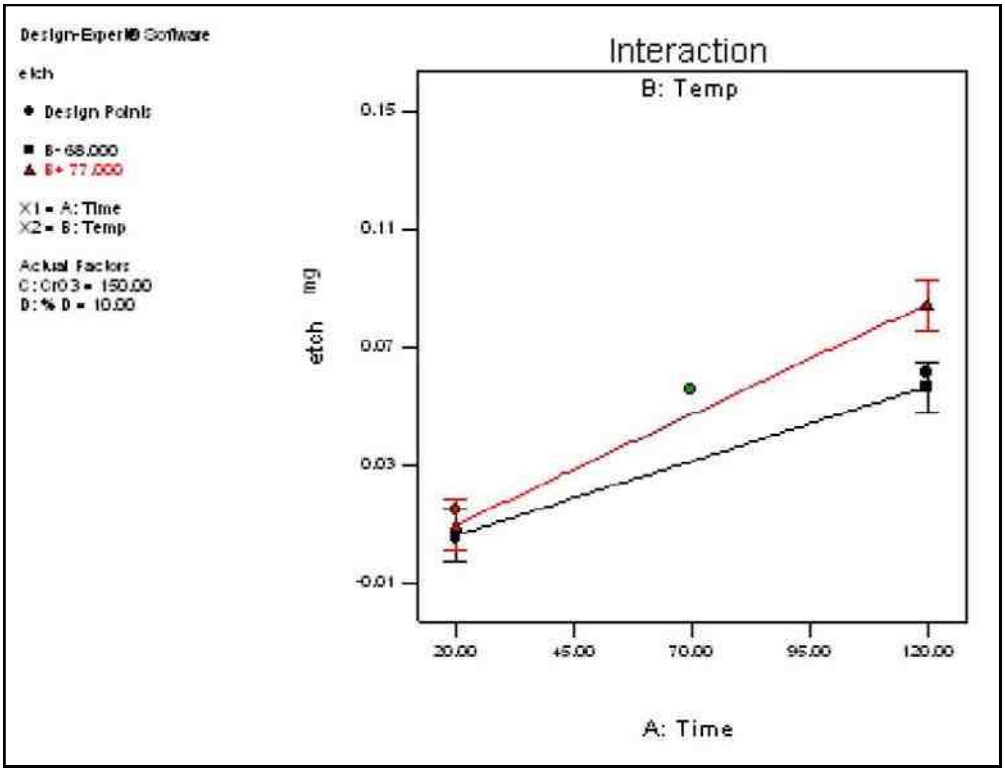

Figure 2—*Chromic/nitric acid etch results.*

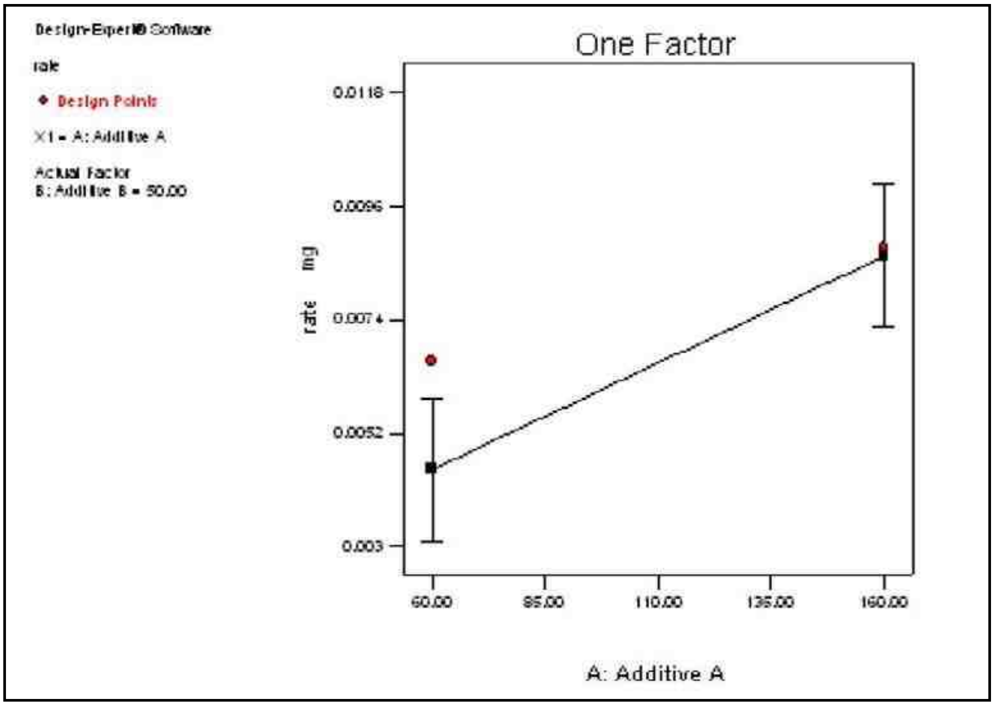

Figure 3—*Alkaline etch results.*

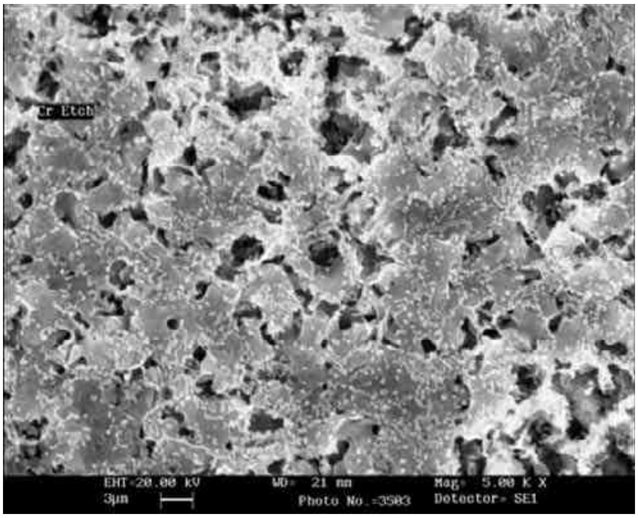

Figure 4—*Chromic/nitric etch, 5000×.*

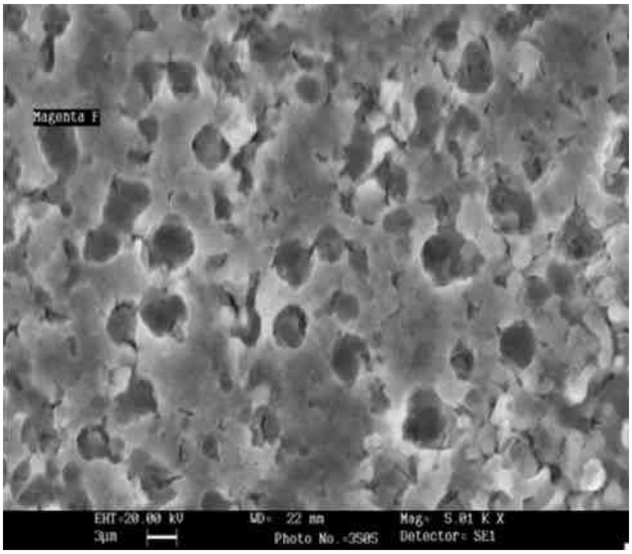

Figure 5—*Alkaline etch, 5000×.*

Table 3
Alkaline etch design matrix

Factor	Name	Units	Type	Low Coded	High Coded
A	Additive A	g/L	Numeric	-1	1
B	Additive B	g/L	Numeric	-1	1

Table 4
Linear polarization measurements of etch

Etch	E(I = 0), mV	I_{corr} (μA):	Corrosion rate, mpy
Chromic/nitric	-782.236	6.97E+03	5.98E+03
Alkaline	-1502.11	1.94E+03	1.58E+03

The next step is to form a chemical film or displacement film, on the surface of the magnesium. In this process, magnesium fluoride, MgF_2, is formed on the surface. Displacement films are used to protect the surface of active metals that will otherwise form oxide films on which plated metals would not adhere. Aluminum, beryllium and magnesium are good examples where the use of a displacement film prior to electrodeposition will provide superior adhesion of the electrodeposited metal. A zinc displacement film works well on all these metals. In addition, stannates work on aluminum, and a fluoride chemical film works on magnesium as a pretreatment for electrolytic or electroless plating.

Looking at the thermodynamics of the formation of magnesium fluoride on magnesium, we see from Fig. 6 that MgF_2 is formed over a wide pH range, from zero to 13. Only in very high alkaline solutions, with fluoride present, will the MgF_2 not be formed on the surface. The thickness of the MgF_2 film, as shown in Fig. 7, is approximately 4.6 μm (0.18 mils), which is about 20 times thicker than an alloy zincate on aluminum.[4]

After the formation of the MgF_2 displacement coating on the magnesium alloy, the part is ready for further processing. The next step is electroless nickel plating onto the magnesium substrate. A special electroless nickel solution is needed to process magnesium. This electroless nickel solution contains fluoride in order to inhibit the dissolution of magnesium to allow the electroless nickel to plate onto the surface of the magnesium. Figure 8 shows the open circuit potential (OCP) of a magnesium AZ-91D panel in an electroless nickel solution with and without fluoride. From this we can see that with the addition of fluoride, the OCP of magnesium is reduced by 0.15 V. This reduction, plus the addition of fluoride, inhibits the formation of magnesium hydride (MgH_2) (See Fig. 6).

As stated earlier, this electroless nickel deposit is only used as a barrier coating to protect the magnesium substrate from further processing solutions and not for corrosion protection itself. This electroless nickel chemistry is designed to produce an electroless nickel coating with 3 to 7 wt% phosphorus, depending on solution age.

Cross-sections of a part plated in electroless nickel-copper-nickel-chromium are shown in Figs. 9a and 9b. The optical microscope photo, Fig. 9a, shows a dark line between the electroless nickel and the substrate. Evaluating this area with a scanning electron microscope (SEM), as in Fig. 9b, the dark line is resolved to show that the magnesium is etched away more than the electrodeposited coatings.

The polishing compounds used to polish the mount seemed to dissolve the magnesium substrate faster than the electroless nickel-copper-nickel-chromium electrodeposits. Using other methods to evaluate the adhesion of the electrodeposit to the magnesium substrate (ASTM B 571-97[5]), we evaluated a bent panel, baking at 200°C (392°F) for 30 min, then quenching in ice water and reverse sawing the panel. All of these tests showed excellent adhesion of the coatings to the magnesium substrate.

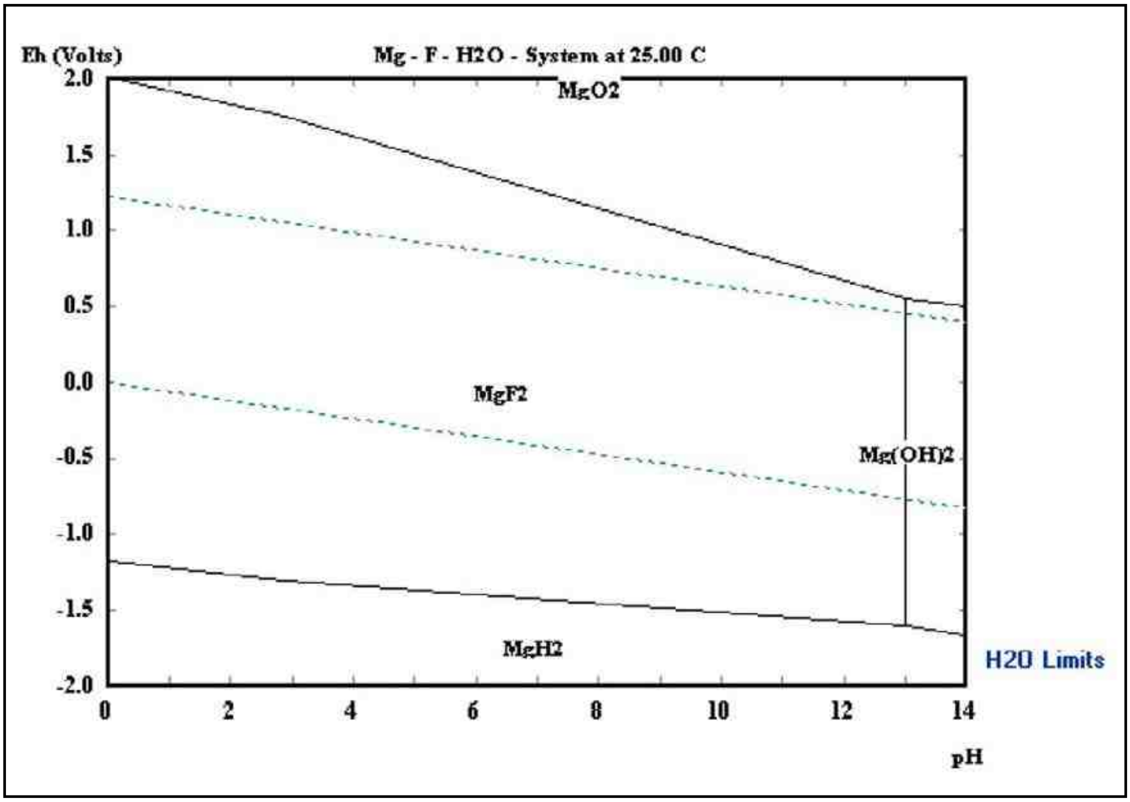

Figure 6—*Potential – pH Diagram of Mg-F-H_2O system.*

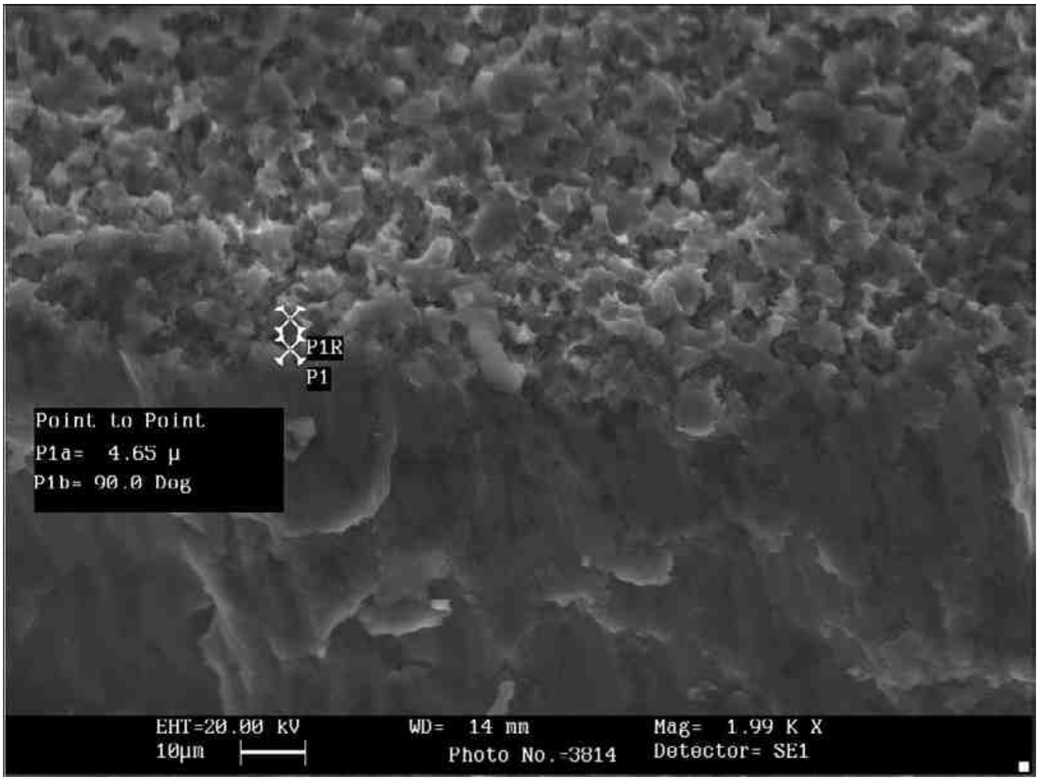

Figure 7—*Cryofracture of magnesium panel with* MgF_2 *on the surface, 2000×.*

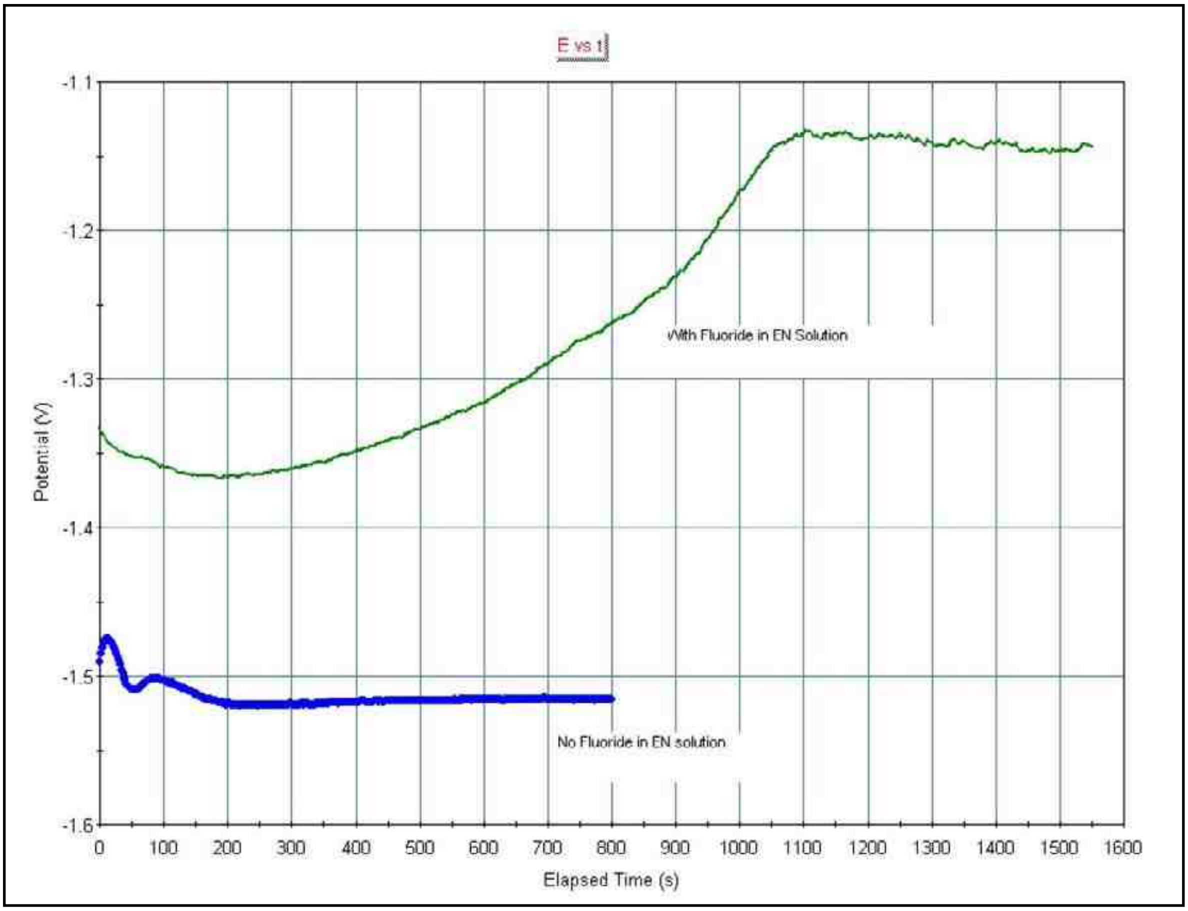

Figure 8—*Open circuit potential of AZ-91D in electroless nickel solution with and without fluoride.*

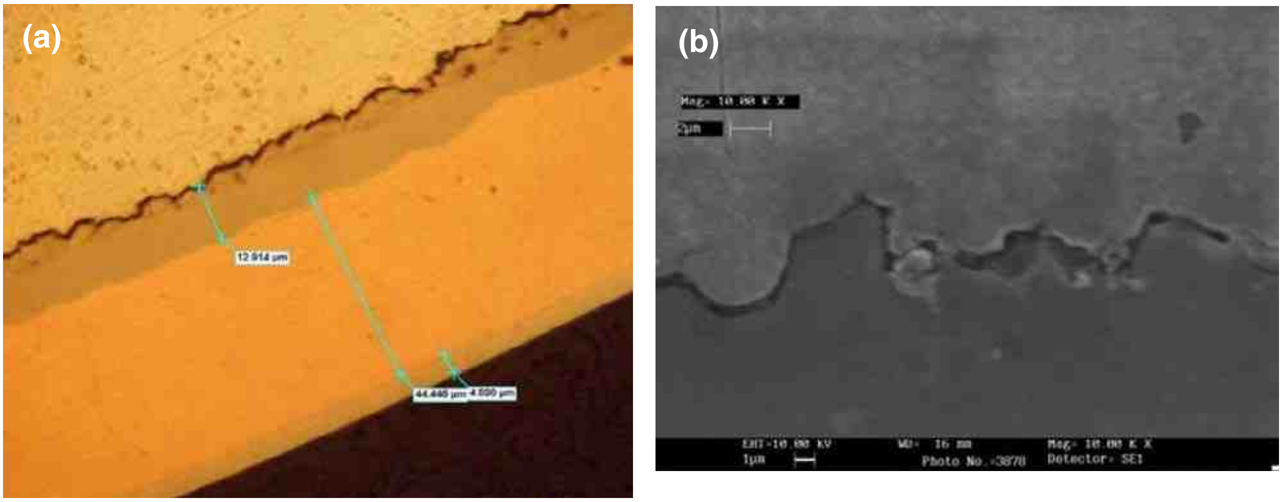

Figure 9—*(a) Optical image of cross section, 1000×; (b) SEM of cross section, 10,000×.*

Corrosion resistance, especially on cast material, is dependent on the substrate. Typical cast defects are porosity, gross segregation, flux inclusions or other imperfections that would tend to cause porosity in the plated coating. Figures 10a and 10b show typical defects in cast parts. Figure 10a shows the surface of an AZ-91D magnesium casting with porosity. Figure 10b shows a cross section of the same casting showing gross cracking in the deposit. Salt spray data shows that other coatings need to be applied after the special electroless nickel coating to achieve any meaningful corrosion resistance. With 12 μm (0.5 mils) of the special electroless nickel, corrosion of the basis metal can be seen in less than 3.0 hr of neutral salt spray. Figure 11a shows the corrosion pits. Figure 11b shows salt spray results for a AZ-91D panel plated with 18 μm (0.7 mils) of high phosphorus electroless nickel over 7.6 μm (0.3 mils) of the magnesium special electroless nickel. This panel was in salt spray for 300 hr without showing any signs of corrosion. Other parts are currently being tested but with copper-nickel-chromium on the surface.

In addition to salt spray testing, electrochemical testing was done to evaluate the porosity of the special electroless nickel deposit. Several panels were run with various times to obtain different thicknesses. Previous studies have shown that 30 min of plating, about 6 μm (0.25 mils), produced a deposit that was pore free, as measured by Tafel plots.[6] In these experiments the open circuit potential of an area of 1 cm^2 was measured in a 5% NaCl solution, with the same composition as the neutral salt solution used in the salt spray cabinet, per ASTM B 117. Figure 12 shows the open circuit potential measurements of three AZ-91D panels plated with various thicknesses of the special electroless nickel. The initial rest potentials of all three panels were very similar, 0.42 ± 0.03V. This shows that the magnesium panel is encapsulated well enough that the salt solution does not immediately penetrate the electroless nickel. With 6 μm (0.23 mils) of electroless nickel, it requires about 600 to 700 sec in the 5% NaCl solution to penetrate the coating. Once the salt solution penetrates the coating, we see a significant change in potential from –0.42V to –1.22V. With 8 μm (0.3 mil)

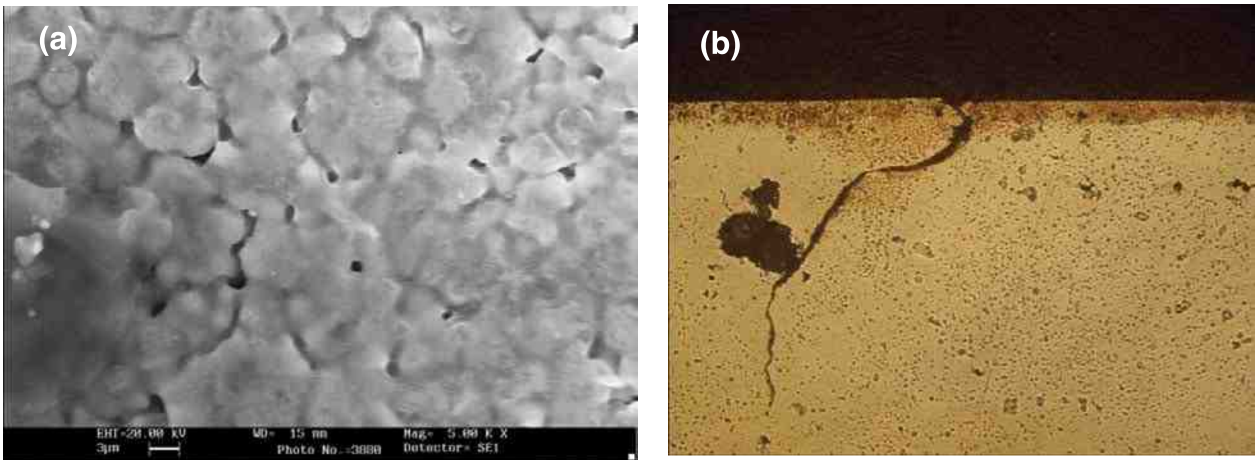

Figure 10—*(a) Surface of raw casting, 5000×; (b) Cross-section of raw casting, 400×.*

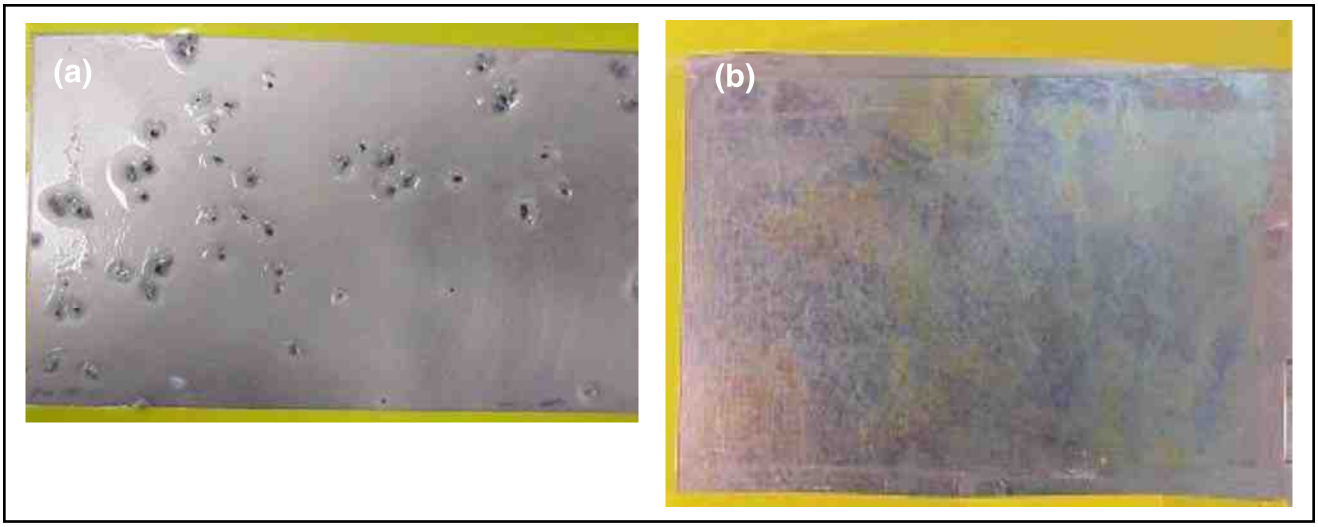

Figure 11—*(a) Special EN 12 µm on magnesium, 24-hr salt spray; (b) high phosphorus EN over magnesium, special EN, 300-hr salt spray.*

of electroless nickel it takes about 1,800 sec to see a significant change in potential and at 2,500 sec, we are completely through the electroless nickel coating. The main difference seen between the 6-µm thick deposit and the 8-µm thick deposit is the shape of the curve. The 6-µm thick coating showed a significant increase in potential in a very short time, whereas the 8-µm thick deposit change was very gradual until it reached the critical point when the coating failed. The 11 µm (0.43 mil)-thick deposit showed no sign of failure over the 3,600-sec test duration. This indicates that the coating, under these test conditions, is more robust than the thinner coatings in protecting the substrate.

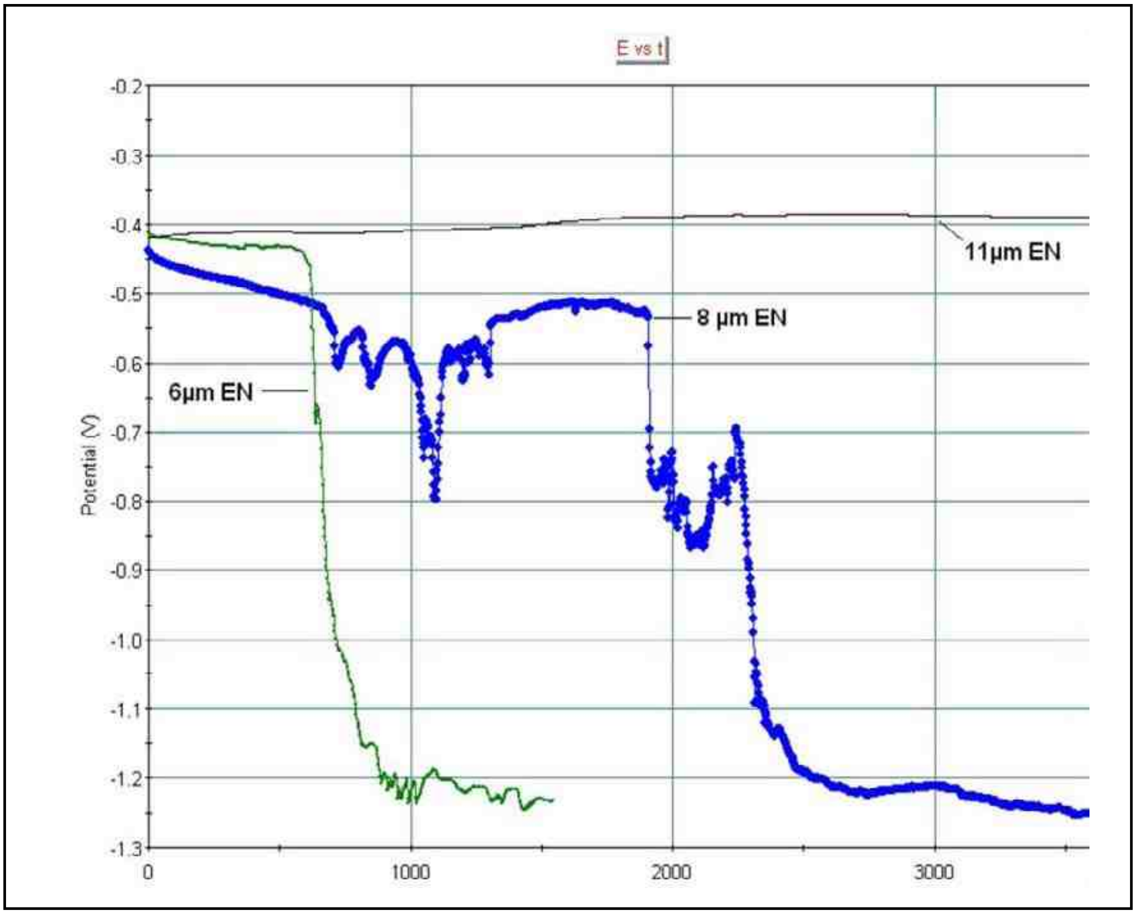

Figure 12—*Open circuit potential of electroless nickel on AZ-91D panel.*

Conclusion

Direct electroless nickel deposition on magnesium alloys offers benefits over the conventional zincate treatment. The direct procedure eliminates the need for rectifiers and a cyanide copper strike which, in turn, simplifies racking and tank design. Also, more parts can be plated at the same time with the direct EN on magnesium.

With the non-chromium etch, there is more control of the etch rate of the magnesium alloy that is being processed. This gives more process control of the chromium-free etch as compared to the chromium-based etch. In addition, the chromium-free etch uses less hazardous chemicals than the chromium etch. The chromium-free etch produces a much finer etch texture, which in turn produces a part that has a much smoother surface finish.

Corrosion resistance was measured by salt spray and electrochemical methods. The salt spray data showed that the special electroless nickel is not very corrosion resistant by itself. By incorporating a high-phosphorus electroless nickel layer over the special electroless nickel for magnesium, the corrosion resistance increased dramatically. Electrochemical data showed that with a thicker initial electroless nickel coating, the salt spray solution took longer to penetrate the special electroless nickel coating. The corrosion resistance of the duplex coating, with a good substrate, should produce salt spray resistance consistent with the type of electroless nickel on the surface.

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George E. Shahin is a Senior Technology Specialist with Atotech USA, Inc. He holds B.S. in Chemistry from Kent State University (Kent, Ohio) and has 24 years with the company. Mr. Shahin has authored or co-authored over thirty papers on various plating processes. In addition he has been awarded three patents in the U.S. and abroad.
