

## THE INFLUENCE OF GALVANIC CURRENT ON CERIUM-BASED CONVERSION COATINGS ON MG, AL, AND GALVANIZED STEEL COUPLES

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### Abstract

The influence of galvanic current on cerium-based conversion coatings (CeCCs) for magnesium (AZ91, AZ31), aluminum (6016), and electro-galvanized steel (EGS) couples has been studied using zero resistance ammeter (ZRA) measurements in prohesion solution. The galvanic current measured between magnesium-aluminum, magnesium-galvanized steel, and aluminum-galvanized steel couples correlated with significant changes in coating morphology and deposition rate. The ZRA galvanic currents (mA) were 0.02 for 6016-EGS, 0.38 for AZ91-EGS, 0.72 for AZ91-6016, 1.08 for AZ31-EGS, and 1.08 for AZ31-6016 couples. The corrosion performance of the coated couples was evaluated by ASTM B117 neutral salt spray testing. Cerium conversion coated couples performed better in salt spray testing compared to uncoated couples. The correlation of galvanic current, cerium deposition, and corrosion performance will be discussed.

### Introduction

Magnesium alloys are being extensively used in automobile industry, aerospace, and electronic applications due to its low density and high strength-to-weight ratio. In an automobile industry, the use of magnesium alloys has doubled in the last decade [1-2]. However, the use of Mg alloys in the automobile industry has been limited due to galvanic corrosion with other structural components [3]. Moreover, the development of a robust paint-line compatible pretreatment process for magnesium intensive vehicles is critical to its expanded use in automotive body and chassis assemblies. Current phosphate electrolyte baths are formulated to treat mixed-metals such as galvanized steel, cold rolled steel, and aluminum in body-in-white (BIW) assemblies. However, because of high solubility of Mg in the phosphate baths magnesium alloys are not compatible with existing phosphate processes used in automotive manufacturing [3-4]. In order to treat a mixed-metal BIW assembly, including magnesium alloy parts, a new conversion coating process needs to be developed.

Chromium-based conversion coatings are one of the most effective ways of preventing corrosion of base metals [5]. However, the carcinogenic nature of chromates restricts the use of chromate baths and extensive effort is being done to find a suitable replacement [6]. Several researchers have reported alternative chromate replacement coatings [7-13]. Among the alternatives, cerium-based conversion coatings (CeCCs) are promising as they offer significant corrosion protection and are environmentally benign [10-15]. Cerium compounds are used in large scale applications such as polishing glass and are not expensive unlike other rare earth materials. The deposition mechanism and corrosion protection of cerium-based conversion coatings on individual alloys have been discussed in numerous publications [10-12]. However, CeCCs on bimetallic couples, such as magnesium-aluminum, magnesium-galvanized steel, and

aluminum-galvanized steel, have not been reported. Therefore, the effect of galvanic current on cerium deposition and corrosion protection of cerium based conversion coatings on bimetallic couples will be examined.

### Experimental procedure

Magnesium (AZ91D, AZ31B), aluminum (6016), and electro-galvanized steel (EGS) samples were sectioned into 2.5 x 2.5 cm coupons for galvanic current measurements (zero resistance ammeter) in prohesion solution of composition 0.6 wt.% NaCl and 0.6 wt.% of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. Similarly, test panels were sectioned into 5 x 10 cm coupons which were then coupled using aluminum rivets for subsequent cerium conversion coating (CeCC). The bimetallic couple schematic diagram is showing in Figure 1. All magnesium alloy samples were first polished using 220, 320, and 400 SiC grit paper cleaned with isopropyl alcohol, and then rinsed with de-ionized water prior to all experiments.

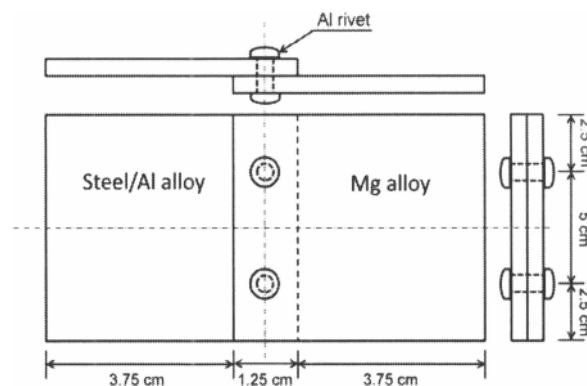


Figure 1. Schematic diagram (not to scale) of bimetallic galvanic couple with aluminum rivets.

The corrosion performance of bimetallic couples with and without cerium conversion coatings was evaluated by ASTM B117 neutral salt spray test. The bimetallic couples were cleaned with 0.5 wt. % tetrafluoroboric acid (HBF<sub>4</sub>) for 20 s at room temperature, rinsed with de-ionized water, cleaned with 5 wt. % sodium hydroxide (NaOH) for 30 s at room temperature, and then rinsed again with de-ionized water. The cleaned couples were immersed in cerium deposition solution for 2 min at room temperature. The composition of the deposition solution was 205 g of stock solution, 25 g of DI water, 0.8 g of gelatin organic (RDH, Rousselot) and 20 ml of H<sub>2</sub>O<sub>2</sub> (Fisher Chemical, 30 vol. %) [14]. Cerium coated couples were post-treated in a phosphate solution for 5 min at 85 °C [10].

Cross-sectional structures of the coated panels were prepared by focused ion beam (FIB) milling (Helios NanoLab 600, FEI). The FIB used a gallium ion beam to selectively mill through coatings

and into the substrates to reveal the coating interface at selected areas. A platinum layer was deposited on the coating surface to protect the area of interest from damage during milling. The scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) capability of the FIB system were then used to image the coating interface and analyze chemical compositions, respectively. All images were taken in secondary electron mode using an acceleration voltage of 5 kV and EDS measurements (Oxford, X-Max Silicon Drift Detector) were carried out at an acceleration voltage of 30 kV.

#### Zero Resistance Ammeter (ZRA) Technique

Galvanic corrosion current ( $I_{gal}$ ) between two electrodes fixed to a cell was measured by a zero resistance ammeter technique. The potentiostat serves as a zero resistance ammeter and measures the current flowing between the anode (Mg alloy) and cathode (Al, EGS). The galvanic currents between couples in different electrolyte solutions were measured by the ZRA technique as follows. The samples were fixed at two ends of a flat cell (Princeton applied research) by modifying the flange arrangement. The two electrodes (Mg alloys and Al/EGS) were placed in the arrangements so as to expose only 1 cm<sup>2</sup> area of each sample to the electrolyte. A saturated calomel electrode (SCE) in saturated KCl served as a reference electrode. The flange for the counter electrode (Pt) was replaced with a flange that contained the working electrode holder. In this manner, samples of 1 cm<sup>2</sup> area would be fixed at the ends of the flat cell. Measurements were made as a function of time using the galvanic current routine in Power-Suite software connected to PARSTAT 2273.

#### **Results and discussion**

Optical images of bare and cerium conversion coated AZ91-6016 bimetallic couple before and after salt spray testing is showing in Figure 2, while, AZ91-EGS, AZ31-6016, and AZ31-EGS couples are showing in Figure 3, Figure 4, and Figure 5, respectively. The optical images revealed that cerium conversion coatings uniformly deposited on both aluminum and EGS panels when coupled with magnesium alloys (AZ91 and AZ31). Cerium coated bimetallic couples had better salt spray corrosion performance compared to bare couples. Among the four couples with different combinations, cerium coated AZ91 bimetallic couple combinations had better corrosion resistance compared to AZ31 couple combinations. For AZ91 couple combinations, the AZ91-6016 couple showed better salt spray corrosion performance than the AZ91-EGS couple, as the EGS panel corroded severely compared to the AZ91 alloy. This may be due to the presence of zinc/zinc oxide under the cerium coating. The open circuit potential of zinc is very close to magnesium alloys and therefore the zinc is probably more active corrosion than AZ91 alloy [16]. It is worth noting that there is no trace of iron rust found in the field of the EGS surface, indicating that the zinc/zinc oxide is serving as a sacrificial anode to the steel panel.

Optical images of salt spray tested bimetallic couples indicated significant galvanic corrosion at the galvanic junction compared to the field away from the junction. It can be seen from the images in Figure 2 to 5 that the galvanic current between the two metals has a significant effect on the overall corrosion behavior of the bimetallic couple. The influence of galvanic current on overall corrosion performance of different couples has been discussed in details by Zhang [16]. In particular, Song et. al. have reported that the galvanic current effect on overall corrosion of magnesium AZ91D alloy coupled with alloys of aluminum, steel, and zinc in a sodium chloride solution [17]. They have reported that the

galvanic current significantly influences the corrosion of magnesium alloys in the presence of other metals and the galvanic effect is more pronounced at the galvanic junction compared to the field away from the junction. However, CeCCs on bimetallic couple significantly change the overall corrosion performance compared to uncoated couples. The bare couple severely corroded within four days of salt spray testing whereas cerium coated couples were able to last more than a week without any major corrosion damage. The cerium conversion coating significantly enhances the corrosion resistance of the bimetallic couples.

The cross-sections of CeCCs and substrate interface was prepared by FIB milling on individual alloys and bimetallic couples as shown in Figure 6 and Figure 7, respectively. The FIB cross-sections of CeCCs deposited AZ91 and AZ31 alloy panels reveal the interface between the magnesium substrate and cerium coating layer was approximately 500 nm thick (Figure 6 a and b). However, there was little or no cerium conversion layer visible on aluminum and EGS substrates. The EDS analysis detected a cerium signal within a few hundred nano-meters of the interface. The FIB analysis indicated that cerium conversion coatings covered magnesium alloy substrates but that the 6016 and EGS panels were lightly coated, if at all, when deposition was done on individual alloys. On the other hand, FIB cross-sections showed cerium coatings on both the aluminum alloy and EGS panels when coupled with magnesium alloys (Figure 7 a through d). The approximate coating thickness on 6016 and EGS panels was about 300 to 400 nm in both bimetallic combinations. Therefore, the galvanic current significantly influences the cerium deposition mechanism on bimetallic couples. Several researchers have reported the influence of micro-galvanic (multiphase alloy) effect on cerium conversion coating mechanism [5, 10-11]. In particular, Pinc et. al. have discussed the influence of metal-matrix and second phase interactions on spontaneous deposition of cerium conversion coatings [11, 12, 18]. They have reported that the micro-galvanic current assists the spontaneous deposition of cerium conversion coatings on multiphase alloys. The galvanic current between bimetallic couples appears to have a similar effect on cerium deposition mechanism. These results clearly demonstrate that the galvanic current significantly influences the deposition mechanism and/or deposition rate. Therefore, galvanic current has a significant effect on spontaneous deposition of cerium conversion coatings on bimetallic anode/cathode couples.

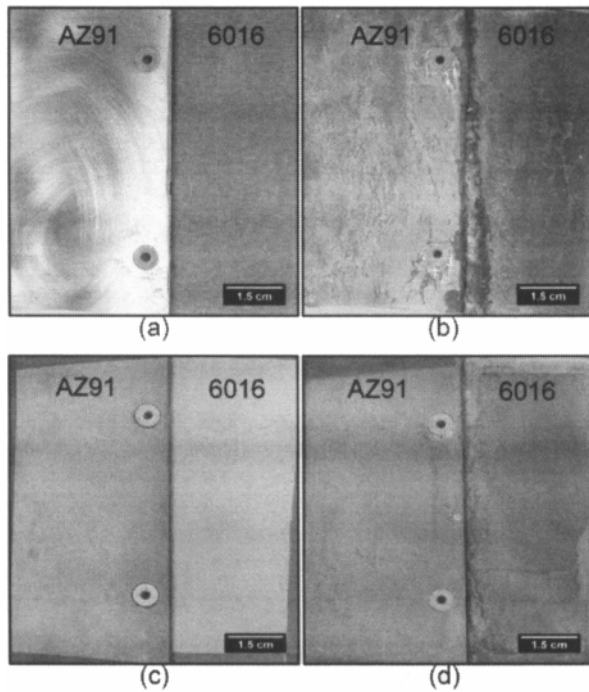


Figure 2. Optical images of AZ91-6016 couple with and without CeCCs, before and after salt spray testing, a) bare couple, b) 4 days salt spray tested bare couple; c) CeCCs deposited couple, and d) 7days salt spray tested CeCCs deposited couple.

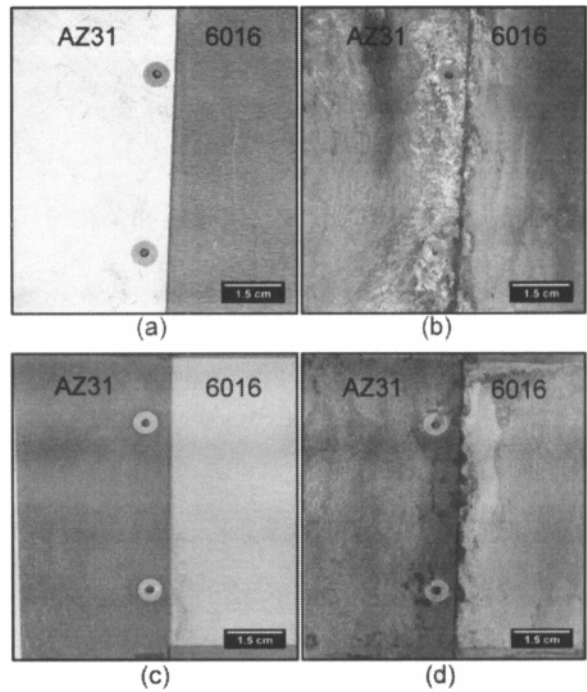


Figure 4. Optical images of AZ31-6016 couple with and without CeCCs, before and after salt spray testing, a) bare couple, b) 4 days salt spray tested bare couple; c) CeCCs deposited couple, and d) 7days salt spray tested CeCCs deposited couple.

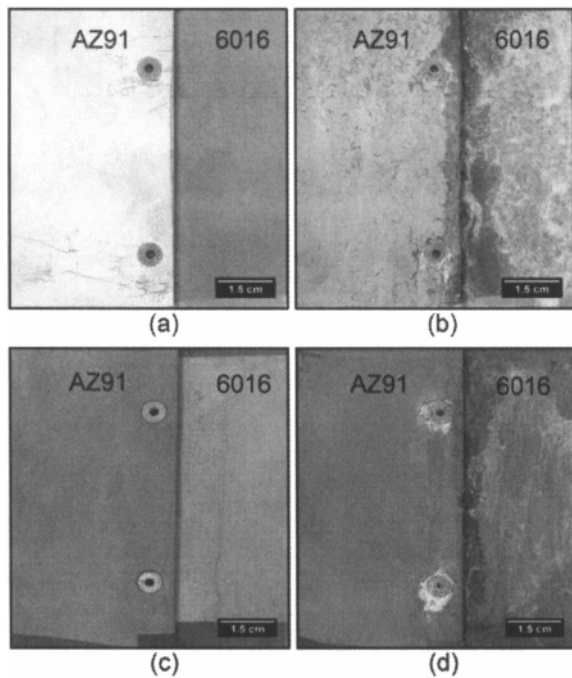


Figure 3. Optical images of AZ91-EGS couple with and without CeCCs, before and after salt spray testing, a) bare couple, b) 4 days salt spray tested bare couple; c) CeCCs deposited couple, and d) 7days salt spray tested CeCCs deposited couple.

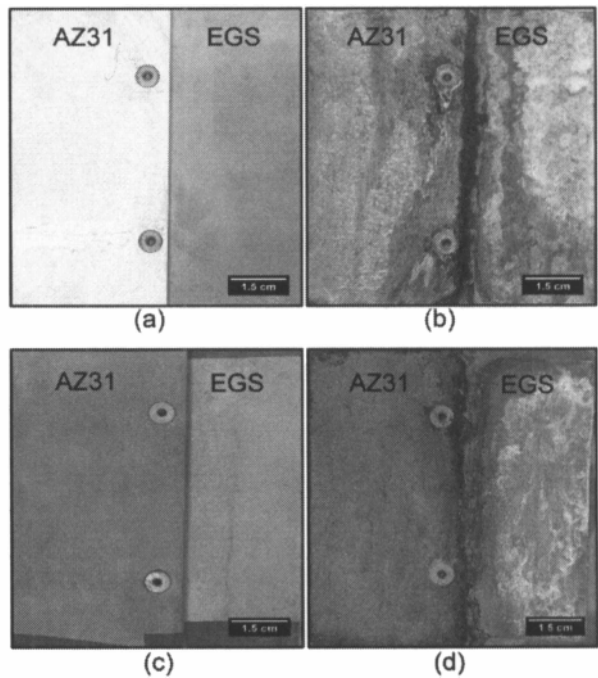


Figure 5. Optical images of AZ31-EGS couple with and without CeCCs, before and after salt spray testing, a) bare couple, b) 4 days salt spray tested bare couple; c) CeCCs deposited couple, and d) 7days salt spray tested CeCCs deposited couple.

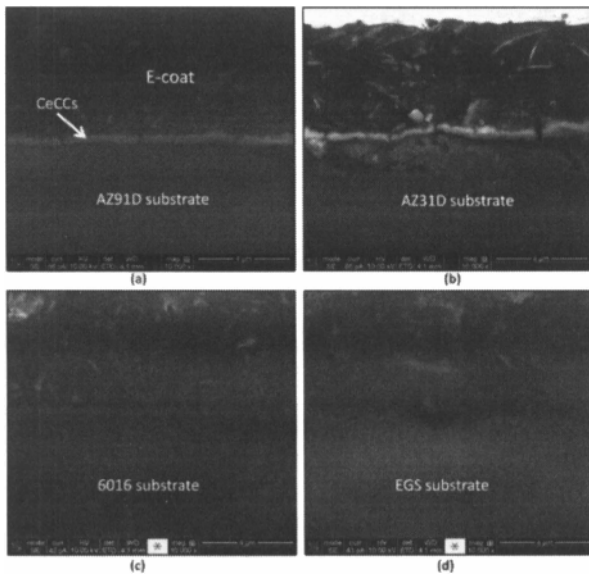


Figure 6. FIB cross-sections of uncoupled CeCCs deposited panels; a) AZ91 alloy, b) AZ31 alloy, c) 6016 alloy, and d) EGS.

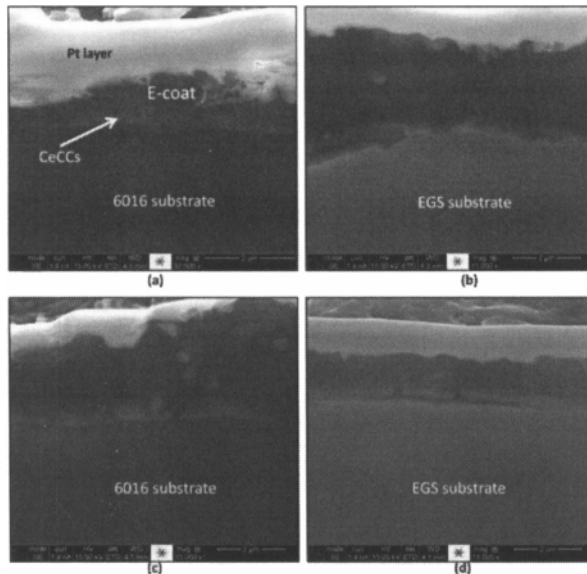


Figure 7. FIB cross-sections of coupled CeCCs deposited aluminum and EGS panels; AZ91 couple a) 6016 alloy b) EGS; and AZ31 couple c) 6016 alloy and d) EGS.

The variation of galvanic current between AZ91-6016 couple in sodium chloride solution was measured by ZRA technique is shown in Figure 8. The experiments were conducted twice with both anodic and cathodic configurations. Similarly, galvanic current was measured between different couples with and without cerium conversion coatings in a sodium chloride solution. The

average galvanic current after stabilization with time was derived and is presented for different combinations of bimetallic couples in Figure 9. The ZRA galvanic currents (mA) were 0.02 for 6016-EGS, 0.38 for AZ91-EGS, 0.72 for AZ91-6016, 1.08 for AZ31-EGS, and 1.08 for AZ31-6016 couples. Overall, the galvanic current between AZ31 Mg coupled with 6016 /EGS was higher compared to AZ91 Mg coupled with 6016/EGS. It was also observed that the galvanic current between 6016-EGS couples is low and showed a corresponding low corrosion rate during salt spray testing. The galvanic current between the AZ91-EGS couple was low compared to the other bimetallic couple combinations and hence showed less galvanic corrosion after salt spray testing (Figure 3). However, AZ31-6016 and AZ31-EGS bimetallic combinations had the highest galvanic current; therefore, AZ31 bimetallic couples combinations showed higher corrosion compared to AZ91 couple combinations (Figure 4 and Figure 5). It is shown in Figure 9 that the bare panels in sodium chloride solution showed higher galvanic current compared to the cerium coated panels. As mentioned above galvanic current not only assisted the cerium deposition mechanism, it also contribute to enhance the corrosion resistance of bimetallic couples.

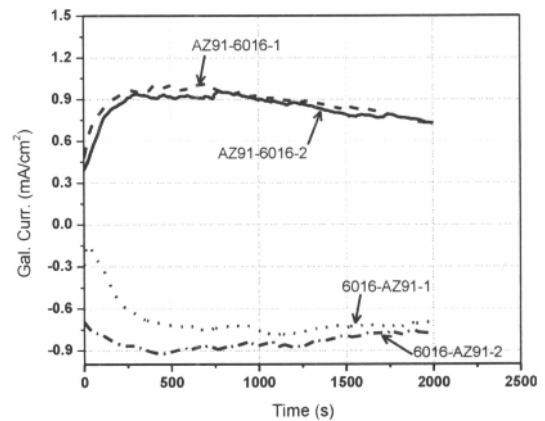


Figure 8. Galvanic current with time between magnesium alloy and aluminum alloy couple in sodium chloride solution.

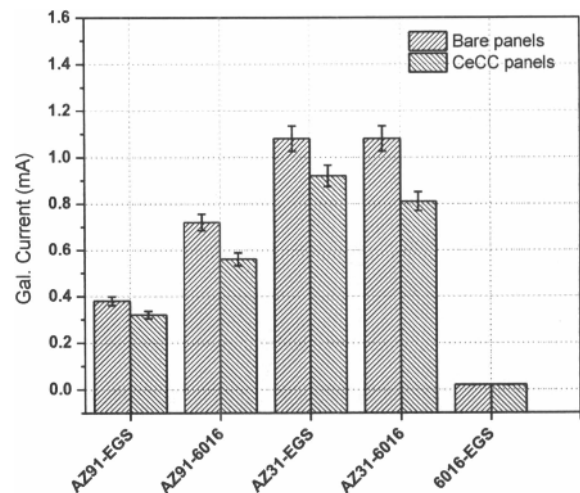


Figure 9. Galvanic current between different couples with and without CeCCs on individual panels in prohesion solution.

## Conclusions

Cerium conversion coatings successfully deposited on bimetallic couples without any contaminating bath. The influence of galvanic current on cerium conversion coatings on magnesium alloys coupled with aluminum and EGS panels has been investigated using ZRA technique in prohesion solution. The ZRA galvanic currents (mA) were 0.02 for 6016-EGS, 0.38 for AZ91-EGS, 0.72 for AZ91-6016, 1.08 for AZ31-EGS, and 1.08 for AZ31-6016 couples. The AZ31-6016/EGS couple combinations had the highest galvanic current compared to the AZ91-6016/EGS couples. Galvanic current significantly influence the conversion coatings on bimetallic couples; moreover, cerium coated bimetallic couples showed better salt spray performance compared to bare couples. Galvanic current significantly changed the coating thickness on coupled Al, and EGS panels compared to uncoupled panels. Cerium coated panels showed less galvanic current compared to the bare couples in prohesion solution.

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