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Advanced Conversion Coatings for Magnesium alloys

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Abstract

Magnesium and its alloys have excellent physical and mechanical properties due to their high strength-to-weight ratio and are ideal for various applications in automotive, aerospace and defense sectors. However, Mg alloys are also highly susceptible to corrosion under harsh environments. Owing to this carcinogenicity as well as environmental impact of hexavalent chromium fueled by stringent environmental regulations, an environmentally green alternative to the carcinogenic hexavalent chromium coatings on magnesium is due.

In this work, a novel trivalent chromium based conversion coating has been developed to improve the corrosion resistance and paint adhesion properties of Mg alloys. Coating performance characterization has been investigated via hydrogen evolution, weight loss measurement and electrochemical corrosion analysis techniques. Results have shown that the novel environmentally green trivalent chromium based coating on magnesium has indeed performed comparable to hexavalent chromium and thus establishing a viable alternative.

Introduction

Magnesium, the eighth most abundant metal on earth, has seen an increase in applications in a variety of sectors ranging from aerospace, military, defense, automobile to commercial mobile phones, sporting goods and handheld tools owing to its high strength-to-weight ratio, machinability, thermal conductivity and weldability [1-4]. Although magnesium alloys have the distinct advantage of high strength-to-weight ratio and high impact resistance, their extremely poor corrosion resistance in aggressive environments especially in assemblies with multiple galvanic couples, limits their usage because of the premature component degradation and replacement. [4-7].

Improving corrosion performance involves a variety of finishing processes including oil applications, wax coating, anodizing, electroplating, conversion coating, painting etc. Metal finishers are often faced with challenges to tailor a better combination of these processes to enhance the product corrosion performance considering various factors ranging from specific applications to environmental conditions. Even though development of new and high purity magnesium alloys and novel surface modification techniques such as ion implantation and laser annealing have mitigated the corrosion problem, magnesium alloys still suffer from performance issues especially under aggressive corrosive environments. High chemical reactivity, complex alloy microstructures, hazardous pretreatment procedures and recycling problems to an extent have discouraged many applications of magnesium [8-10].

Among the typical surface modification techniques, conversion coating, electroplating with alloys like Zn, Ni and Cr and anodizing processes such as DOW 17, HAE, and Tagnite have become widely popular for the surface treatment of magnesium alloys.

Majority of the magnesium alloys are either sand-cast or die-cast and hence are prone to microstructural inhomegeniety, surface imperfections such as porosity and impurities. Magnesium and its alloys are also prone to galvanic corrosion and alloy dissolution owing to lesser nobility of magnesium. Design of a process routine that results in an effective barrier to corrosion as well as wear would be ideal. Hexavalent chromium (Cr^{6+}) based conversion coatings have been used for a long time as a coating material on aluminum, magnesium and other metals in order to increase the corrosion protection, paint adhesion, and adhesive bonding characteristics. However, solutions containing Cr6+ are highly toxic and adversely affect the environment and human health.

A recent Under Secretary of Defense memo, dated April 2009, regarding the elimination and restriction of the Cr6+ from Department of Defense (DoD) weapon systems and platforms shows the importance of novel non-hexvalent technologies for the U.S. military departments. The U.S. and International market needs for a Trivalent Chromium Conversion Coating is predicated on three severe and stringent European Union (EU) Directives: Restriction of Hazardous Substances (RoHS), Waste Electrical & Electronic Equipment (WEEE), and End of Life Vehicle (ELV). Global manufacturing demands compliance even though these directives are implemented in the EU. EU member nation states have established regulations and enforcement of these Directives. In the U.S., heavy regulations from both EPA and OSHA are continuing to be issued and implemented. OSHA has mandated a Permissible Exposure Level (PEL) of 5 ppm of Hexavalent Chromium, an unrealistic level for the vast majority of metal finishers and manufacturers to attain. Compliance to the Directives and OSHA requirements are not an option, they are mandatory. In addition, the EPA Executive Order 12856 showed the need to reduce or eliminate the release of chromates during aircraft coating applications.

There is, therefore, a need for environmentally green conversion coatings that can provide high corrosion resistance and increase the adhesive bonding strength characteristics of the metal surface. Although there are other conversion coatings, which do not contain Cr6+, their corrosion performance and paint adhesion characteristics are not as effective as the Cr6+ based conversion coatings.

Our aim is to at develop an environmentally friendly conversion treatment for magnesium alloys. In this present study, trivalent chromium based environmentally conversion coating for AZ92A magnesium alloy was developed. Furthermore, the performance was gauged against hexavalent chromium coatings using hydrogen evolution test, weight loss measurement techniques and potentidynamic studies.

Experimental set up

Experimental process routine for the study was conducted in accordance with AMS -3171-C, [11]. Sand cast magnesium Alloy AZ92A discs (1.5 in. dia and 0.5 in. thickness) conforming to AMS 4434 [12], have been purchased from Metalmart Inc., with the following compositions.

Al	Zn	Si	Mn	Cu
9.0	2.0	0.3 max	0.10 min	0.25 max

Table 1 : Elemental compositions of AZ92A sand casting in percentages.

Conversion coating samples underwent the following identical process routine for neutral coating-performance comparisons.

Mechanical Grinding: Samples have been ground to 1200p using SiC wafers, rinsed in D.I water and dried.

Pretreatment Process: Ground samples are then wiped with acetone and rubbing alcohol. Samples are then subjected to the pretreatment routines for effective coating depositions as shown below.

Alkaline Cleaning: Sodium Hydroxide based cleaner has been chosen for alkaline cleaning of magnesium alloys for 5 minutes at 140F and a pH> 12.0. Magnesium is very resistant to corrosion by alkalis if the pH exceeds 10.5 which corresponds to the pH of a saturated $Mg(OH)_2$[13]; a $Mg(OH)_2$film is formed on the magnesium surface [3,13]. Dilute alkali solutions show negligible attack at temperatures up to the boiling point [14]. Consequently, a 10% caustic solution is commonly used for cleaning at temperatures up to the boiling point [15].

Surface activation via Acid Pickling: Chromic-Nitric-HF acid pickle in compositions recommended in the AMS-3171-C - specification [11], has been observed to be beneficial in contrast to phosphoric and sulfuric acid etches on AZ92A and hence has been adopted. A 2 minute immersion in an agitated mixture of Ammonium Bifluoride + Nitric acid has been observed to effectively remove the acid smut adhering to the surface in the trial studies.

Conversion Coating: Hexavalent chromium based conversion coatings were applied in accordance with the Type VIII treatment in the AMS-3171-C specification [11]. Iridite #15 was used for hexavalent chromium conversion coating of AZ92A.

Once conversion coated samples are stored in a dehumidifier chamber for a minimum of 24 hour curing period prior testing.

Performance characterization

Hydrogen Evolution and Weight loss measurement:

Hydrogen evolution studies have been conducted on bare AZ92A discs ground to 1200p grit and hexavalent chromium conversion coated samples for base line test criteria. Trivalent chromium conversion coated samples processed and cured were tested for amount of hydrogen evolved under 3.5% NaCl solution and was compared to the baseline criteria for rate of hydrogen evolution per surface area. Hot chromic acid 24 oz/gal at 190F, 8 minutes was used to remove any corrosive products on the alloy surface followed by a rinse in D.I. ,dried and weighed to evaluate the amount of weight loss per surface area due to salt immersion.

DC Polarization studies

Potentiodynamic measurements were performed on the conversion coated and bare AZ92A discs. The experiments were carried out in an aggressive 3.5% NaCl electrolyte. A three-electrode configuration was employed: conversion coated magnesium substrate as working electrode, a carbon rod as a counter electrode, and a SCE (Standard Calomel Electrode) as reference electrode. The amplitude of the perturbation was 10mV and the OCP (Open Circuit Potential) was chosen as bias potential. The examined frequency range was from 10mHz to 100kHz. Results obtained from these tests are used to determine the corrosion current, potential and corrosion rate.

Results and discussion

Hydrogen evolution experiment:

Magnesium dissolution in aqueous environments are often influenced by an electrochemical reaction with water that produces magnesium hydroxide and hydrogen gas. Under film-breakdown agents such as chlorides the stable oxide/hydroxide layers experience surface film break-down followed by the evolution of hydrogen. A stable coating negates this surface film limits this surface film break down vis-à-vis lesser hydrogen evolution. After conversion coated and cured, substrates are submerged in a bath of 3.5% NaCl solution to measure the amount of hydrogen released and the amount of weight loss per surface area. The volume of hydrogen displaced in the inverted burette is used to calculate the amount of hydrogen released per surface area.

Results obtained from the above measurements were used to evaluate the corrosion rate of the alloy (mm/y) with respect to their coating configurations using the following formulae.

$$\text{Corrosion rate [mm/y]} = 2.2785\ (\text{hydrogen evolution rate per Surface area [ml/cm}^2\text{/d]}).$$

$$\text{Corrosion rate [mm/y]} = 2.10\ (\text{weight loss rate [mg/cm}^2\text{/d]});$$

Figure 1 and 2 details the results of the hydrogen evolution test conducted on various conversion coated and bare magnesium samples as well as the calculated corrosion rates. It is clear from these values that the novel trivalent coating enhanced the corrosion protection compared to the uncoated bare substrate and performed close to the hexavalent coating. Figure 3 details the calculated corrosion rates via weight loss measurement tests and it can be observed that in both cases Trivalent chromium conversion coating processed samples performed on par with hexavalent IRIDITE coating by offering comparably effective film breakdown protection.

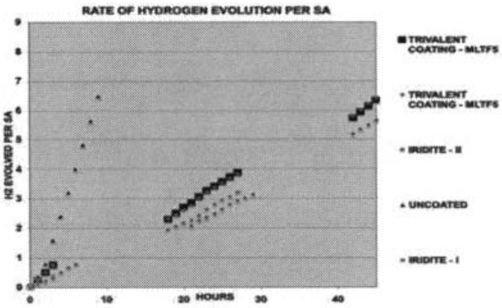
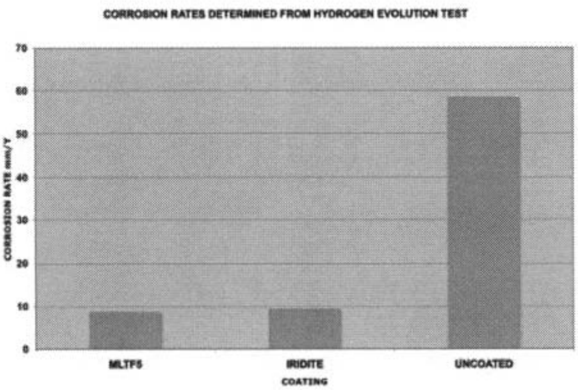


Figure 1: Rate of hydrogen evolution per surface area for various coated surfaces.



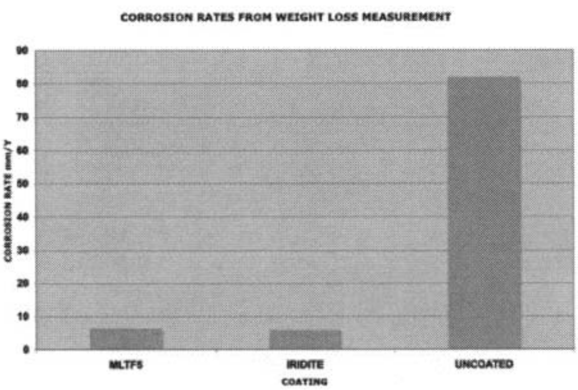


Figure 2 & 3: Corrosion rates calculated from the hydrogen evolution experiment and weight loss measurement tests on various coated surfaces.

DC Polarization studies:

DC polarization tests were conducted on bare as well as conversion coated substrates. Potentiodynamic studies revealed that the trivalent based conversion coating offered much nobler corrosion potential as shown in Figure 4 and Table 2 displays the corrosion current, corrosion potential and corrosion rates from Tafel plots generated using Gamry DC105 corrosion techniques software. It can be observed from these values that the corrosion rate for trivalent chromium based conversion coating on AZ92A has been reduced than for the hexavalent chromium based conversion coating as wells as the bare substrate.

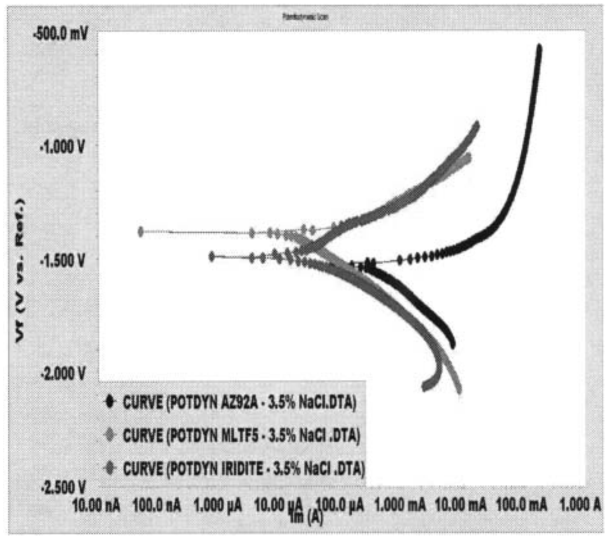


Figure 4: Potentiodynamic study results of various coating surfaces under 3.5% NaCl electrolyte.

Coating	Icorr-Amperes	Ecorr - Volts	Corrosion Rate (MPY)
Uncoated	4.48 mA	-1.53	6.82E+02
Iridite – Cr^{+6}	24.6 µA	-1.49	11.23
MLTF5 – Cr^{+3}	18.1 µA	-1.38	8.26

Table 2: Corrosion current, voltage and corrosion rates obtained from Potentiodynamic tests on AZ92A.

Conclusions

The novel trivalent chromium based conversion coating developed for magnesium alloys has in fact enhanced the corrosion resistance comparable to hexavalent chromium. Based on the results from various tests it can be concluded that;

- Rate of hydrogen evolution per surface area for magnesium substrates with trivalent chromium based conversion coatings is less than bare substrates and comparably same as hexavalent chromium coated substrates.
- Corrosion rates obtained from hydrogen evolution tests and weight loss measurement tests have shown that the trivalent chromium based coatings have indeed enhanced the corrosion resistance of the magnesium alloys.
- DC polarization studies have shown that the trivalent chromium based conversion coatings have offered significant amount of resistance when exposed to harsh chloride environment.

Acknowledgment

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