

Chemical Conversion Coatings on Magnesium Alloys - A Comparative Study

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Comparative studies on some of the important chemical conversion coatings viz, stannate, cerium oxide, chromate and galvanic black anodizing on magnesium alloy AZ31B have been conducted. The surface morphology and composition of the coatings were examined by SEM and EDX techniques. Corrosion resistance of these coatings was compared by polarization studies, salt spray test and electrochemical impedance spectroscopy [EIS]. The space worthiness of the coatings was evaluated by environmental tests viz., humidity, thermal cycling and thermo vacuum performance. The optical properties (solar absorptance and infrared emittance) of the coatings were measured before and after environmental tests. The corrosion resistance investigated was found in the following order, Galvanic black anodizing > Chromate conversion coating > Cerium Oxide coating > Stannate coating.

Keywords: Magnesium Alloys; Polarization; Electrochemical Impedance Spectroscopy; Thermal Cycling; Humidity Test

1. INTRODUCTION

Magnesium and its alloys are increasingly used in aerospace and automotive applications because of their ultra lightness and high strength to weight ratio with a density that is two thirds of aluminum and one fourth of iron [1]. Unfortunately, magnesium has high chemical affinity and reacts with atmospheric oxygen and water resulting in the formation of porous oxide carbonate film on the surface [2, 3] which does not offer protection. The metal corrodes even in moist air and in distilled water. The situation is even more complex for magnesium alloys.

In earlier days, hexavalent chromium compounds were widely used for producing conversion coatings [3, 4] to protect magnesium alloy. However, the use of Cr⁶⁺ is reduced in recent years as it is found to be carcinogenic [5]. Other alternative such as stannating [6] and salts of lanthanide elements

have been used in producing eco friendly corrosion protection coatings on aluminum and magnesium alloys [7-12]. Cerium oxide conversion coatings were developed by various authors [13, 14]. Photo electrochemical investigation for nucleation and growth process [15] of stannate conversion coatings has been studied. Galvanic black anodizing on magnesium lithium alloys for thermal control applications has been studied [16-18]. These chemical conversion coatings provide better corrosion resistance and acts as an excellent base for paints and adhesives.

In the present work comparative studies have been carried out on stannate, cerium oxide, chromate and galvanic black anodizing coatings on magnesium alloy AZ31B. The corrosion resistance of the coatings was compared using polarization, neutral salt spray and impedance tests. The environmental stability of the coatings was compared using humidity, thermal cycling and thermo vacuum performance tests.

2. EXPERIMENTAL PART

Chemical conversion coatings were obtained on magnesium alloy AZ31B (with chemical composition 3% Al, 1% Zn and balance Mg) test samples of dimension 5 x 5 x 0.2 cm as per the following sequence of operations.

1. Solvent degreasing in isopropyl alcohol using an ultrasonic bath for 10 min. at room temperature.
2. Alkaline cleaning in a solution containing 50 g/L Sodium hydroxide and 10 g/l Tri sodium orthophosphate for 10 min. at 55 ± 5 °C followed by water rinsing.
3. Acid cleaning in a solution containing Chromic acid 180 g/L, Ferric nitrate 40 g/L, Potassium fluoride 4.5 g/L for 2-3 min. at room temperature followed by water rinsing.

In addition to above, acid pickling was carried out only for stannate coating. Acid pickling was performed in a solution containing 280 ml/L 40% Hydrofluoric acid (%V/V) for 10 min. at room temperature followed by water rinsing.

4. Different chemical conversion coatings were then obtained by using the following bath formulations and operating conditions.
 - a) **Stannate conversion coatings** were produced by immersing the substrate in a solution containing 10-12 g/L Sodium hydroxide, 40-50 g/L Potassium stannate, 10–25 g/L Sodium acetate and 40–50 g/L Tetra sodium pyrophosphate at 82 °C, pH 11.6, for 20 min with continuous agitation [19]

- b) **Cerium oxide coatings** were obtained by dipping the pretreated samples in a solution containing 5 g/L Cerium sulphate and 40 ml/L Hydrogen peroxide at room temperature, pH 2.0 for 3-4 min.
 - c) **Chromate conversion coating** process was performed by dipping the samples in a solution containing 10 g/L Chromic acid and 7.5 g/L Calcium sulphate at room temperature, pH 1.2 for 30-60 sec. [3].
 - d) **Galvanic black anodizing** was carried out in a solution composed and operated as follows: 25 g/L Potassium dichromate; 25 g/L Ammonium sulphate; pH 5.8; temperature $28 \pm 1^\circ\text{C}$; anode to cathode ratio 1:10; for 15 minutes, galvanic current $0.8\text{-}2.4 \text{ mA/cm}^2$ with agitation in an anodizing (stainless steel) tank [17].
6. Water rinse and air drying at room temperature for 5-6 hours.

All the chemicals used were of LR grade and the solutions were prepared by using de-ionized water. The pH of the solution was adjusted upwards with dilute ammonium hydroxide and downward with dilute sulphuric acid solutions.

3. MEASUREMENT TECHNIQUES

The coatings were examined visually under 4X magnification for any degradation in physical appearance before and after corrosion and environmental stability tests.

Surface morphological studies were carried out with scanning electron microscope JEOL, JSM , 840 which is equipped with an energy dispersive X- Ray spectroscopic micro analyzer, Oxford Instruments Analytical, UK, for elemental analysis of the coatings.

Corrosion resistance of the coatings was evaluated by

- a) Galvanostatic polarization experiments using potentiostat/ galvanostat (362 A, PG and PAR, USA) in a three compartment cell containing corrosive medium (5% NaCl) at pH 5.0 with platinum foil and a saturated calomel electrode as counter and reference electrode, respectively.
- b) Salt Spray test was conducted in a salt spray chamber, CMI equipments Private Limited, Bangalore as per ASTM B117 standard using 5% NaCl solution as corrosive medium for 96 hours. Salt solution was prepared by dissolving 5% Sodium Chloride in distilled water and filtered before use. The test specimens were cleaned by dipping in isopropyl alcohol and dried. The test specimens were placed in salt spray chamber so that all the specimens are exposed to free setting of fog. The test chamber was closed, chamber temperature was set to 38°C and fog

was turned on. The test samples were visually examined after every two hours for any degradation of the coating.

- c) Impedance spectra were recorded at the corrosion potential using an Auto lab PGSTAT 30 (USA) potentiostat/ galvanostat with pilot integration controlled by GPES 4.9 software. The electrochemical cell consisted of a 3-electrode Pyrex glass cell. A saturated calomel electrode (SCE) was used as the reference electrode and a platinum foil was used as the auxiliary electrode. 5% NaCl solution at pH 5.0 was used as the test electrolyte. A time interval of 5-10 minutes was given for the system to attain a steady state open circuit potential (OCP). AC potential of 10mV was superimposed over the steady state potential. The AC frequency was varied from 10 kHz to 100 mHz. The real part (Z^I) and imaginary part (Z^{II}) of the cell impedance were measured in ohms for various frequencies. All impedance data were fit to appropriate equivalent circuit using a complex non linear squares fitting with both the real and imaginary components of the data.

Humidity tests were carried out in a thermostatically controlled humidity chamber (Heraeus Votsch type 08, 500, Germany). The relative humidity in the chamber was maintained at $95\pm 0.5\%$ at 50°C .

Thermal cycling test was carried out in a thermostatically controlled hot and cold chamber Brabender Real Test Umweltsimulatoren, (Germany).

Optical properties of the coatings viz, solar absorptance and infrared emittance were measured by using a solar reflectometer version 50, Model SSR – ER and emissometer model RD1, respectively, from Devices and Services Co (USA). Both these instruments provide an average value of solar absorptance and infrared emittance digitally over the entire solar (200-2500nm) or infrared (2.5 μm -25 μm) region.

4. RESULTS AND DISCUSSION

4.1. Surface morphology and EDX studies

The scanning electron micrograph of stannate, cerium oxide, chromate and galvanic black anodizing coatings on magnesium alloy AZ31B are shown in Figure 1. Stannate coating consists of uniform spherical and cubic grains. Cerium conversion coating consists of a thin fine cracked surface with 'dry mud' morphology. Chromate coatings and galvanic black anodizing was having a gel like structure which after drying, harden to give a microcracked pattern.

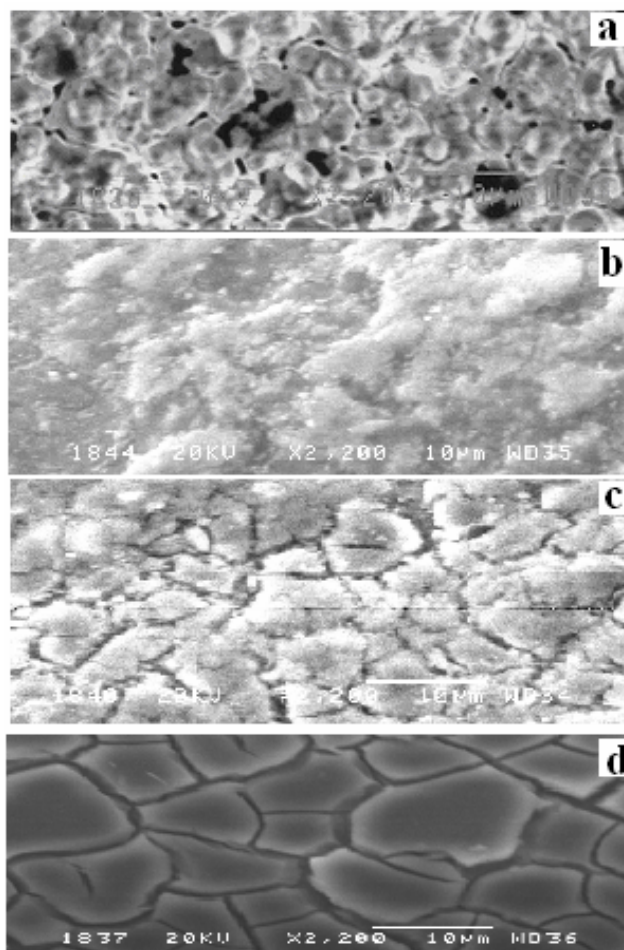


Figure 1. Scanning electron micrograph of (a) Stannate (b) Cerium (c) Chromate and (d) Galvanic black anodizing on magnesium alloy AZ31B .

Elemental composition of the conversion coatings were obtained from EDX. The composition (weight %) of different metals in the various conversion coatings is tabulated in Table1.

Table 1. Elemental composition (weight %) of various chemical conversion coatings

Type of conversion coating	Mg	Cr	Ce	Sn	O	Al	Zn
Stannate	56.82			8.31	32.70	1.17	1.00
Cerium oxide	56.42		4.52		33.06	4.51	1.49
Chromate	57.07	9.46			30.36	2.49	0.62
Galvanic black anodizing	48.66	12.16			34.54	3.52	1.12

4.2. Testing and evaluation

4.2.1. Polarization Studies

Galvanostatic polarization experiments were carried out in a three compartment cell containing 5% NaCl solution at pH 5.0 using potentiostat / galvanostat to study the corrosion resistance of the coatings. Platinum foil and saturated calomel electrodes were used as counter and reference electrodes, respectively. The polarization diagrams for different conversion coatings are given in Figure 2. The corrosion resistance of the different coatings was calculated using the following equation

$$I_{\text{corr}} = b_a b_c / (b_a + b_c) 2.303 R_p$$

I_{corr} corrosion current in $\mu\text{A}/\text{cm}^2$

b_a, b_c are anodic and cathodic Tafel slopes

R_p polarization resistance

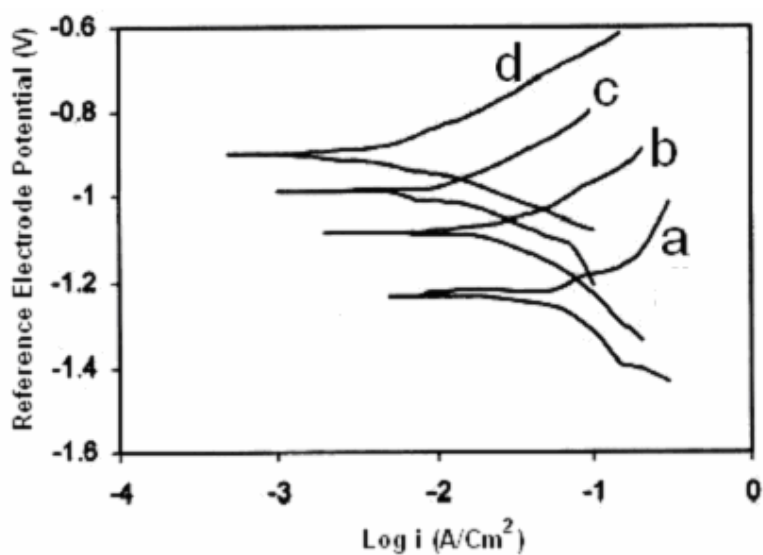


Figure 2. Polarization diagram of conversion coatings on Mg-AZ31B in 5% NaCl solution, a) Stannate b) Cerium c) Chromate d) Galvanic black anodizing

The polarization data of the conversion coatings is tabulated in Table 2.

From the Figure and Table it is clear that the corrosion current for different conversion coatings are in the following sequence

$$(I_{\text{corr}})_{\text{Black anodizing}} < (I_{\text{corr}})_{\text{chromate}} < (I_{\text{corr}})_{\text{ceriumoxide}} < (I_{\text{corr}})_{\text{stannate}}$$

Table 2. Polarization data of different conversion coatings on Mg-AZ31B in 5% NaCl solution.

Type of conversion coating	b_a (mV/dec)	b_c (mV/dec)	R_p (Ohm)	I_{corr} $\mu A/cm^2$
Stannate	201.6	271.09	4.4	11.4
Cerium oxide	87.05	228.7	3.4	8.05
Chromate	103.3	106.67	4.5	5.06
Galvanic black anodizing	172.9	86.12	5.2	4.8

4.2.2. Salt spray test

After neutral salt spray test the coating was carefully examined for any discoloration and formation of corrosion spots on the surface by 4X magnification lens. Stannate coating was stable up to 18 hours and slow degradation started from 18-20 hours. After 20 hours the corrosion rate was increased, a significant increase in the values of α_s and ϵ_{IR} was observed after salt spray test. Cerium oxide coating was found to be stable up to 28 hours. After 28 hours, degradation and darkening of the coating is observed. An increase in α_s and ϵ_{IR} value by 0.075 and 0.10 respectively was observed. On the other hand chromate is found to be stable up to 68 hours. After 70 hours degradation in terms of white patches were observed. The measured α_s and ϵ_{IR} values increased by 0.008 and 0.01, respectively. However, the galvanic black anodizing was found to be stable up to 90 hours. A negligible change (decrease) in solar absorptance and infrared emittance was noticed. This decrease in the optical properties may be due to the white patches found after the salt spray test.

Stannate coating is found to be corroded extensively, followed by cerium oxide conversion coating. However, the extent of corrosion in case of chromate and galvanic black anodizing coating were found to be less. And only a negligible degradation was observed in galvanic black anodizing.

The solar absorptance (α_s) and emittance (ϵ_{IR}) of the samples before and after the test was recorded and is tabulated in Table 3.

Table 3. Variation in optical properties of different conversion coatings before and after salt spray test

Type of conversion coating	α_s		ϵ_{IR}	
	Before Test	After Test	Before Test	After Test
Stannate	0.391	0.606	0.31	0.57
Cerium oxide	0.457	0.532	0.26	0.36
Chromate	0.796	0.804	0.27	0.26
Galvanic black anodizing	0.942	0.938	0.95	0.88

4.2.3. Impedance studies

When a metal surface is covered with a protective layer, the corrosion is controlled by the transportation of the species in the protective film through diffusion channels as a result of open pores or micro cracks [20]. Figure 3 presents impedance diagram (Z''/Ω versus Z'/Ω) recorded at OCP at different conversion coatings. It is evident from the figure that the semicircle diameter decreases in the following order.

Galvanic black anodizing < Chromate < Cerium oxide < Stannate

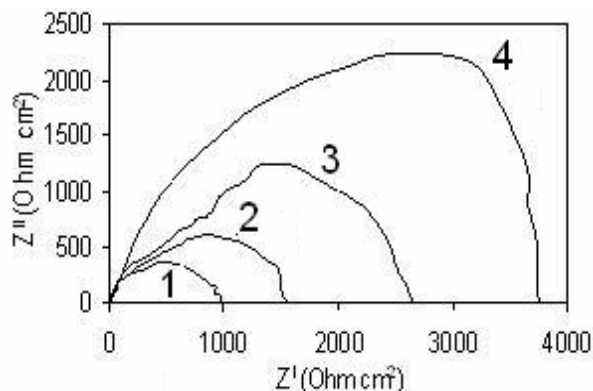


Figure 3. Nyquist diagram for different coatings, 1) Stannate 2) Cerium 3) Chromate and 4) Galvanic black anodizing

Since the diameter of the capacitive semicircle represents the resistance of the coatings, it can be said that the resistance decreases significantly with the decrease in diameter. This indicates that the corrosion resistance of anodic coating is greater than the other coatings, which is in good agreement with salt spray and polarization tests.

Figure 4a and 4b gives the Bode amplitude and Bode phase angle plot for different conversion coatings, respectively. From Nyquist plot it is clear that galvanic black anodic coating exhibits impedance values higher than the other coatings. There is an increase in the impedance for anodic coating and chromate coatings compared to cerium oxide, and stannate coatings. However, the more significant differences on the electrochemical behavior can be inferred from the analysis of the Bode phase angle plots, which are different for different conversion coatings. There is a clear displacement to lower frequency of the phase angle maximum for the anodic coating, indicating the hindrance of interfacial charge transfer phenomenon by the presence of conversion layer. The impedance and phase angle maximum in the high frequency region decreases from anodic coating, chromate, cerium to stannate coating indicating decrease in the protective properties of the coating, which can be attributed to electrolyte penetration through cracks in stannate and cerium coatings, reacting with the underlying magnesium substrate and resulting in the formation of magnesium hydroxy corrosion products which destabilize the coating by increasing its porosity [7].

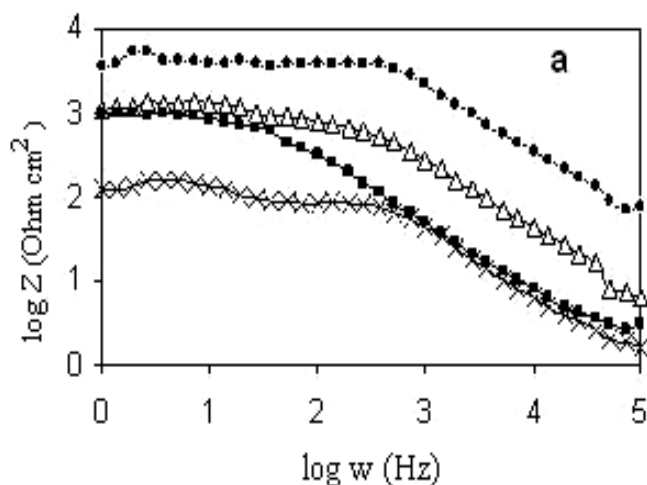


Figure 4(a). Bode amplitude diagram X – Stannate, ♦ - Cerium, △ - Chromate, • - Galvanic black anodizing

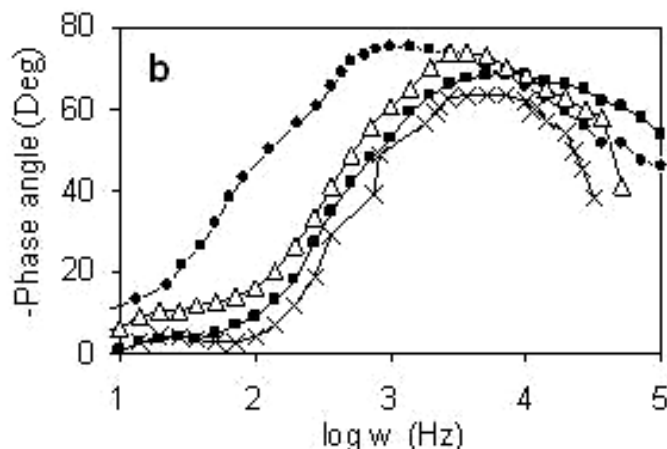


Figure 4(b). Bode phase angle diagram X – Stannate, ♦ - Cerium, △ - Chromate, • - Galvanic black anodizing

4.2.4. Humidity test

The humidity test was carried out to examine the resistance of the coating to the corrosive pre launch atmosphere. The test was conducted in a thermostatically controlled humidity chamber for 48 hrs. A relative humidity of $95 \pm 0.5\%$ was maintained in the chamber at $50 \pm 1^\circ\text{C}$. The test specimens were then examined visually, and their optical properties were measured. The α_s and ϵ_{IR} for different samples before and after humidity test is tabulated in Table 4. No change in color and degradation of the coating was observed in case of chromate and galvanic black anodizing. However, in case of stannate darkening of the coating and also some black degradation spots were observed. The increase in the α_s and ϵ_{IR} is ~ 0.092 and 0.10 , respectively. In case of cerium oxide darkening of the coating is

observed without any degradation or black dots. However, the increase in the α_s and ϵ_{IR} is as high as 0.125 and 0.10, respectively.

Table 4. Variation in optical properties of different conversion coatings before and after humidity test

Type of conversion coating	α_s		ϵ_{IR}	
	Before test	After test	Before test	After test
Stannate	0.391	0.483	0.30	0.40
Cerium oxide	0.457	0.582	0.25	0.35
Chromate	0.796	0.796	0.29	0.31
Galvanic black anodizing	0.942	0.943	0.94	0.94

4.2.5. Thermal Cycling test

A satellite in orbit becomes too hot when exposed to direct sun light and experiences low temperature when it dives in to earth shadow. The thermal cycling test is designed to evaluate the effect of cycling temperature on the deposit that is likely to be encountered throughout the life span of a spacecraft. The test was conducted in thermo statistically controlled hot and cold chambers. A total of 100 cycles were applied. A cycle consists of placing the samples in to a chamber operating at -45°C for 5 minutes, bringing them to an ambient temperature with a dwell of 15 minutes then shifting them to a hot chamber at 85°C for another 5 minutes. After thermal cycling test, specimens were inspected visually and their optical properties were measured. The α_s and ϵ_{IR} for different samples before and after thermal cycling test is tabulated in Table 5. No change in color and degradation of the coating was observed in case of chromate and galvanic black anodizing. Further no change in optical properties was observed. In case of cerium conversion coating visually no degradation was noticed but a slight increase in α_s and ϵ_{IR} value ~ 0.003 and 0.02 was observed. However, in case of stannate coating darkening and black spots were observed with increase in α_s and ϵ_{IR} value by ~ 0.042 and 0.11 , respectively.

Table 5. Variation in optical properties of different conversion coatings before and after thermal cycling test

Type of conversion coating	α_s		ϵ_{IR}	
	Before test	After test	Before test	After test
Stannate	0.391	0.433	0.30	0.41
Cerium oxide	0.457	0.460	0.25	0.27
Chromate	0.796	0.796	0.29	0.29
Galvanic black anodizing	0.942	0.942	0.94	0.94

5. CONCLUSIONS

1. Different chemical conversion coatings such as cerium oxide, stannate, chromate and galvanic black anodizing coating were carried out on precleaned Magnesium alloy AZ31B. The corrosion resistance and thermal stability of the different coating was compared.
2. Scanning electron micrographs showed that the stannate coating has uniform spherical and cubic grains. Cerium coating consists of a thin and cracked coating with 'dry mud' morphology. A gel like structure with 'mud crack' pattern was observed in case of chromate and black galvanic coating.
3. The corrosion resistance of the coatings was investigated by the polarization, impedance and salt spray techniques. From polarization studies the corrosion resistance of the coatings was found in the following order: galvanic black anodizing > chromating > cerium oxide > stannate coating. The electrochemical impedance studies also showed that galvanic black anodizing offer good corrosion resistance compared to other coatings which is in agreement with polarization and salt spray studies.
4. The space worthiness of the coatings was examined by the humidity and thermal cycling tests and evaluation of their optical properties. No degradation was noticed in case of galvanic black anodizing and chromate conversion coatings. A small change in optical properties was observed in case of cerium oxide coating while large scale degradation was observed with stannate coatings.

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