Passivation of the surface of AZ31B magnesium alloy in solutions based on salts of rare-earth metals

A.A. Abrashov,¹ * N.S. Grigoryan,¹ M.A. Simonova,¹
T.A. Vagramyan¹ and I.A. Arkhipushkin²

¹Federal State Budgetary Educational Institution of Higher Education “Russian Chemical-Technological University named after D.I. Mendeleev”, Miusskaya sq., 9, 125047
Moscow, Russian Federation

²A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Leninsky pr. 31, 119071 Moscow, Russian Federation

*E-mail: abr-aleksey@yandex.ru

Abstract

A solution has been developed for applying protective-adhesive lanthanum-, manganese-containing coatings under paintwork on the surface of magnesium alloy AZ31B instead of high-toxic chromate coatings, as well as independent anticorrosive coatings under mild operating conditions, for example, for inter-operation storage of products. A solution containing 1–6 g/l $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 0.5–2 g/l KMnO_4 , allows at pH 2.0–3.0 and at a temperature 18–30°C to form conversion coatings consisting of La_2O_3 , MnO_2 , MgO , $\text{Mg}(\text{OH})_2$ on the surface of AZ31B magnesium alloy in 2 minutes. Titanium-, zirconium- and lanthanum-, manganese-containing coatings can be used as adhesion layers under paintwork instead of high-toxic chromate coatings, and also as independent anticorrosive coatings under mild operating conditions, for example, for inter-operation storage of products. Using ellipsometry, it was found that the thickness of the cerium-containing coatings is 175 ± 5 nm. Corrosion tests in a salt-spray chamber according to ISO 4536 (SD test) ASTM B117 have shown that the developed lanthanum-, manganese-containing coatings are superior in protective ability to the currently widely used chromate coatings and are not inferior to titanium-, zirconium-containing coatings. The developed coatings also have good adhesion properties. Ti-, Zr- and La-, Mn-containing coatings in terms of protective characteristics and adhesion strength with paintwork are not only not inferior to the currently used chromate coatings but even surpass them.

Keywords: corrosion protection, conversion coatings, cerium-containing coatings, lanthanum-containing coatings, titanium-, zirconium-containing coatings, surface treatment, chromate-free passivation, rare-earth metals.

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Introduction

The growing demand of the aviation, space, military and other industries for light materials with high strength characteristics, capable of withstanding high loads in various environments and operating conditions, predetermines the ever-increasing scale of

application of magnesium alloys [1–3]. The disadvantages of magnesium and its alloys are low corrosion resistance and scrub resistance. The low corrosion resistance of magnesium alloys is due to the high negative values of their standard potentials (-2.37 V). In real chloride environment, for example, in a 3% solution of sodium chloride, the potential of the AZ31B magnesium alloy is -1.38 V, which is also much more negative than that of other structural metals and alloys [4].

In order to protect magnesium alloys from corrosion and wear and tear, protective coatings are applied to their surface: paint, galvanic (including conversion) hydride, anodic oxide, gas-plasma coatings, *etc.* [5–7]. According to [8], the leading place among the methods and means of protecting magnesium and its alloys belongs to conversion coatings, both independent and in combination with paintwork.

Chromatic coatings are widely used as adhesion layers under the paintwork before painting magnesium and its alloys.

Due to the high toxicity of chromating solutions, which contain hexavalent chromium compounds, and the conversion coatings formed in them, which also contain up to $200 \text{ mg/m}^2 \text{ Cr}^{6+}$, in many countries the use of conversion chromate coatings is significantly limited or prohibited [9–14].

In recent years, in world practice, as an alternative to chromate layers on magnesium and its alloys, conversion titanium- and/or zirconium-containing adhesive coatings have been used. Such coatings are formed from solutions based on hexafluorozirconic and hexafluorotitanic acids [6, 15–18]. Along with this, salts of rare-earth metals, in particular cerium and lanthanum salts, which are ecologically safe and effective corrosion inhibitors of such metals as aluminum and zinc and their alloys, are described in the literature as corrosion inhibitors alternative to chromates [19–23]. In view of the foregoing, cerium- or lanthanum-containing conversion coatings can become a possible substitute for adhesive conversion chromate coatings.

At the Department of Innovative Materials and Corrosion Protection (Mendeleev University of Chemical Technology of Russia), technological processes for the deposition of titanium-, zirconium-containing conversion coatings were previously developed. Within the framework of this study, cerium- and lanthanum-containing coatings were developed and compared with titanium-, zirconium-containing and chromate coatings on the AZ31B magnesium alloy.

Methods and Materials

Magnesium plates AZ31B of the size of 3×4 cm were used as samples.

To prepare the solutions, the chemical reagents of grades “pure”, “chemically pure”, and distilled water were used.

Passivating coatings were formed by immersing samples of magnesium alloy AZ31B in the test solution for a specified time, after which the samples were removed and dried by blowing hot air at a temperature of 80°C for 10 minutes.

As objects of comparison, chromate and titanium-containing coatings were selected, for the formation of which the following solutions were used:

- $\text{K}_2\text{Cr}_2\text{O}_7$ 40 g/l; K_2SO_4 20 g/l; $t = 75^\circ\text{C}$; 1–14 min [24].
- H_2TiF_6 0.5–1 g/l; H_2ZrF_6 1.5–2 g/l; $\text{HOOCCH}(\text{OH})\text{CH}(\text{OH})\text{COOH}$ 1–2 g/l; $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ 0.3 g/l; pH 4–5; $t = 20\text{--}30^\circ\text{C}$; 2–3 min [6].

The protective ability of the coatings was determined by the “express drop method” using a 10 g/l solution of lead acetate, $\text{Pb}(\text{CH}_3\text{COO})_2$. The criterion for assessing the quality of the coating was the time until the color of the control area under the drop changed from gray to dark black for the magnesium base. The “express drop method” using a solution containing 50 g/l of $\text{Pb}(\text{CH}_3\text{COO})_2$ is intended for evaluating protective ability on galvanized steel [25]. When using a solution of this concentration in relation to a magnesium base, the color change of the control area under the drop of the solution occurred too quickly due to the high activity of magnesium. For this reason, it was not possible to visually assess the differences in the protective ability of magnesium-based coatings when using a solution of such a concentration. It has been experimentally established that for a visual assessment of the protective ability on a magnesium basis, the solution should be diluted (up to 10 g/l). The correctness of the application of the “drop method” using a diluted solution is due to the fact that it was used for comparative assessment of coatings and prompt rejection of unsuitable options. Subsequently, the protective ability of the developed coatings was determined by standard corrosion tests.

The thickness of the coatings was determined by an ellipsometric method using a spectroscopic ellipsometer by Sentech SENresearch (SENTECH Instruments GmbH, Krailling, Germany) 4.0 SER 800 with a high-speed monochromator. The measurements were carried out in the spectral range of wavelengths of 240–1000 nm at a goniometer angle of 70° . For calculations, a three-layer model was used, including two Drude–Lorentz layers and 1 Cauchy layer. The model parameters (thickness d , refractive index n_2) from the measured values Ψ and Δ (inverse problem of ellipsometry) were determined by the software of the device in accordance with the selected mathematical model. The calculated result was considered valid if the result of the parameters of the physical model corresponded to the mathematical model and did not exceed the limits of the established errors [26]. The thickness measurement error was ± 5 nm.

The composition of the surface layers was studied using X-ray photoelectron spectroscopy (XPS) on an OMICRON ESCA+XPS device (Germany) [27–30]. The panoramic spectra were also recorded after argon-ion etching of the coating in different depths. Thus, the composition of the coating at different distances from the substrate was determined. The pressure of the inert gas in the working chamber was maintained at this level, so that the ion energy and the ion current rate, and consequently, the etching rate, were constant. When analyzing the obtained spectra, it was considered that the analyzing beam penetrates the material to the depth of 5 nm, *i.e.*, the resulting spectra correspond to a layer of material 5 nm thick [31].

Corrosion tests of conversion coatings on magnesium surface using a saline solution according to ISO 4536 (SD test) were carried out in a solution simulating the composition of seawater (in g/l): NaCl 26.5; MgCl₂ 2.4; MgSO₄ 3.3; CaCl₂ 1.1; KCl 0.73; NaHCO₃ 0.2; NaBr 0.28. This solution, in accordance with the method, was applied to the samples using a spray gun at a temperature of 23°C, the relative humidity at the same time was 90% [32].

The adhesion of the coatings was determined by the normal detachment method using the PosiTest AT digital adhesion meter. The method is based on measuring the minimum breaking tension required to separate or rupture the coating in a direction perpendicular to the substrate surface [33].

Corrosion tests of magnesium samples in combination with powder paint were carried out in a salt spray chamber of Ascott S450iP (Great Britain) in accordance with the international standard ASTM B117 [34].

Polyester powder paint was applied to the samples with adhesion conversion coatings using an electrostatic coating pistol. Then, to melt the paint, the samples were placed in a drying oven for 10–15 minutes at a temperature of 180–200°C. After the melting process was completed, the samples were removed and cooled in air.

Current–voltage and impedance studies were carried out using an IPC potentiostat with an FRA attachment and a three-electrode glass cell thermostated at 25°C in 3% NaCl. The counter electrode was a titanium plate, the surface area of which significantly exceeded the overall area of the working electrode. The potentials were measured relative to a saturated silver-chloride electrode and then recalculated to the scale of a standard hydrogen electrode. The potential sweep rate when obtaining voltammograms was 50 mV/s. The impedance was measured in a potentiostatic mode at a stationary potential in the frequency range 0.1 Hz–20 kHz at a potential oscillation amplitude of 10 mV.

To analyze the equivalent circuits and calculate the denominations of their elements, the DCS program (Dummy Cell Solver), created by V.E. Kasatkin (IPCE RAS), was used. This program allows you to calculate the theoretical frequency dependence of the impedance of the selected circuit and compare it with the experimentally obtained dependence. The optimization of the nominal values of the elements of the selected equivalent circuit is performed according to the criterion of minimizing the relative error between the experimental and simulated values of the impedance vectors for each measurement in the investigated range.

Results and Discussion

Cerium and lanthanum salts such as phosphates, cinnamates and silicates [35–37], as well as nitrates and chlorides are described in the literature as corrosion inhibitors for aluminum and magnesium alloys [19,20,23,38].

Taking into account the manufacturability, safety, availability in the present work, nitrate salts of cerium and lanthanum (Ce(NO₃)₃·6H₂O and La(NO₃)₃·6H₂O) were chosen as the main components of the conversion solutions.

According to the literature, the formation of a coating on the surface of magnesium in solutions based on cerium or lanthanum salts begins at the cathode areas of the surface as a result of an increase in pH in the solution adjacent directly to the metal surface due to oxygen reduction (metal corrosion with oxygen depolarization). The formation of films can be accelerated by introducing oxidizing agents into the solution, which catalyze the cathodic reaction [19–23].

In the present work with the accordance of literature data, hydrogen peroxide and potassium permanganate were tested as oxidants.

The experiments made it possible to determine the concentration regions of the solution components (1–6 g/l $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ or $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 15–20 ml/l H_2O_2), in which conversion homogeneous coatings had a good appearance and high adhesion strength to the substrate. However, the protective ability of the coatings is low – the color of a drop of the control solution changes on them within 15–20 s.

It should be noted, that using 0.5–2 g/l potassium permanganate instead hydrogen peroxide leads to an increase in the protective ability of the cerium-containing coatings formed up to 30–34 s and lanthanum-containing coatings up to 50–54 s, which is apparently explained by their lower porosity. At the same time, the permissible range of concentrations of rare-earth metal salts is preserved.

The above experiments were carried out at a working solution temperature of 18–25°C. It was found that heating the solution to 40°C practically does not affect the protective ability of the coatings, further heating is undesirable, since it leads to some decrease in protective ability. Thus, heating the solution in the summer without damage to the deposited coatings is permissible up to 30°C.

The study of the effect of the acidity of the solution on the protective ability of coatings showed that the acceptable pH values are in the range of 2.0–3.0, and the optimal values are in the range of 2.5–3.0 pH units. At $\text{pH} < 2.0$ coatings are not formed. When the pH of the solution rises to $\text{pH} \geq 4$, a precipitate of insoluble rare-earth metal compounds precipitates in the solution.

Taking into account possible transformations in accordance with the Pourbaix diagram for the Ce– H_2O_2 and La– H_2O_2 systems, the mechanism of formation of coatings in a solution with hydrogen peroxide at $\text{pH} = 2–3$ may be described by the following reactions:

At the same time, the magnesium base is dissolved and the solution is alkalized at the interface:

Magnesium ions, as well as Ce^{3+} ions unoxidized by hydrogen peroxide, form magnesium and cerium hydroxides:

During subsequent drying, the resulting coatings are dehydrated and a mixed oxide is formed:

Lanthanum is included in the coating, apparently, in the form of an oxide formed by the following reactions:

According to the above mechanism, the forming cerium-containing coating would appear to consist of oxides: Ce_2O_3 , CeO_2 и MgO , and La-containing coatings – from oxides La_2O_3 and MgO .

Potassium permanganate also acts as an oxidizing agent at the initial stage, which leads to a local increase in the pH value and allows the precipitation of $\text{Ce}(\text{OH})_3$ or $\text{La}(\text{OH})_3$.

A decrease in the concentration of H^+ further contributes to the following reactions:

or

In this regard, manganese oxide can also be included in the formed coatings along with magnesium, cerium and lanthanum oxides.

The chemical composition of the forming cerium- and lanthanum-containing coatings has been investigated. The survey XPS spectra of the coating formed in the working solution $\text{Ce}/\text{H}_2\text{O}_2$ indicate the presence of oxygen, cerium, and magnesium in the coating. From the individual spectra of cerium (Figure 1a) and magnesium (Figure 1b), it can be seen that cerium is present in the coating in the form of Ce_2O_3 and CeO_2 , and magnesium in the form of MgO and $\text{Mg}(\text{OH})_2$. Lanthanum from the working solution $\text{La}/\text{H}_2\text{O}_2$, as expected, is included in the coating in the form of La_2O_3 (Figure 2). Manganese from the working solutions Ce/KMnO_4 and La/KMnO_4 is included in the coating in the form of manganese(VI) oxide (Figure 3). These data are consistent with the above-described mechanism of coating formation.

Figure 1. Individual XPS spectra of cerium (a) and magnesium (b) in the coating.

The spectra in Figures 1 and 3 show that, in the presence of hydrogen peroxide in the solution, 10 times less magnesium is included in the coating than in the presence of potassium permanganate, and the proportion of Ce(IV) oxides significantly increases: the ratio Ce(IV)/Ce(III) in the coating in this case increases 3.5 times (Table 1). This is most likely due to the greater oxidizing ability of potassium permanganate in relation to magnesium: the standard potentials of oxidants are $E_{\text{H}_2\text{O}_2/2\text{OH}^-}^0 = +0.88\text{V}$ and $E_{\text{MnO}_4^-/\text{MnO}_2}^0 = +1.692\text{V}$, respectively.

Figure 2. Individual XPS spectra of lanthanum in the coating.

Table 1. Chemical composition of the coatings (X-ray photoelectron spectroscopy (XPS)).

Name	Peak name	Quantitative composition, %
Ce/H ₂ O ₂		
Cerium	Ce3d ⁴⁺	7.89
	Ce3d ³⁺	2.40
Oxygen	O1s	86.56
Magnesium	Mg2p	3.14
Ce/KMnO ₄		
Cerium	Ce3d ⁴⁺	2.02
	Ce3d ³⁺	0.85
Oxygen	O1s	60.28
Manganese	Mn2p ₃	6.20
Magnesium	Mg2p	30.65

Figure 3. Individual XPS spectra of cerium (a) magnesium (b) and manganese (c) in the coating.

Figure 4 shows the results of corrosion tests according to ISO 4536 (SD test) of magnesium samples with cerium- and lanthanum-containing coatings, as well as chromate and Ti, Zr-containing layers. It can be seen that La, Mn-containing coatings have the greatest protective ability. The first local spot of corrosion appeared after 30 hours of testing. Ce- and Ce, Mn-containing coatings are characterized by the least protective ability: corrosion products begin to appear after 6 and 8 hours, respectively. Samples with chromate and Ti, Zr-containing coatings begin to corrode after 20 and 24 hours of exposure under the salt drops, respectively. It should be noted that the first local spot of corrosion on a magnesium base without coating appear after 0.5 hours of corrosion tests.

Figure 4. Saline drop test results.

With the help of ellipsometry, the thicknesses of the developed and selected as objects of comparison conversion coatings on magnesium alloy were determined (Figure 5).

Figure 5. Thickness value depending on the type of coating.

It should be noted that at a significantly lower thickness, La, Mn-containing coatings are superior to chromate coatings in terms of protective ability, and Ti, Zr-containing coatings are comparable to them.

In this work, impedance spectroscopy was also used to compare the protective characteristics of conversion coatings.

Protective coatings can be described by an equivalent circuit (Figure 6), consisting of active resistance (R_0), which is the resistance of the electrolyte, the capacitance of the electric double layer (CPE_1), which is the geometric capacity of the conversion film, and the active resistance (R_1), which is the polarization resistance of the conversion coating, the pseudo-inductive resistance (R_2), which is the polarization resistance to the corrosion process, and the pseudo-induction capacitance (CPE_2), which is the capacitance of the metal/coating interface.

Nyquist diagrams (hodographs) for magnesium alloy samples with various conversion coatings are shown in Figure 6. Parameter values calculated according to the equivalent circuit are shown in Table 2.

Figure 6. Nyquist diagrams and equivalent circuit for magnesium samples with protective coatings: 1 – uncoated Mg; 2 – Ce; 3 – Ce+Mn; 4 – Cr(VI); 5 – La; 6 – Ti+Zr; 7 – La+Mn.

It is known that hodographs show charge transfer resistance from solution to metal and vice versa, so the larger the hodograph loop, the more hindered this process is, and, therefore, the hodographs can be used to assess the barrier characteristics of the coatings. The given hodographs indicate that the greatest difficulties in charge transfer occur in the case of a La,

Mn-containing coating. The hodograph radii of samples with La, Mn- and Ti, Zr-containing coatings are comparable.

Table 2. Parameter values calculated according to the equivalent circuit.

System	E, mV	R_0 , Ohm	R_1 , Ohm	CPE T1	CPE f1	R_2 Ohm	CPE T2	CPE f2
Cr	–1313	15.1668	–762.697	–0.00022	1	1409.31	$2.14 \cdot 10^{-5}$	0.897291
Ce	–1323	13.2585	–420.98	–0.00028	1	663.433	$3.89 \cdot 10^{-6}$	0.938318
Ti-Zr	–1358	11.1396	260.47	0.00012	1	1522.9	$3.34 \cdot 10^{-6}$	0.888408
Ce-Mn	–1363	13.3263	–624.023	–0.00046	1	863.098	$4.40 \cdot 10^{-6}$	1
La	–1298	20.6885	–736.783	–0.00043	1	1139.49	$1.81 \cdot 10^{-6}$	1
La-Mn	–1313	8.03443	–1314.69	–0.00014	1	2084.13	$6.45 \cdot 10^{-6}$	0.84411
Mg	–1318	8.51841	–36.2972	$-4.29 \cdot 10^{-3}$	1	75.1038	$9.22 \cdot 10^{-4}$	1

It should be noted that the results of impedance spectroscopy are consistent with the above results of corrosion tests.

Corrosion tests (ASTM B117) in a salt spray chamber of AZ31B magnesium alloy samples with applied conversion coatings, painted with polyester powder paint (Ecocolor PE RAL 9016/P), were carried out. The thickness of the paintwork was 90–100 microns.

Tests have shown that the developed coatings in terms of protective ability satisfy the requirements for adhesive layers under the paintwork, since the width of corrosion penetration from the place of incision in these cases does not exceed 2 mm after 240 hours of testing according to the international standard ISO 9227 (Table 3).

Table 3. Results of corrosion tests.

No.	Coating type	The width of corrosion penetration from the place of incision, h (ISO 9227)	Corrosion spread assessment from the place of incision (ASTM D 1654-08)	
			Corrosion spread from the place of incision, mm	Class (from 0 to 10)
1	Mg	9.58	6.32	4
2	Ti+Zr	0.2	0.1	9
3	Ce	0.86	1.08	7
4	La	0.6	0.56	8
5	Ce+Mn	0.78	1.03	7
6	La+Mn	0.26	0.16	9
7	Cr(VI)	0.15	0.2	9

It should be noted that the smallest depth of corrosion penetration under the paintwork film from the place of incision is observed for samples with adhesion chromate, Ti, Zr- and La, Mn-containing coatings (class 9 on a ten-point scale according to the American standard ASTM D 1654-08).

The pull-off adhesion strength of the LCP to the surface of AZ31B with an adhesive sublayer (the “fungi” method), is shown in Table 4.

Table 4. The results of determining the adhesion strength of coatings to the substrate.

№	Coating type	Adhesion strength, MPa		The decrease in adhesion, %
		Before corrosion tests	After corrosion tests (240 h)	
1	Mg	6.14	2.42	60.6
2	Ti/Zr	13.83	11.61	16.0
3	Ce	10.42	4.24	59.3
4	La	12.7	6.42	49.4
5	Ce, Mn	11.19	8.35	25.4
6	La, Mn	13.65	11.18	18.1
7	Cr	13.15	10.42	20.8

It can be seen that the adhesion strength of the samples with titanium-, zirconium- and lanthanum-, manganese-containing adhesive coatings is higher than that of the sample with chromate coating: 13.83 and 13.65 versus 13.15 MPa. It should be noted that the decrease in adhesion (%) after 240 hours of corrosion tests in a salt spray chamber for these coatings is 16.0%, 18.1 and 20.8%, respectively.

Conclusion

A solution containing 1–6 g/l $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 0.5–2 g/l KMnO_4 , allows at pH 2.0–3.0 and at a temperature 18–30°C to form on the surface of AZ31B magnesium alloy conversion coatings 175±5 nm thick consisting of La_2O_3 , MnO_2 , MgO , $\text{Mg}(\text{OH})_2$ for 2 minutes.

Titanium-, zirconium- and lanthanum-, manganese-containing coatings in terms of protective characteristics and adhesion strength with paintwork are not only not inferior, but also surpass the currently used chromate coatings.

Titanium-, zirconium- and lanthanum-, manganese-containing coatings can be used as adhesion layers under paintwork instead of high-toxic chromate coatings, as well as independent anticorrosive coatings in light operating conditions, for example, for interoperative storage of products.

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