Physicochemical studies of composite coatings during accelerated tests for atmospheric corrosion

Mariia Gerasimenko[1,2], Konstantine Nadaraia[1,2], Dmitry Mashtalyar[1], Igor Imshinetskiy[1], Sergey Sinebryukhov[1] and *Sergey Gnedenkov[1]*

[1]Institute of Chemistry FEB RAS, 159 pr. 100-letiya Vladivostoka, Vladivostok 690022, Russia
[2]Far Eastern Federal University, 10 Ajax Bay, Russky Island, Vladivostok 690922, Russia

Abstract. In the present paper, the formation of protective coatings on the MA8 magnesium alloy by plasma electrolytic oxidation (PEO) with subsequent treatment of fluoropolymer is considered. The morphology of coatings after accelerated climatic tests was investigated and the elemental composition of coatings was studied after tests in a salt spray chamber (SSC). The analysis of the obtained results demonstrated a higher corrosion resistance of the fluoropolymer-containing layers in comparison with the base PEO coating.

1 Introduction

Magnesium alloys are one of the lightest metal of all known structural materials. Therefore, the use of magnesium alloys is found in various fields of engineering, transport, and industry. Magnesium alloys have many advantages over other alloys based on non-ferrous metals [1]. Unfortunately, these materials also have some drawbacks. The main disadvantages of magnesium and its alloys, which prevent their widespread use, are low corrosion and wear resistance [2]. These disadvantages can be eliminated by forming multifunctional composite coatings with high protective properties on the surface of magnesium alloys using the method of plasma electrolytic oxidation (PEO) with subsequent application of organofluorine compounds. The PEO is the most promising electrochemical method for the fabrication of protective coatings on magnesium alloys [3–5]. The presence of developed surface morphology in PEO coatings allows us to consider these layers as the basis for the formation of composite coatings (CC) [6], for example, by applying chemically stable substances to a rough oxide surface.

This work presents the results of a study of changes in the morphology of samples with various types of surface treatment during accelerated climatic tests in a salt spray chamber.

2 Experimental

Samples made of MA8 magnesium alloy were used in the work. Previously, the samples were sequentially treated with grinding paper to remove defects, then washed with distilled water and degreased with ethanol. The dimensions of all samples were 30 mm × 40 mm × 1 mm.

All of the above operations were carried out in order to standardize the surface of the samples. The PEO process was carried out in 2 stages in the electrolyte containing NaF and Na_2SiO_3. At the first stage, the voltage in the anodic component was increased from 30 to 240 V at a sweep rate of 1 V/s, the cathodic component had a constant value of –40 V. At the second stage, the voltage in the anodic part was changed from 240 to 200 V at a sweep rate of 0.07 V/s, whereas cathodic one was changed from –40 to –10 V at a sweep rate of 0.05 V/s. The duration of the first stage was 200 s and the second one was 600 s [7].

Then, the samples were washed and dried in a FD 53 drying oven (BINDER, Germany) for the further formation of composite coatings (CC) using 15 wt. % alcohol suspension of superdispersed polytetrafluoroethylene (SPTFE) [8]. The polymer-containing layer was applied by spraying followed by heat treatment at 315° C for 15 min. SPTFE was sprayed 1-3 times (CC-1X, CC-2X, CC-3X). Since significant differences in the properties of coatings were observed only between samples with a single and triple application of fluoropolymer, data on the formation of composite layers with a double application of SPTFE are not given in the work.

The samples were placed in a salt spray chamber (SSC) for 4, 10, 20, 30 and 40 days according to ISO 9227:2017 [9]. Water NaCl solution in concentration of 5 wt. % was used as a corrosive medium.

An EVO 40 scanning electron microscope (Carl Zeiss, Germany) was used to study the morphology of the surface and the analysis of the coatings. The scanning electron microscopy (SEM) method, which is actively used to study the surface of oxide layers, provides extensive qualitative information about the morphology of the surface. Additionally, this microscope was equipped with an INCA X-act energy dispersion analysis (EDS) device (Oxford Instruments, UK). Before analysis, a thin layer (100 nm) of conductive material (chromium) was sprayed on samples. The sprayed film provided enough electrical conductivity of the surface layer of the sample, necessary to prevent the formation and accumulation of a volumetric electric charge on the surface.

3 Results and Discussion

At the end of the general test lasting 4, 10, 20, 30 and 40 days, the salt deposit from the samples was washed off with a weak stream of water, then dried with warm air.

Analysis of SEM images of the uncoated sample (MA8) after accelerated tests in SSC revealed serious damage. After 4 days, the formation of multiple corrosion defects is observed in the SSC (Figure 1a). The condition of the samples after 10 days is described by a higher degree of destruction (Figure 2a), while the surface is almost completely covered with corrosion products. Due to significant violations of the integrity of the uncoated magnesium alloy on the 10th day of exposure in SSC, further climatic tests for this type of samples were considered inappropriate.

A sample with a PEO coating after 4 days in SSC shows changes in surface morphology and the formation of a small number of corrosion products on the surface (Figure 1b). In the future, on the 10th, 20th, 30th and 40th days, more corrosion products are formed and the integrity of the protective coating is violated (Figure 2b, 3a, 4a,-5a), which is a consequence of the penetration of the corrosive medium through the pores of the coating to the metal substrate. Note that after 40 days of testing, most of the surface of the PEO coating is covered with corrosion products. Thus, this type of coating is suitable either as a short-term protection of magnesium alloys in highly aggressive corrosive environments, or for use in less harsh operating conditions.
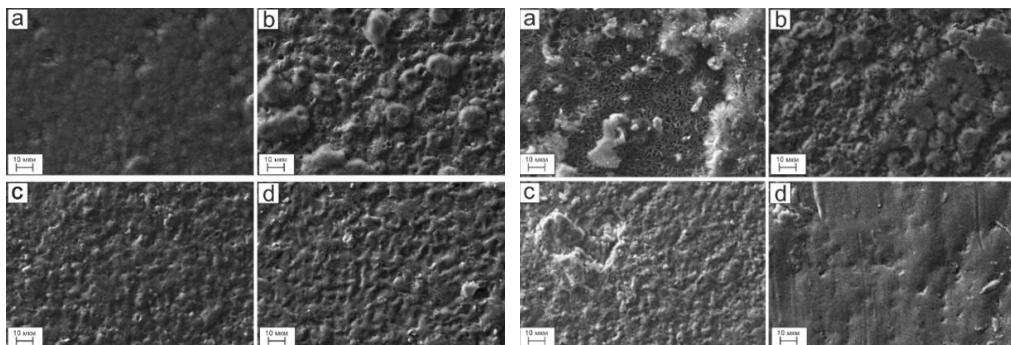
Fig. 1. SEM images of the uncoated sample (MA8) (a), PEO coating (b), CC-1X (c) and CC-3X (d) after 4 days of corrosion tests in SSC.

Fig. 2. SEM images of the uncoated sample (MA8) (a), PEO coating (b), CC-1X (c) and CC-3X (d) after 10 days of corrosion tests in SSC.

Composite coatings with a single application of SPTFE (CC-1X) after 4 days in SSC demonstrate high stability to aggressive conditions (Figure 1c). The first areas with defects appear on the 10th day (Figure 2c). Then the area of such areas becomes larger with increasing time spent in the SSC (Figure 3-5b), and there is an increase in the roughness of the coating, which is due to the gradual penetration of a corrosive medium through unsealed pores in the base PEO layer to the substrate material.
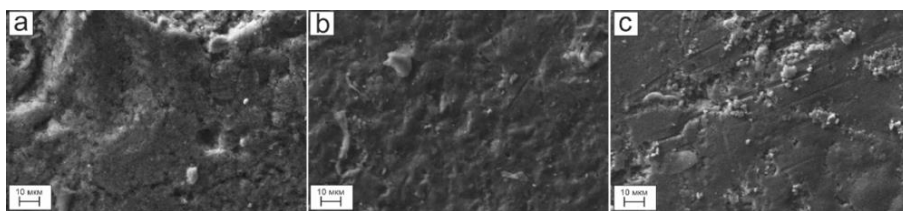

Fig. 3. SEM images of a sample PEO coating (a), CC-1X (b) and CC-3X (c) after 20 days of corrosion tests in SSC.

The highest corrosion resistance among the formed composite coatings was found in samples with triple application of SPTFE (CC-3X). After 10 days in an aggressive corrosive environment (Figure 1d), corrosion was not observed, and after 40 days of testing (Figure 5c), the CC-3X showed the lowest degree of destruction. The reason for the high durability of the composite coating is the presence of a polymer component in its composition – SPTFE, which during the formation of CC penetrates into the pores of the PEO coating, gradually sealing them as the multiplicity of application increases. Thus, in CC-3X, almost all pores and defects of the base PEO layer are filled, and a smooth continuous coating is formed, in contrast to the heterogeneous surface structure of the CC with a lower frequency of SPTFE treatment (Figure 1c, 2c, 3b, 4b, 5b).
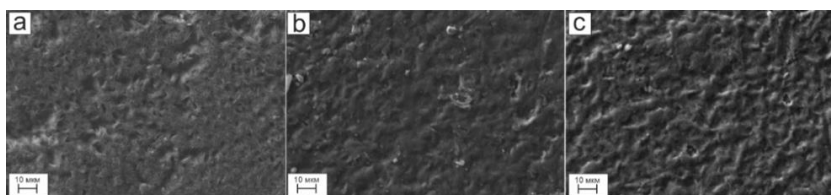

Fig. 4. SEM images of a sample PEO coating (a), CC-1X (b) and CC-3X (c) after 30 days of corrosion tests in SSC.
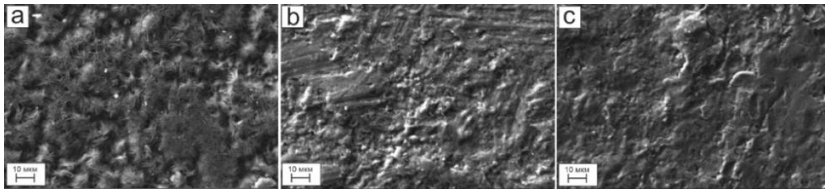
Fig. 5. SEM images of a sample PEO coating (a), CC-1X (b) and CC-3X (c) after 40 days of corrosion tests in SSC.

Analysis of the data obtained using energy-dispersive X-ray spectroscopy (EDS) after 4 days in SSC (Figures 6-8) indicates the presence of the Mg and O. And if the presence of magnesium for all samples is due to the use of a magnesium alloy in the work, then the presence of oxygen is the result of several reasons.

It is known that one of the main components of the PEO coating is MgO, formed during the oxidation process, part of the O detected by the EDS during the study of PEO coatings is part of this compound (Figure 7). However, it should be noted that oxygen is also present on the surface of uncoated samples. In this case, O is included in the compound $Mg(OH)_2$: the main corrosion product of magnesium and its alloys. Taking into account the presence of corrosion products on the surface of the PEO coating (Figure 1b), it can be concluded that for the PEO coating, part of the detected O is also part of $Mg(OH)_2$.
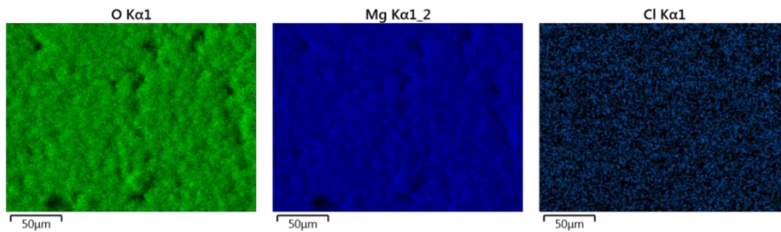

Fig. 6. Map of the distribution of elements over the surface of uncoated MA8 alloy after 4 days of corrosion tests in SSC.
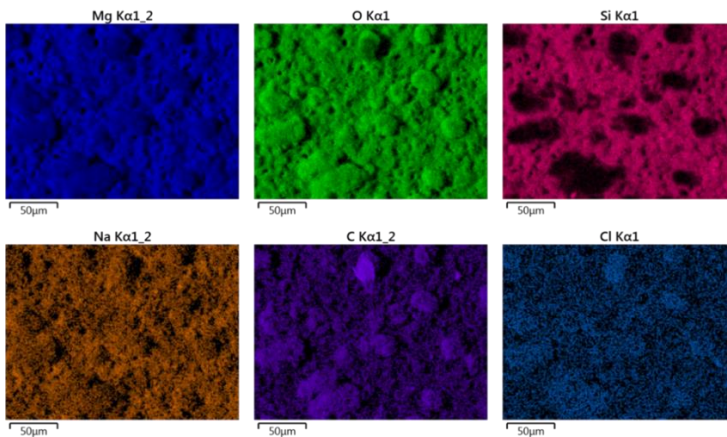

Fig. 7. Map of the distribution of elements over the surface of the PEO coating after 4 days of corrosion tests in SSC.

The presence of oxygen in CC is also of particular interest (Figure 8). Probably, in this case, the reason is the penetration of radiation during EDS through a thin polymer film on the surface of the composite layer. Thus, the detected oxygen, as for the PEO coating, is a component of magnesium oxide. This assumption is confirmed by the fact that no corrosion damage was detected during the SEM data analysis of CC-3X (Figure 1d).
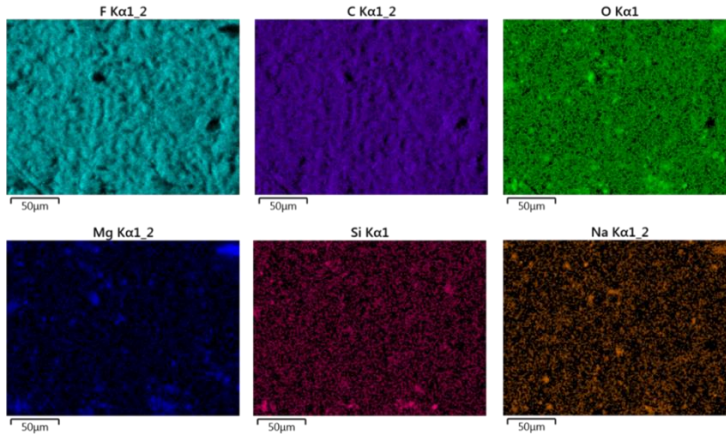

Fig. 8. Map of the distribution of elements over the surface of the CC-3X coating after 4 days of corrosion tests in SSC.

The presence of chlorine seems to be due to salt deposits during the tests, which were not completely removed during the washing of the samples (Figures 6-8). At the same time, this element was not detected on the surface of the composite coatings. Which is a consequence of the high hydrophobicity of the synthesized composite layers and, consequently, the ability to self-clean (Figure 8).

Carbon is also present on the surface of the samples, which is due to some contamination of the samples during testing (Figure 7, 8). Additionally, for a polymer-containing layer, the presence of C is also a consequence of the presence of PTFE in the composition. The same reason explains the presence of F in CC (Figure 8). The presence of Na and Si in the composition of PEO and composite coatings is explained by the transport of these elements from an electrolyte containing Na_4SiO_4 (Figures 7, 8).

After 40 days of testing, the same elements were found in the composition of PEO coatings and CC as after 4 days (Figure 9, 10). The presence of these elements is due to the same reasons as in the case of the samples that were 4 days in the SSC.
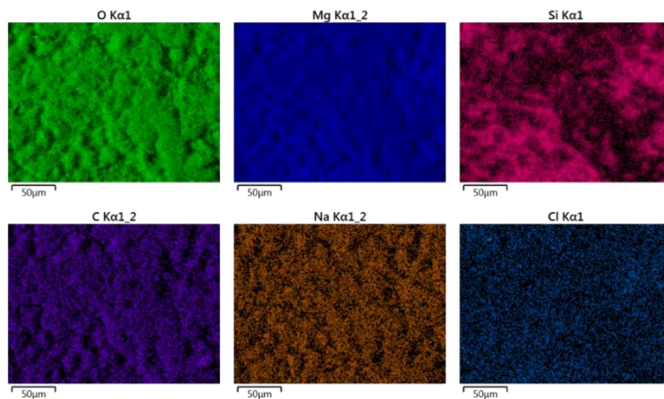
Fig. 9. Map of the distribution of elements over the surface of the PEO coating after 40 days of corrosion tests in SSC.
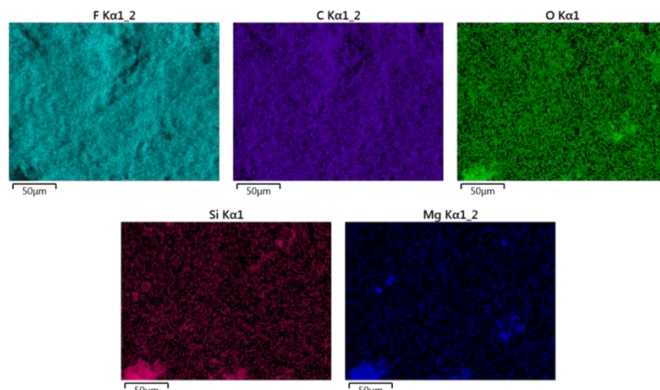

Fig. 10. Map of the distribution of elements over the surface of the CC-3X coating after 40 days of corrosion tests in SSC.

4 Summary

According to the results of the conducted studies, it can be concluded that composite polymer-containing coatings are substantially resistant to long-term exposure to an aggressive environment during accelerated climatic tests.

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