The protective properties of coatings on a magnesium alloy formed by plasma electrolytic oxidation in silicate electrolytes

S.V. Oleynik,[1]* V.S. Rudnev,[2,3] Yu.A. Kuzenkov,[1] T.P. Jarovaja,[2] L.F. Trubetskaja,[1] N.N. Degtiarenko[2] and P.M. Nedozorov[2]

[1]*A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Leninsky pr. 31, Moscow, 119071 Russian Federation*
[2]*Institute of Chemistry, Far-Eastern Branch of the Russian Academy of Sciences, pr. 100-letiya Vladivostoka 159, Vladivostok, 690022 Russian Federation*
[3]*Far Eastern Federal University, Suhanova str. 8, Vladivostok, 690022 Russian Federation*
E-mail: oleynik@ipc.rssi.ru

Abstract

The protective properties and features of formation of plasma electrolytic coatings (PEO) on MA8 magnesium alloy in various silicate electrolytes were studied. It is shown that the addition of sodium fluoride to the silicate electrolyte reduces the number of pores in PEO coatings by increasing their size. PEO coatings formed in the electrolytes in the presence of fluorides possess greater protective properties both in the initial state and upon subsequent filling with corrosion inhibitors. A correlation between the stages of galvanostatic PEO machining and the corrosion resistance of the coatings was detected. The best coating characteristics are obtained at the stage of spark discharge and at the beginning of action of microarc discharges.

1. Introduction

Magnesium alloys are widely used in industry due to their unique properties [1]. However, the low corrosion resistance limits the use of magnesium alloys in aggressive environments [2]. Plasma electrolytic oxidation is one of the methods to obtain corrosion resistant coatings on magnesium alloys that currently receives much attention in literature [3–5].

A literature review shows that alkaline solutions based on silicates, together with phosphate or aluminate solutions are the most common electrolytes for PEO of magnesium and its alloys [3, 6]. Despite the large number of works in this field [7–12], the issue of the influence of electrolyte composition and modes of PEO treatment on the protective properties of coatings on magnesium alloys and justification of optimal conditions of their formation are still topical.

The aim of this work was to study the influence of PEO on the composition, structure and anticorrosive properties of coatings formed on magnesium alloy MA8 in an alkaline silicate electrolyte with and without additives in the presence of sodium fluoride.

2. Materials and methods

2.1. Sample preparation, composition of electrolytes, coating formation

Coatings were obtained on flat samples (50×50 mm) of magnesium alloy MA8 (Table 1). Before oxidation, the samples were treated mechanically to remove burrs on the ends, the surface was sanded to remove the protective factory grease, washed, dried at room temperature and degreased with ethanol just before the oxidation.

Table 1. Composition of MA8 alloy.

Fe	Si	Mn	Ni	Ce	Al	Cu	Be	Zn	Mg
0.05	0.1	1.3–2.2	0.007	0.15–0.35	0.1	0.05	0.002	0.3	Balance

Coatings were formed in the following electrolytes:

(I) $Na_2SiO_3 \cdot 5H_2O$ (10.6 g/l) + NaOH (2 g/l)

(II) $Na_2SiO_3 \cdot 5H_2O$ (10.6 g/l) + NaOH (2 g/l) + NaF (2 g/l).

The PEO treatment of samples was carried out in galvanostatic mode at effective current density of 0.1 A/cm^2 and treatment time from 3 to 30 minutes. A stainless steel bath served as the cathode. After oxidation, the samples with coatings were washed with running water, rinsed with distilled water and dried in air.

The coatings were formed using a computer-controlled multi-functional current source created on the basis of a commercial reverse thyristor unit "TER-4/460H-2-2UHL4" (Russia).

2.2. PEO coating characterization, corrosion and electrochemical tests methods

The thickness of the coatings formed was evaluated using a "VT-201" thickness gauge (Russia). Radiographs of the samples with coatings were shot on a "D8 ADVANCE" X-ray diffractometer (Germany) in CuKα radiation. The X-rays patterns were analyzed using the "EVA" search program with the "PDF-2" data bank. The elemental composition of the coatings was determined by a JXA-8100 X-ray analyzer (JEOL, Japan) with an "Oxford Instrument INCA-sight" energy dispersive unit (UK).

The coatings were filled by immersion of samples for 1 h into a solution containing corrosion inhibitors (95–100°C). Anodic polarization curves of alloys with PEO coatings (working area 0.5 cm^2) were recorded in a standard thermostatically controlled electrochemical cell at $t = 20 \pm 2$°C in a borate buffer solution (pH 7.36) containing 0.01 M NaCl. Pyrographite was used as the auxiliary electrode, and the potential of the working

electrode was measured relative to a saturated Ag/AgCl electrode with subsequent recalculation to the normal hydrogen electrode scale. Polarization of the electrode (1 mV/s) was usually started from the free corrosion potential (E_c) after its exposure for 20–30 min in the solution being studied.

The corrosion resistance of the coatings was evaluated at the time of pitting formation that was initiated by a 1.5 V potential difference, upon contact of the coating with 3% NaCl aqueous solution [13]. A horizontally mounted sample is brought into contact with a drop of 3% NaCl solution, squeezed out onto the coating surface from a metal syringe needle. The metallic needle was connected to the minus clamp of the power source; the plus clamp was connected through a milliammeter to the cleaned bare metal of the sample. The time interval (τ_p) was measured by a stopwatch from the moment of contact of the drop with the surface until a sharp increase in the corrosion current through the coating.

3. Experimental results and discussion

In the formation of PEO coatings in the silicate electrolyte and in the electrolyte with fluoride addition, their thickness raises monotonically with increasing treatment time (Figure 1). However, the thickness of the coatings obtained in the electrolyte with addition of sodium fluoride is on average 1.5 times higher than that of the coatings obtained in the base alkaline silicate electrolyte. As can be seen from Figure 2, the resistance of the coatings obtained in both electrolytes to local corrosion in chloride solution little depends on the thickness of the coatings, although a small peak is observed for coatings obtained in 8–10 minutes of oxidation. The addition of sodium fluoride to the electrolyte has a greater effect on the barrier properties. In such coatings, the time to breakdown is by an order of magnitude higher than for coatings obtained in silicate solution.
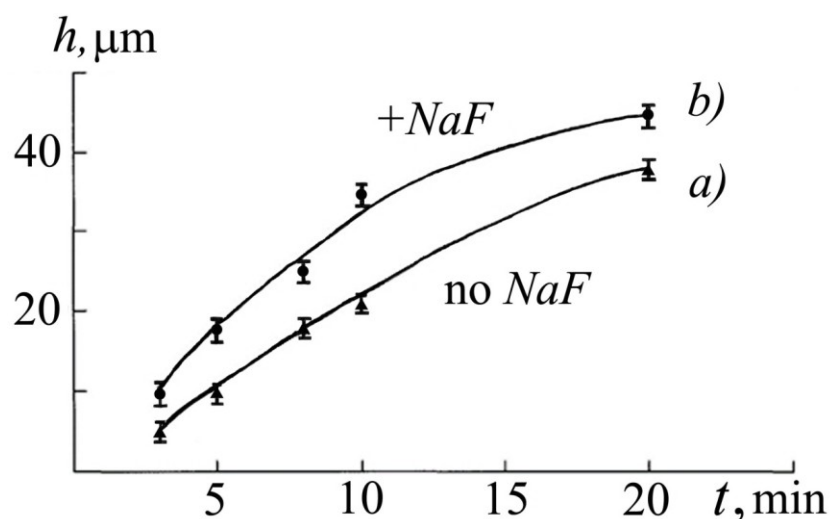

Figure 1. Thickness of PEO coatings depending on the treatment time of MA8 magnesium alloy in a silicate electrolyte and in a silicate electrolyte with the addition of NaF.
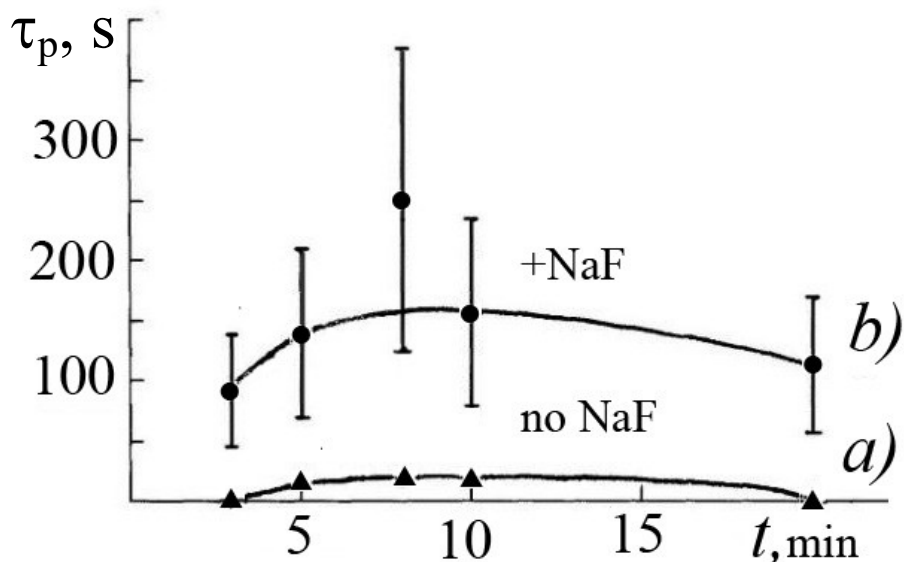
Figure 2. Time to pitting of PEO coatings depending on the treatment time of MA8 magnesium alloy in a silicate electrolyte and in a silicate electrolyte with the addition of NaF.
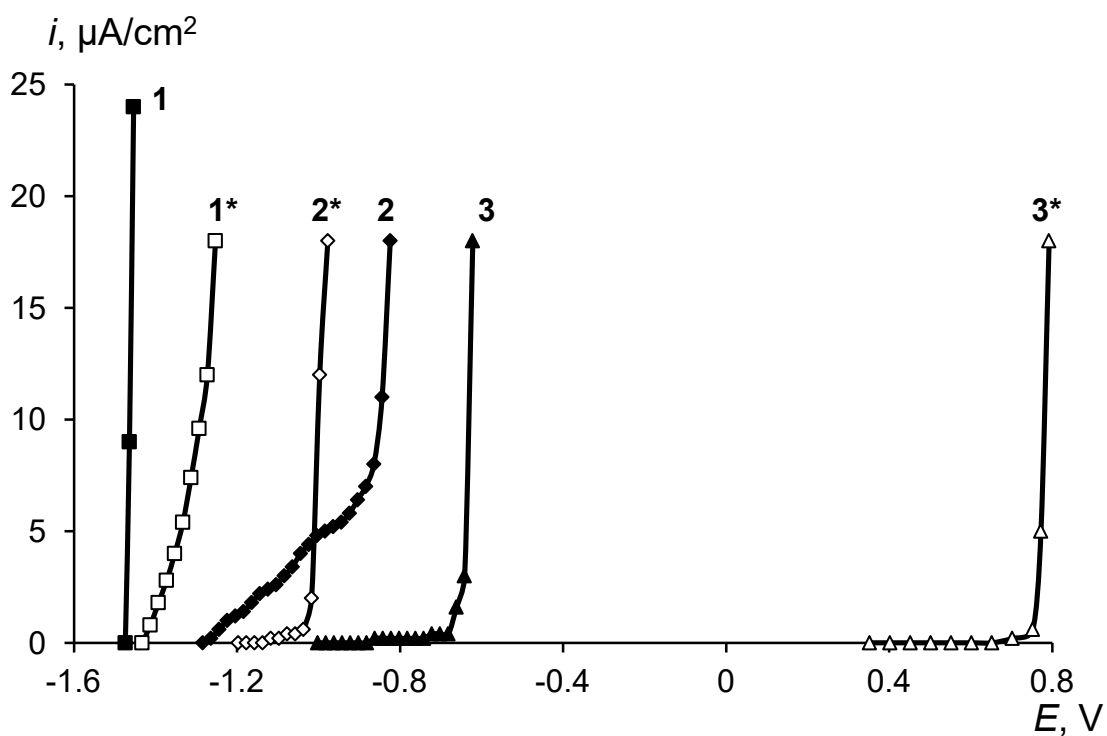

Figure 3. Anodic polarization curves recorded in 0.01 M NaCl solution (pH 7.4) on MA8 magnesium alloy covered with PEO coatings (8 min) obtained in a silicate electrolyte and in a silicate electrolyte with addition of NaF (*): 1 – without a PEO coating, 2 – additional treatment in NaOH solution, 3 – additional treatment in NaOH solution and in a carboxylate inhibitor solution.

Anodic polarization curves of the samples with the investigated coatings in chloride environments (Figure 3) confirm the data obtained by the previous method. Whereas in the case of coatings obtained in silicate electrolyte, breakdown of PEO films starts from the corrosion potential, breakdown of the coatings obtained in the electrolyte with fluoride addition is observed after a short period of current growth. An increase in resistance of PEO coatings formed in silicate and aluminate electrolytes in the presence of fluoride to local corrosion in chloride environments was also observed on magnesium alloys AZ31 and AZ91 [12, 14]. Furthermore, coatings obtained in electrolytes with addition of fluoride are more resistant to local anodic activation in chloride environments after additional treatment in a sodium hydroxide solution in comparison to those obtained in the absence of fluoride. The most significant difference in the anodic behavior of PEO coatings obtained in the absence and in the presence of fluoride is observed after filling in a corrosion inhibitor solution. In the latter case, the corrosion potential and breakdown potential are ennobled by 1 V, which may indicate a smaller number of through pores in the coating obtained in the fluoride-containing electrolyte.

This is confirmed by analysis of the surface morphology of the coatings (Figure 4). For coatings obtained after 8 min of oxidation, it is clear that the number of pores on the surface of the coating obtained in the electrolyte with addition of fluoride is smaller, but they are larger, which is consistent with other data [12]. Apparently, the decrease in the total number of pores, rather than the increase in their size, is the determining factor in the protective properties of the coatings. A smaller number of through pores are more likely to be passivated by subsequent treatment in a sodium hydroxide solution, while large non-through pores contribute to the adsorption of corrosion inhibitors.
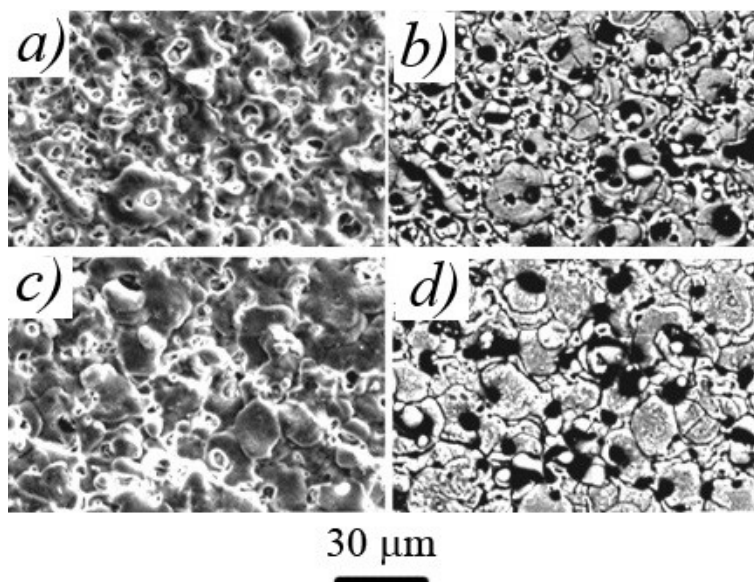

30 μm

Figure 4. SEM images of the surface of the PEO coatings (8 min) in the amplitude (a, c) and phase (b, d) representations for PEO coatings obtained in a silicate electrolyte (a, b) and in a silicate electrolyte with addition of NaF (c, d).

Comparison of X-ray diffraction patterns of coatings (Figure 5) obtained in both electrolytes shows that the main difference in the phase composition is the presence of a phase of magnesium fluoride (MgF_2) in the coatings formed in the electrolyte Na_2SiO_3 + NaOH + NaF. Also, these coatings have less intense peaks of forsterite, which is associated with a lower average content of silicon. Using a high resolution electronic scanning analyzer, the compositions of the coating, the pores and rollers surrounding the pores were analyzed (Figure 6). The content of oxygen, magnesium and silicon is approximately the same in the pores, around then, and on average for the surface. In pores and around the pores, the content of fluorine and sodium is increased. The specific surface porosity of the coatings varies widely (Figure 7). In coatings with addition of sodium fluoride, the estimated surface porosity is much lower and the difference increases with the duration of PEO treatment.
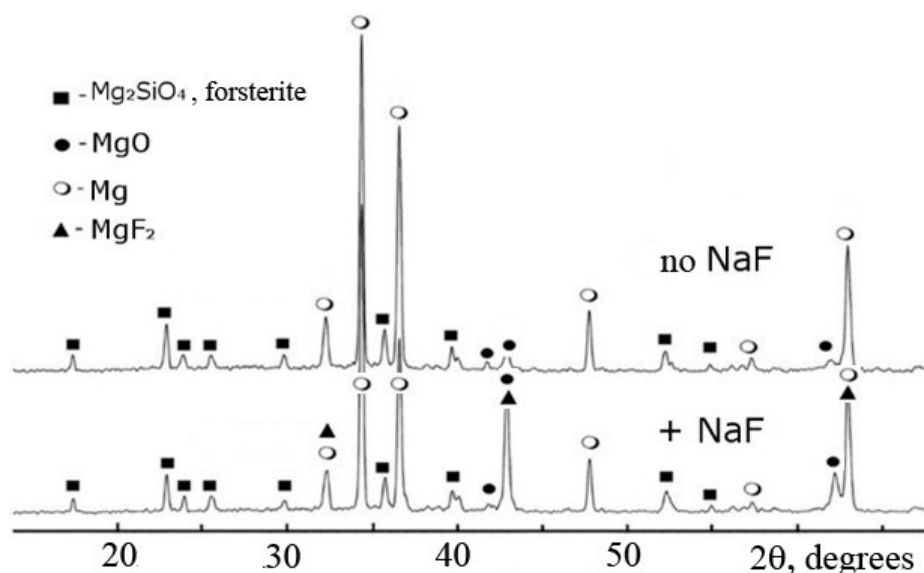

Figure 5. X-Ray diffraction patterns of PEO coatings (8 min) obtained in a silicate electrolyte and in a silicate electrolyte with addition of NaF.
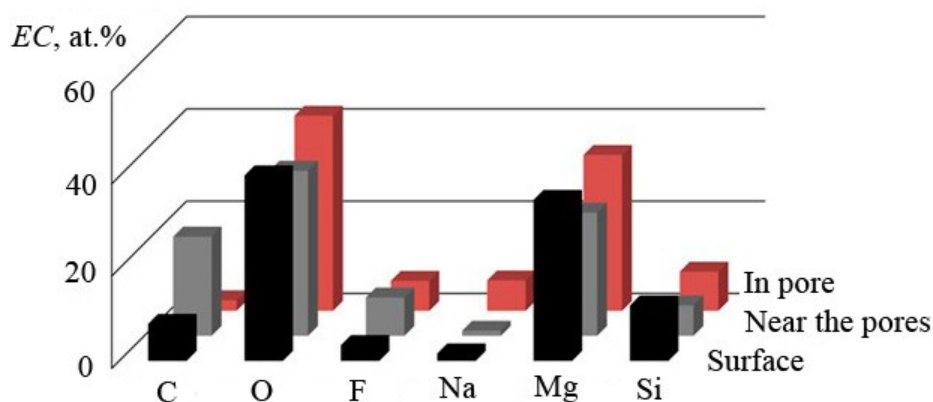

Figure 6. Elemental composition of surface, pores and rollers of PEO-coatings (8 min) obtained in a silicate electrolyte with addition of NaF.
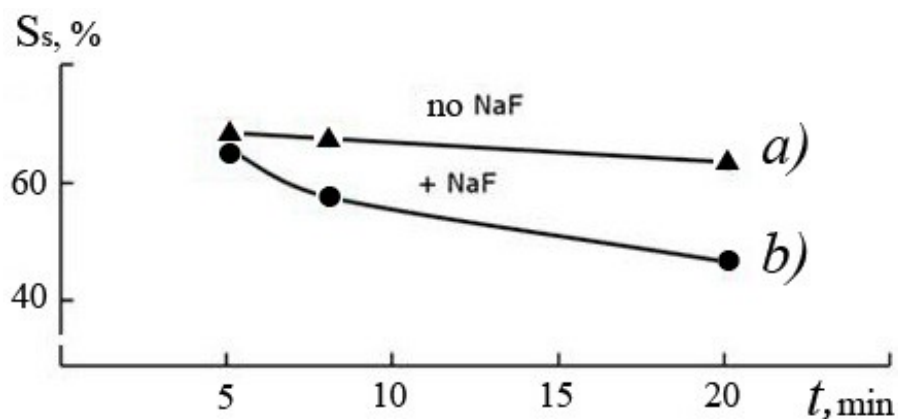
Figure 7. Calculated specific surface porosity of PEO-coatings depending on the treatment time of MA8 magnesium alloy in a silicate electrolyte and in a silicate electrolyte with addition of NaF.

As follows from the data in Figure 8, if the time τ_p of pitting formation is normalized per unit of thickness h in each case, we see that until the formation time of ~8 minutes the value of τ_p/h remains constant and then decreases sharply (Figure 8b). It is known that in galvanostatic formation of coatings, growth mechanism changes with increasing treatment duration. At short times, traditional anodizing occurs (I – pre-sparc stage), followed by the spark stage (stage II) and that of stronger micro-arc discharges (stage III). Figure 8a shows these typical regions, the duration of which was determined from analysis of the forming curve behavior. From these data it is seen that in the spark stage and in the region of transition to the micro-arc stage, coatings are formed, which are characterized by a constant time of pitting formation per unit of coating thickness. That is, at this stage, the coatings grow with roughly the same internal structure as the rate of pitting formation is permanent.

On transition to the micro-arc stage, the anticorrosive properties of coatings deteriorate sharply. A correlation is observed between the spark and micro-arc stages of coating growth and the anticorrosive properties of the coatings. The coatings formed in the spark stage have the same time of the formation of pitting attributed to the thickness of the coatings. Transfer to the micro-arc treatment stage leads to degradation of the protective properties of coatings. An increase in the treatment duration is accompanied by a monotonic increase in the thickness of coatings and a decrease in the specific surface porosity. However, there is no direct relationship between these parameters and the anticorrosion properties of the coatings. Large pores are formed in the micro-arc region under the influence of powerful micro-arc discharges. Apparently, they can have not only a big mouth but also a considerable depth, which ultimately leads to a sharp decrease in the resistance of coatings to the formation of pitting.
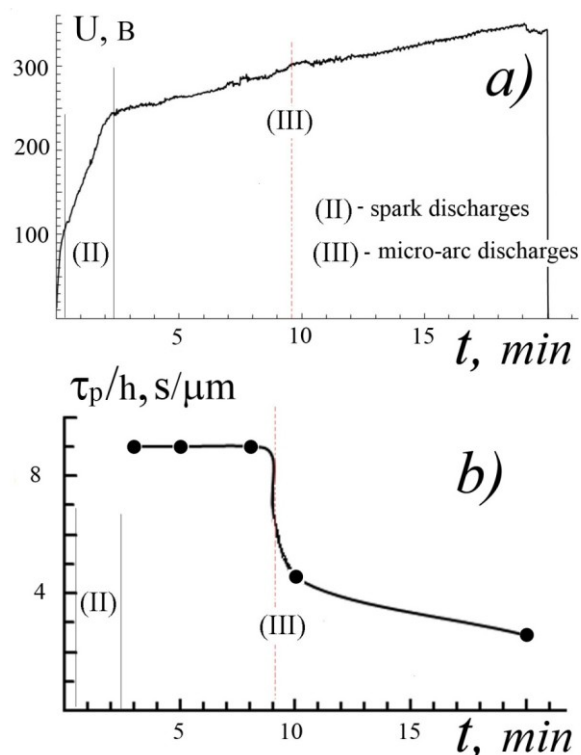
Figure 8. Calculated τ_p/h value depending on the treatment time of MA8 magnesium alloy in a silicate electrolyte with addition of NaF.

Conclusions

1. Addition of fluoride to a sodium silicate electrolyte enhances the protective properties of both the original PEO coatings on MA8 magnesium alloy and of these coatings subsequently filled with corrosion inhibitors.
2. Addition of sodium fluoride to a silicate electrolyte reduces the number of pores in PEO coatings while increasing their size.
3. A correlation was detected between the stages of galvanostatic PEO treatment and the corrosion resistance of coatings. The best coating characteristics are obtained at the stage of spark discharge and in the beginning of action of micro-arc discharges.

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