THE INFLUENCE OF FLUORIDE ADDITIVES ON THE PROPERTIES OF OXIDE LAYER PRODUCED BY PLASMA ELECTROLYTIC OXIDATION

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Abstract
The addition of fluoride ions to the alkaline electrolyte for the Plasma Electrolytic Oxidation (PEO) processing of aluminum and magnesium alloys produces significant changes in the structure and properties of the coating [1-3], however the mechanism of these changes is not clear. A study of the influence of the fluoride concentration on the composition, structure and morphology of thin (to 20 µm) PEO layers was performed. The oxide layer on aluminum is significantly thinner and less continuous than that on magnesium. Fluorine is detected as an amorphous phase in the vicinity of the base metal.

Introduction
Plasma Electrolytic Oxidation (PEO) allows the production of oxide ceramic layer on valve metals such as aluminum, magnesium, titanium and others. The oxide layer normally has high adhesion to the base metal, is much harder than the base metal and has certain decorative value. In spite of relatively high porosity, PEO layers effectively protect the base metal against corrosion due to the fact that the pores are always capped with a barrier oxide layer and are therefore non-penetrable by corrosion media. The improvement of corrosion stability of PEO treated metals as compared to bare metals has been reported for aluminum [4, 5] and magnesium alloys [6, 7].

PEO layers can be produced in several types of electrolytes [8], whose components can dissolve the base metal (acidic and alkaline
electrolytes), passivate it (phosphate and polymer electrolytes) or interact with it in more complex and less understood ways (fluoride electrolytes).

The role of fluoride additives to electrolytes is intriguing. It has been established quite reliably that the addition of fluorides to alkaline electrolytes significantly improves technological parameters of PEO layers on magnesium alloys. As it was reported by Tao Xu et al., the addition of KF into Na$_2$SiO$_3$–KOH electrolytes results in the decrease of pore diameter and surface roughness and increase of the compactness, surface hardness and wear resistance of the microarc oxidation layer on magnesium alloys [9]. In fact, potassium fluoride has become a standard component of various electrolytes for the production of PEO coating on magnesium and its alloys.

The situation with the effect of fluoride on the production of PEO coatings on aluminum alloys is quite different. Only few studies of PEO of aluminum alloys have involved any fluorine containing additives. Thus, two earlier works [3, 10] proved the principal possibility of producing PEO coatings on aluminum alloys and reported that amorphous oxide layers were formed. Two more recent papers by Zhaohua Jiang et al. investigated the addition to alkaline electrolytes of several silicates and aluminates including Na$_2$SiF$_6$ [1] and the effect of NaF on the production of PEO coating on aluminum alloys [2]. It was reported there that both Na$_2$SiF$_6$ and NaF additives made the PEO coating denser and harder.

It was observed in 1960s and confirmed more recently [12 – 14] that if potassium fluoride is added to an alkaline electrolyte in the process of anodizing of magnesium alloys, sparking starts and the process proceeds as plasma oxidation rather than anodizing. The explanation to that phenomenon was that the addition of fluorides favors the formation of a dielectric layer of magnesium fluoride, in which then breakdowns occur and cause plasma discharges [12, 13]. In fact, this means that KF serves as an initiator of PEO process for magnesium alloys. For aluminum alloys, aluminum fluoride should be formed on the surface of the metal. Aluminum fluoride is a better dielectric (relative permittivity 2.2) than magnesium fluoride (relative permittivity 4-5 dependently on the crystallographic direction), therefore more energy is supposed to be needed for its breakdown.
Normally, the oxide layer in a PEO process grows at the rate of 0.5-1 µm/min and it takes 30-60 minutes to obtain technologically acceptable coating of 40-80 µm. However, the structure changes are less unambiguous for layers of that large thickness because of their complex structure and compression deformations in the course of the process. The difference between the fluoride-supported PEO of magnesium and aluminum alloys, if any, should be better pronounced at the beginning of the oxidation process, when the structure is simpler and internal deformations are smaller. For that reason, at the first stage we decided to limit ourselves with the first 15 minutes of PEO, when the produced layer is too thin for the evaluation of technological parameters such as hardness or corrosion behavior, but its structure changes are more evident. Here we present more detailed as compared to our paper published elsewhere [15] results of the study of the first 15 minutes of PEO process on magnesium and aluminum alloys.

**Experimental**

Aluminum A5052 alloy (Al as the base and approximately 2.5% of Mg) and magnesium AZ9110D alloy (Mg as the base and 8.3-9.7% Al, 0.15% Mn min., 0.35-1.0% Zn, 0.10% Si max., 0.005% Fe max., 0.030% Cu max., 0.002% Ni max., 0.02% max. others) were taken for the comparison. Rectangular plates (3 x 15 x 30 mm) of each alloy were prepared. Samples were polished with #1200grit SiC abrasive paper and rinsed in tap water before being coated by the PEO process. The oxidation was performed in AC mode by 50 Hz saw edged voltage (± 400 V) at the end current density 6.6 ± 0.2 A / dm² for 15 minutes on a home-made 40 kVA PEO station with a water-cooled bath made of stainless steel, which served as the counter electrode. Sodium silicate Na₂SiO₃ having the silicate index \( n = 1 \) (pentahydrate, Spectrum, practical grade), KOH (Finkelman Chemicals, technical grade) and KF (Merck, 99%) were used for the electrolytes. Each electrolyte contained 0.08 mol /L KOH, 0.08 mol / L Na₂SiO₃ and 0 – 0.2 mol / L KF in tap water.

Conductivities and pH of the electrolytes were measured by a YK-2005WA pH/CD meter, the thickness of coatings was measured by a micrometer, coating thickness gauge CM-8825 and by SEM. The surface morphology, structure and composition were measured on SEM JEOL JSM6510LV equipped with an NSS7 EDS analyzer (Correction
Method Proza – Phi-Pho-Z was used for the quantitative analysis. Cross-section samples prepared according to standard metallographic protocols were used for SEM, EDS and XRD. X-ray Diffractometer (XRD) Panalytical X’Pert Pro with Cu Kα radiation (λ=0.154 nm) was used with the full pattern identification made by X’Pert HighScore Plus software package, version 2.2e (2.2.5) by PANalytical B.V. Materials identification and analysis made by the PDF-2 Release 2009 (Powder Diffraction File). Phase analysis identification made by XRD, 40kV, 40mA. The XRD patterns were recorded in the GIXD geometry at a=1° and 5° in the range of 20-80° (step size 0.05° and time per step 2s).

Results

The surface morphology for both the magnesium and the aluminum alloys is normal for PEO coatings and consists of “volcanic” pores chaotically distributed on a fused surface (Fig. 1). In the basic electrolyte (0.08 mol/L KOH + 0.08 mol/L Na2SiO3) without fluoride addition the 15 minute PEO process produces approximately 20 μm thick non-continuous oxide layer on the magnesium alloy and only about 5 μm thick non-continuous layer on the aluminum alloy (Fig. 2). It should be noted that for longer processing times (30-90 min) much thicker coatings have been obtained, but the initial stages demonstrate clear difference between the two metal alloys. Both on the magnesium and on the aluminum alloys the coating is porous, but the porous are blind. Element compositions at points 1, 2 and 3 along lines drawn from the pure base metal to the outer border of the coatings (Fig. 2) are given in Table 1.

As seen from Fig. 2 and Table 1, the oxidized layer on the magnesium alloy is not only thicker, but also more uniform than that on the aluminum alloy, for which large voids containing relatively high amounts of oxygen are formed between the base metal and the oxide layer. It deserves to be noted that the percentage of oxygen is lower than what should be expected according to the stoichiometry of magnesium and aluminum oxides (Mg : O = 1:1 and Al : O = 2 : 3). Therefore, the oxide layer never consists of the oxides, but is combined by the oxides and the excess metals.
Fig. 1. Typical morphology of PEO surface. SEM image (x2000) on aluminum alloys obtained after 15 minute oxidation.

Fig. 2. SEM images (x3000) with EDS linear scans of cross-sectioned PEO coatings on (a) the magnesium and (b) aluminum alloys obtained after 15 minute oxidation. Black zone in the topmost parts is polymer tar fixing the specimen. The base metals are in the bottom part of each image. Element composition at points 1, 2, 3 of each image is specified in Table 1.
Table 1
Element compositions at representative points 1, 2 and 3 as shown in Fig. 2

<table>
<thead>
<tr>
<th></th>
<th>Mg alloy</th>
<th>Al alloy</th>
</tr>
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<tbody>
<tr>
<td>Point 1</td>
<td>Mg 82 at%, Al 8 at%, O 9 at%, Si 1 at%</td>
<td>Point 1</td>
</tr>
<tr>
<td>Point 2</td>
<td>Mg 67 at%, Al 13 at%, O 17 at%, Si 3 at%</td>
<td>Point 2</td>
</tr>
<tr>
<td>Point 3</td>
<td>Mg 60 at%, Al 9 at%, O 27 at%, Si 4 at%</td>
<td>Point 3</td>
</tr>
</tbody>
</table>

Fig. 3. BSE SEM images (x3000) with EDS linear scans of cross-sectioned PEO coating on the magnesium alloy obtained after 15 minute oxidation in the electrolyte containing 0.01 mol/L KF.

As KF is added to the electrolytes, the situation with the oxidation of magnesium alloy becomes different. While the total thickness of the coating remains relatively the same (~ 20 μm after 15 minutes), its structure and composition are clearly distinguished from what was observed without the fluoride. Already for the lowest studied KF concentration (0.01 mol/L) the coating is continuous and consists of two very different sublayers (Fig. 3). The inner sublayer is only 2-3 μm thick and contains about 70 at% of Mg, 25 at% of O and 5 at% of Al. The outer sublayer is 15-18 μm thick, porous and contains large voids.
filled by light elements (dark sites in Fig. 3). The typical composition of the outer layer is 50-60 at% O, 35-40 at% Mg, 10 at% Si and 2-4 at% Al. As the content of KF in the electrolyte increases, the structure of the layers does not change, but significant amounts of fluorine are detected in the coating.

Fig. 4. Element composition profiles (EDS linear scan) across the PEO coating on the magnesium alloy obtained after 15 minute oxidation in the electrolyte containing 0.2 mol/L KF.

Interestingly, the maximal amount of fluoride was detected in the most inward part of the outer sub-layer (Fig. 4). According to small angles (1°-5°) XRD measurements, the surface consists of Periclase MgO (77%) and metal Mg (23%). Deeper layers of the coating demonstrate the increase of Mg at the expense of MgO. No fluorine-containing phases could be identified with confidence (Fig. 5).

The addition of KF to the electrolytes has another effect. While for lower concentrations of KF (<0.05 mol/L) only a very thin porous coating layer is formed, higher KF contents result in the formation of 5-10 µm oxide layer. As the thickness of the coating increases, two sublayers are revealed. As for the magnesium alloy, the thin inner sublayer is denser and the thicker outer one is more porous (Fig. 6). As evidenced by EDS, the outer sublayer contains 60 at% of O and 40 at% of Al. As much as 9% fluorine is found in the inward part of the outer sublayer. XRD measurements show that the surface (1° incident beam)
consists of two crystal phases, whose composition is Al2MgO4 (56%) and MgO (44%). Deeper layers (5° incident beam) are formed by metal Al (78%) and MgO (22%). A sample of an XRD pattern is given in Fig. 7.

Fig. 5. Small angle (1°) XRD pattern for the surface of the PEO coating on the magnesium alloy obtained after 15 minute oxidation in the electrolyte containing 0.02 mol/ L KF

Fig. 6. BSE SEM images (x3000) with EDS linear scans of cross-sectioned PEO coating on the aluminum alloy obtained after 15 minute oxidation in the electrolyte containing 0.2 mol/ L KF
Discussion

The most obvious observation, which can be made from the comparison of the PEO of the magnesium and of the aluminum alloys, is that magnesium is oxidized much more easily than aluminum. While for all the studied magnesium systems 20 \( \mu \)m coating was produced after 15 minutes of the PEO, only 5-10 \( \mu \)m coating on the aluminum alloy could be obtained for the same process time. An interesting issue is the ratio “Mg:Al” at different depth of the coatings (Table 2).

Table 2

<table>
<thead>
<tr>
<th>( \text{C}_{\text{KF}}, \text{ mol} / \text{L} )</th>
<th>( \text{Mg alloy} )</th>
<th>( \text{Al alloy} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Base metal</td>
<td>Inner sublayer</td>
</tr>
<tr>
<td>0</td>
<td>10.3</td>
<td>6.7*</td>
</tr>
<tr>
<td>0.01</td>
<td>10.3</td>
<td>14</td>
</tr>
<tr>
<td>0.1</td>
<td>10.3</td>
<td>15</td>
</tr>
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</table>

*No sublayers were observed for this PEO layer

As seen from Table 2, magnesium content at the inner sublayer is always higher than in the base metal, except for the oxidation of the magnesium alloy in the electrolyte containing no fluoride, when no sublayers can be seen. The trend is less straightforward for the outer sublayer, which can be explained by the fact that the latter is thicker,
more porous and much less uniform. XRD phase analysis confirms that the key role at the initial stage of the oxidation is played by magnesium oxide and only on the surface aluminum starts to be oxidized to form Al₂MgO₄. These can be explained by two facts: (1) that the amphoteric aluminum is readily dissolved by the alkaline electrolyte while magnesium is not; (2) that according to Ellingham diagrams [12] the oxidation of magnesium is thermodynamically more favorable than that for aluminum in the entire range of temperatures below 1500K.

Many authors report that they could not identify a fluoride containing phase in PEO coatings on aluminum or magnesium alloys obtained in alkaline fluoride-containing electrolytes (see, for instance [1-3, 14]). This is consistent with our XRD observation; however we could clearly see the presence of fluoride on EDS cross-sectional profiles of the coatings (Fig. 4). This means that considerable amounts of amorphous fluorides are found in the coatings very close to the base metal. Summarizing, the action of fluoride additives can be assumed as follows: (1) fluoride anions are first chemisorbed to the metal surface and create on it barrier layer; (2) as the dielectric breakdown occurs, oxide layer is formed due to the exchange of fluorine by oxygen atoms from the electrolyte; (3) fluoride remains in the vicinity of the metal and takes part in the formation of an amorphous phase. This process is much more favorable for the magnesium alloy due to the easier breakdown of magnesium fluoride as compared to aluminum fluoride.

Conclusions
1. The formation of PEO coating on magnesium and aluminum alloys in the presence of fluoride starts with the fluorination of the metal surface and formation of a dielectric metal fluoride layer. Electric breakdowns destruct this layer and form oxide layers containing also amorphous fluorides.
2. The fluoride-supported PEO process proceeds more easily for the magnesium than for the aluminum alloys.
3. The external surface of the coating is enriched by magnesium as compared to the base metal.

Acknowledgements
References