

# ELECTROLYTES FOR PLASMA ELECTROLYTIC OXIDATION OF MAGNESIUM

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## Abstract

The classification of electrolytes for PEO treatment of magnesium is given. The probable mechanism for the formation of refractory compounds is considered. Several sealing methods are described. Some experimental results obtained on magnesium coted in silicate- and aluminate containing electrolytes are presented.

## 1. Introduction

In the literature devoted to plasma electrolytic oxidation (PEO) of magnesium, dozens of electrolyte compositions and electrical regimes are given [1]. At the same time, many publications contain sketchy information concerning electrolyte recipes connected with the characteristics of coatings. The absence of significant technological details in the description of the experiments did not allow us to analyse all the variety of works that appeared in recent years. This paper covers only those publications that contain a fairly complete description of the regimes, electrolytes, and chemical composition of the coatings obtained.

## 2. Typical electrolytes and coatings composition

At present, a number of universal solutions have been developed [2], suitable for plasma oxidation of both magnesium and aluminium (Table 1).

Table 1. Electrolytes and regimes applicable for both aluminium and magnesium

| Components of electrolytes and electrical regimes | Content, g.l <sup>-1</sup> |           |
|---|----------------------------|-----------|
|   | Aluminium                  | Magnesium |
| Na <sub>2</sub> SiO <sub>3</sub>                  | 3-10                       | 0         |
| KOH   | 1-3                        | 0-2       |
| Na <sub>2</sub> P <sub>4</sub> O <sub>7</sub>     | 0-5                        | 0-5       |
| NaF   | 0                          | 2-7       |
| NaAlO <sub>2</sub>                                | 0                          | 4-10      |
| Time of electrolysis, min                         | <120                       | 20        |
| Current density, A.m <sup>-2</sup>                | <2000                      | <1000     |
| Temperature, °C                                   | 10-40                      |           |
| Thickness, µm                                     | <70                        | <30       |

According to the main component forming polymer anions, all known compositions can be classified into four groups: silicate, aluminate, phosphate and borate. Within each group, the composition of electrolytes can vary, for example, silicate-phosphate,

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aluminate-fluoride, etc. To adjust the pH, ammonia, alkalis and acids are usually added. To improve the uniformity of the coatings, organic and surface-active substances can be used.

Table 2 represents main conditions of electrolysis and composition of coatings obtained on different Mg alloys. These data were taken from publications that, in the opinion of the authors, contain the most complete information concerning the relationship between the composition of the electrolytes and coatings.

Table 2. Electrolytes and regimes for PEO of magnesium alloys

| №                     | Magnesium alloy   | Regime  | Electrolyte, g.L <sup>-1</sup>   | Coating composition  | References                                       |
|-----------------------|---|---|--|--|--|
| Silicate electrolytes |   |   |  |  |  |
| 1                     | AM60B   | 600 A.m <sup>-2</sup><br>Pulse regime   | KOH 1<br>Na <sub>2</sub> SiO <sub>3</sub> ·9H <sub>2</sub> O 10<br>KF 8  | MgO, KMgF <sub>3</sub> ,<br>Mg <sub>2</sub> SiO <sub>4</sub> ,<br>MgAl <sub>2</sub> O <sub>4</sub> ,<br>MgF <sub>2</sub> | [3]  |
| 2                     | AZ31D   | 400-900 AM <sup>-2</sup><br>Pulse regime,<br>f= 700 Hz  | KOH 3<br>Na <sub>2</sub> SiO <sub>3</sub> ·9H <sub>2</sub> O 6-15<br>KF·2H <sub>2</sub> O 3<br>Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O 4 | MgO, Mg <sub>2</sub> SiO <sub>4</sub>  | [4]  |
| 3                     | AZ31B   | 300 AM <sup>-2</sup> ,<br>Direct current  | KOH 2<br>Na <sub>2</sub> SiO <sub>3</sub> ·9H <sub>2</sub> O 6<br>KF 2<br>Glycerol 12.6  | Mg <sub>2</sub> SiO <sub>4</sub> , MgO   | [5]  |
| 4                     | Mg<br>(99.95%)  | 400 AM <sup>-2</sup><br>Direct<br>current,<br>t=1-22 min  | NaOH 30<br>Na <sub>2</sub> SiO <sub>3</sub> ·9H <sub>2</sub> O 160<br>Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O 160                        | Mg <sub>2</sub> B <sub>2</sub> O <sub>5</sub> ,<br>Mg <sub>2</sub> SiO <sub>4</sub> ,<br>SiO <sub>2</sub>                | [6]  |
| 5                     | AZ91HP  | 400 AM <sup>-2</sup><br>f=2000 Hz,<br>duty cycle<br>20%,<br>t=3 min   | NaOH 10<br>Na <sub>2</sub> SiO <sub>3</sub> 18<br>NaOH 10<br>C <sub>6</sub> H <sub>18</sub> O <sub>24</sub> P <sub>6</sub> (phytic<br>acid) 12                     | Amorphous<br>structure, MgO  | [7]  |
| 6                     | AZ31  | Pulsed<br>current, t=70<br>min  | Na <sub>2</sub> SiO <sub>3</sub> 10<br>Na <sub>2</sub> WO <sub>4</sub> , KOH,<br>Na <sub>2</sub> EDTA  | MgO, MgAl <sub>2</sub> O <sub>4</sub> ,<br>MgSiO <sub>3</sub>  | [Error!<br>Book<br>mark<br>not<br>defin<br>ed.8] |
| 7                     | Mg<br>(99.9%),<br>AZ31,<br>AZ61,<br>AZ91D,<br>ZC71,<br>ZE41,<br>WE43-T6 | 650 A.m <sup>-2</sup><br>rectangular<br>pulses,<br>asymmetric<br>current,<br>i <sub>c</sub> /i <sub>a</sub> =1.2;<br>f= 50 Hz<br>t=15 min | Na <sub>2</sub> SiO <sub>3</sub> (ρ=1.5<br>g.cm <sup>-3</sup> ) 37.5<br>Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub> ·10H <sub>2</sub> O 15                       | MgO, Mg <sub>2</sub> SiO <sub>4</sub>  | [Error!<br>Book<br>mark<br>not<br>defin<br>ed.9] |
| 8                     | AZ91D   | 3-5 A<br>f= 500Hz   | Na <sub>2</sub> SiO <sub>3</sub> 15<br>NaOH.....3  | MgAl <sub>2</sub> O <sub>4</sub>   | [10]   |

|                        |                      |  |   |  |      |
|------------------------|----------------------|--|---|--|------|
| 9                      | AZ91D                | AC mode 50 Hz<br>10.0 A.dm <sup>-2</sup><br>t=60 min   | Na <sub>2</sub> SiO <sub>3</sub> 0.05 mol.L <sup>-1</sup><br>KOH 0.04 mol.L <sup>-1</sup><br>KF 0–0.2 mol.L <sup>-1</sup>   | Mg, O  | [11] |
| 10                     | AZ31B                | 1000 A.m <sup>-2</sup>   | Na <sub>2</sub> SiO <sub>3</sub> 6<br>KF 2<br>KOH 2<br>Glycerol 12.61<br>Surfactant (sodium dodecyl sulphate, diphenylamine 4-sulphonate or sodium dodecylphenylsulphonate) 0.25            | Mg <sub>2</sub> SiO <sub>4</sub><br>TiO <sub>2</sub> (rutile and anatase)<br>MgO<br>Mg | [12] |
| 11                     | AZ31                 | Bipolar pulses<br>i <sub>a</sub> =i <sub>c</sub> =350 Am <sup>-2</sup><br>duty cycle 10-40%,<br>f=600 Hz<br>t=30 min | Na <sub>2</sub> SiO <sub>3</sub> 15<br>KF 3.2<br>KOH 20<br>Glycerol 12.61   | Mg<br>MgO<br>Mg <sub>2</sub> SiO <sub>4</sub>  | [13] |
| 12                     | AZ91D                | Bipolar pulses f=700 Hz, 60 V  | Na <sub>2</sub> SiO <sub>3</sub> ·9H <sub>2</sub> O 6-15<br>Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O.... 4<br>KOH..... 3<br>KF <sub>2</sub> H <sub>2</sub> O.....3 | MgO..... 41%<br>Mg <sub>2</sub> SiO <sub>4</sub> ..... 59%                             | [4]  |
| 13                     | AZ91D                | 150-250 A.m <sup>-2</sup>  | KOH 10<br>K <sub>2</sub> SiO <sub>3</sub> 16  | MgO<br>Mg(OH) <sub>2</sub><br>MgSiO <sub>3</sub>                                       | [9]  |
| 14                     | AZ91D                | U= 500 V,<br>f= 600 Hz,<br>duty cycle 8%,<br>t=5 min   | Na <sub>2</sub> SiO <sub>3</sub> 15<br>NaOH 10<br>KF 8<br>Glycerol 6.3<br>Titanium sol to 1   | MgO<br>Mg <sub>2</sub> SiO <sub>4</sub><br>TiO <sub>2</sub>                            | [14] |
| Aluminate electrolytes |                      |  |   |  |      |
| 15                     | Al 2-12,<br>Mg rest  | 40 A.m <sup>-2</sup><br>Direct current   | KOH 168<br>Na <sub>3</sub> PO <sub>4</sub> 4.44<br>KF 34.8<br>NaAlO <sub>2</sub> 32.8-90.2  | MgAl <sub>2</sub> O <sub>4</sub><br>γ-Al <sub>2</sub> O <sub>3</sub>                   | [15] |
| 16                     | AZ91D                | 100 A.m <sup>-2</sup><br>Direct current  | NaAlO <sub>2</sub> 3-15<br>KF 0-15  | Al <sub>2</sub> Mg<br>MgAl <sub>2</sub> O <sub>4</sub>                                 | [16] |
| 17                     | AJ62                 | Monopolar pulses, duty cycle - 80%,<br>f= 2 kHz;<br>t=10-20 min  | NaAlO <sub>2</sub> 10-20  | MgAl <sub>2</sub> O <sub>4</sub>   | [17] |
| 18                     | Magnesium alloy wire | Keronite <sup>®</sup>  | Keronite <sup>®</sup> (Na <sub>2</sub> SiO <sub>3</sub> ,   | MgO<br>MgAl <sub>2</sub> O <sub>4</sub>  | [18] |

|                        |                                 |  |   |  |  |
|------------------------|---------------------------------|--|---|--|--|
|                        | (2% Al, 1% Zn, 0.2% Mn)         | Bipolar pulses, 200-100 A.m <sup>-2</sup><br>$\tau=3.5-7$ min<br>$f=1000$ Hz                   | NaOH, Na <sub>3</sub> PO <sub>4</sub> )   | MgO<br>Al <sub>2</sub> O <sub>3</sub>  |  |
| 19                     | AZ91HP<br>(Mg-9.Al-1, Zn-alloy) | 70 -90 V,<br>200 - 5000<br>A.m <sup>-2</sup><br>$\tau=10$ min                                  | KOH 165<br>Al(OH) <sub>3</sub> 34<br>KF 34<br>Na <sub>3</sub> PO <sub>4</sub> 34<br>KMnO <sub>4</sub> 20  | MgO<br>MgF <sub>2</sub>  | [19]   |
| Phosphate electrolytes |                                 |  |   |  |  |
| 20                     | AZ91D                           | 400-900<br>A.m <sup>-2</sup><br>Pulse current,<br>$f=700$ Hz                                   | KOH 5<br>(NaPO <sub>3</sub> ) <sub>6</sub> 5-15<br>Na <sub>3</sub> AlF <sub>6</sub> 5-10<br>Triethanolamine 4   | Mg<br>MgO  | [4]  |
| 21                     | WE43<br>AZ91D                   | 600 A.m <sup>-2</sup><br>Pulse current   | KOH 1<br>NaAlO <sub>2</sub> 8<br>Na <sub>3</sub> PO <sub>4</sub> 10   | MgO<br>MgAl <sub>2</sub> O <sub>4</sub>  | [23]   |
| 22                     | AZ91D                           | 50 A.m <sup>-2</sup><br>Direct current   | KOH 168<br>Na <sub>3</sub> PO <sub>4</sub> 4.44<br>KF 34.8<br>Al(NO <sub>3</sub> ) <sub>3</sub> 32  | MgO<br>Al <sub>2</sub> O <sub>3</sub><br>Al(OH) <sub>3</sub>   | [20]   |
| 23                     | WE43-T6<br>AZ91D                | 300 A.m <sup>-2</sup><br>Direct<br>current,<br>$t=2400$ s                                      | Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O 167.7<br>NH <sub>4</sub> OH 52.56   | MgO<br>Mg <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>   | [21]   |
| 24                     | AM50                            | 420 V<br>$t=10$ min  | Na <sub>3</sub> PO <sub>4</sub> 8<br>NH <sub>4</sub> OH 18<br>K <sub>2</sub> ZrF <sub>6</sub> 3<br>NaH <sub>2</sub> PO <sub>2</sub> 1   | ZrO <sub>2</sub><br>MgO<br>MgF <sub>2</sub>  | [22]   |
| 25                     | AM60B                           | 70-80-90 V<br>Voltastatic<br>regime,<br>$t=15$ min   | KOH 3.0<br>Na <sub>3</sub> PO <sub>4</sub> 0.21<br>Al(NO <sub>3</sub> ) <sub>3</sub> 0.15   | MgO  | [23]   |
| 256                    | AM50                            | 300 A.m <sup>-2</sup> ,<br>Alternating<br>pulses (2 ms)<br>and pauses<br>(18 ms)<br>$t=15$ min | Ca(OH) <sub>2</sub> 2<br>Na <sub>3</sub> PO <sub>4</sub> 5-15   | MgO<br>Mg <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub><br>CaH(PO <sub>4</sub> ) <sub>2</sub><br>CaO <sub>2</sub> (calcium<br>peroxide) | [24 <b>Er<br/>ror!<br/>Book<br/>mark<br/>not<br/>defin<br/>ed.</b> ] |
| 27                     | AZ31                            | 4 A.m <sup>-2</sup><br>85-80 <sup>0</sup> C<br>$t=60$ min.                                     | Ca(NO <sub>3</sub> ) <sub>2</sub> 6.9<br>NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> 2.88<br>NaNO <sub>3</sub> 13.9<br>HNO <sub>3</sub> or NH <sub>4</sub> OH<br>(adjusting pH =5) | Mg<br>Ca <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub><br>CaHPO <sub>4</sub> ·2H <sub>2</sub> O                      | [25]   |
| 28                     | Mg-Zn-Ca                        | Asymmetric<br>pulses,<br>$i_c/i_a=2$ ;   | Ca(NO <sub>3</sub> ) <sub>2</sub> 6.9<br>NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> 2.88<br>NaNO <sub>3</sub> 13.9  | Ca-P with<br>atomic ratio<br>1.33:1.65   | [24]   |

|                     |                |  |  |     |      |
|---------------------|----------------|--|--|-----|------|
|                     |                | $i_a$ 100 A.m <sup>2</sup><br>t=30 min       | HNO <sub>3</sub><br>(CH <sub>2</sub> OH) <sub>3</sub> CNH <sub>2</sub> ,<br>NH <sub>4</sub> OH adjusting<br>pH =5  |     |      |
| Borate electrolytes |                |  |  |     |      |
| 29                  | AZ31,<br>AZ91D | Alternative<br>current,<br>120 V<br>t= 3 min | NaOH 50<br>H <sub>3</sub> BO <sub>3</sub> 10<br>Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O 20<br>C <sub>6</sub> H <sub>5</sub> O <sub>7</sub> Na <sub>3</sub> 10<br>Na <sub>2</sub> WO <sub>4</sub> ·2H <sub>2</sub> O<br>A<br>(organic additive) 2 | MgO | [26] |

Electrolytes for PEO treatment of AZ31 alloy were classified according to their pH [27] (Table. 3).

Table 3. Electrolytes for PEO of alloy AZ31

| Silicate electrolytes (mol.L <sup>-1</sup> )  |  | pH          |
|---|--|-------------|
| 1   | 0.035Na <sub>2</sub> SiO <sub>3</sub> +0.07KOH (M <sub>Na</sub> :M <sub>K</sub> =1:1)  | 12.99       |
| 2   | 0.07Na <sub>2</sub> SiO <sub>3</sub> +0.07KOH (M <sub>Na</sub> :M <sub>K</sub> =2:1)   | 12.91       |
| 3   | 0.07Na <sub>2</sub> SiO <sub>3</sub> +0.07KOH+0.085KF+ glycol  | 12.96       |
| 4   | 0.07 Na <sub>2</sub> SiO <sub>3</sub>  | 12.7        |
| 5   | 0.07Na <sub>2</sub> SiO <sub>3</sub> +KOH(ρ=32 mS.cm <sup>-1</sup> )   | 13.3        |
| Phosphate electrolytes (mol.L <sup>-1</sup> ) |  |             |
| 6 <sup>1</sup>                                | H <sub>3</sub> PO <sub>4</sub> +K <sub>2</sub> ZrF <sub>6</sub> <sup>2</sup> (M <sub>H3PO4</sub> : M <sub>K2ZrF6</sub> =1:9)       | 2.33        |
| 7   | NaH <sub>2</sub> PO <sub>4</sub> +K <sub>2</sub> ZrF <sub>6</sub> (M <sub>NaH2PO4</sub> : M <sub>K2ZrF6</sub> =1:9)                | 3.68        |
| 8   | Na <sub>2</sub> HPO <sub>4</sub> +K <sub>2</sub> ZrF <sub>6</sub> (M <sub>Na2HPO4</sub> : M <sub>K2ZrF6</sub> =1:9)                | 5.73        |
| 9   | Na <sub>5</sub> P <sub>3</sub> O <sub>10</sub> +K <sub>2</sub> ZrF <sub>6</sub> (M <sub>Na5P3O10</sub> : M <sub>K2ZrF6</sub> =1:9) | 9.46        |
| 10  | 0.07 Na <sub>3</sub> PO <sub>4</sub>   | 12.45       |
| 11  | 0.07 Na <sub>3</sub> PO <sub>4</sub> +KOH (ρ=32 mS.cm <sup>-1</sup> )  | 13.38       |
| Aluminate electrolytes (mol.L <sup>-1</sup> ) |  |             |
| 12  | 0.07 NaAlO <sub>2</sub>  | 12.46-12.50 |
| 13  | 0.07 NaAlO <sub>2</sub> +KOH(ρ=32 mS.cm <sup>-1</sup> )  | 13.30       |
| Others (mol L <sup>-1</sup> )                 |  |             |
| 14  | 0.07 KF  | 9.08        |
| 15  | 0.07 KF+KOH (ρ=32 mS.cm <sup>-1</sup> )  | 13.18       |
| 16  | 0.07Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> +KOH (ρ=32 mS.cm <sup>-1</sup> )   | 13.01       |
| 17  | 0.07Na <sub>2</sub> CO <sub>3</sub> +KOH (ρ=32 mS.cm <sup>-1</sup> )   | 13.04       |
| 18  | 0.69 KOH   | 14.00       |

<sup>2</sup>The molar concentration of K<sub>2</sub>ZrF<sub>6</sub> was 0.025; the content of K<sub>2</sub>ZrF<sub>6</sub> in the reagent exceeded 98% by weight.

The structure of the coatings is determined by five main factors: chemical composition of the electrolyte and the alloy, current density, electrical processing regime and duration of the process. As a rule, the surface of PEO coatings has a fairly coarse porous structure and needs subsequent removal of the top layer, or to be sealed. It was considered [12] that spherical pores of PEO coating surrounded by a halo of fused material are formed by outgoing gases. So, any measures limiting gas generation at the electrode and contributing to a decrease in temperature on the surface of the coating will positively affect the morphology of the surface.

It was found [28] that the coatings obtained from silicate ( $10 \text{ g.L}^{-1} \text{ Na}_2\text{SiO}_3 + 1 \text{ g.L}^{-1} \text{ KOH}$ ) and phosphate ( $10 \text{ g.L}^{-1} \text{ Na}_3\text{PO}_4 + 1 \text{ g.L}^{-1} \text{ KOH}$ ) electrolytes by the pulses with equal anodic and cathodic current densities  $600 \text{ A.m}^{-2}$  were slightly different. At the same time, the "phosphate" coating had a more compact and continuous structure than the "silicate" one.

There are indirect data about the positive influence of magnesium fluoride on the structure and morphology of PEO coatings [29]. The introduction of fluorides in magnesium oxide at the high temperature ( $635 - 705^\circ\text{C}$ ) treatment in  $\text{SF}_6$  atmosphere was found. Fluorine particles diffused through the oxide layer and formed magnesium fluoride in the interphase space between the metal and the oxide film. In some cases, a layer enriched in fluoride was detected between the oxide crystals. It has been suggested that magnesium fluoride increases the Pilling-Bedworth ratio of  $\text{Mg/MgO}$  to 1 due to incorporation into the oxide structure.

### 3. Corrosion resistance

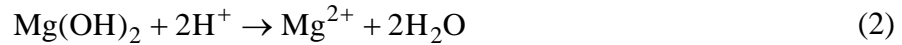
A comparative characteristic of anticorrosive coatings on magnesium is given in [30]. The total corrosion rate was determined by immersion in 3.5% (by weight)  $\text{NaCl}$  solution at  $20^\circ\text{C}$  for 48 hours. The protective ability was carried out by results of salt spray tests after 336 hours of exposure in accordance with ASTM B893-98 (Table 4).

Table 4. Corrosion resistance of the coatings on magnesium

| Process               | Electrolyte  | Regime   | Thickness ( $\mu\text{m}$ ) | Average corrosion rate ( $\text{mg.m}^{-2} \cdot \text{h}^{-1}$ ) | Defensive ability (score) |
|-----------------------|--|--|-----------------------------|---|---------------------------|
| Bare Mg               |  |  |                             | 257.97  | 0                         |
| HAE                   | $\text{KOH}$ ,<br>$\text{Al(OH)}_3$ ,<br>$\text{KF}$ ,<br>$\text{Na}_3\text{PO}_4$ ,<br>$\text{KMnO}_4$          | $t=15-30^\circ\text{C}$<br>$U=70-90 \text{ V}$<br>$I(\sim)=20-25$<br>$\tau=8-60 \text{ min}$                           | 19                          | 148.82  | 2-3                       |
| DOW17                 | $\text{NH}_4\text{HF}_2$ ,<br>$\text{Na}_2\text{Cr}_2\text{O}_7$ ,<br>$\text{H}_3\text{PO}_4$                    | $t=71-82^\circ\text{C}$<br>$U=70-90 \text{ V}$<br>$I(\sim/-)=5-50$<br>$\text{mA.cm}^{-2}$ ;<br>$\tau=5-25 \text{ min}$ | 31                          | 221.81  | 7-8                       |
| PEO (silicate-borate) | $\text{KOH}$ ,<br>$\text{Na}_2\text{CO}_3$ ,<br>$\text{Na}_2\text{SiO}_3$ ,<br>$\text{Na}_2\text{B}_4\text{O}_7$ | $t=8...85^\circ\text{C}$<br>$U=150 \text{ V}$<br>$I(\sim/-)=5-500$<br>$\text{mA.cm}^{-2}$ ;<br>$t=10-80 \text{ min}$   | 10<br>17<br>33              | 49.85<br>42.16<br>32.54   | 7-8<br>>8<br>9            |

It was mentioned above that the stability of the protective oxide/hydroxide layer  $\text{MgO/Mg(OH)}_2$  is observed at  $\text{pH } 11.46 - 13.83$ . Reducing the  $\text{pH}$  to 7.4, for example, in biological media, leads to a slow dissolution of the oxide [31]:





In the corrosion media with  $\text{Cl}^-$  ions magnesium forms soluble salt  $\text{MgCl}_2$ .

The optimization of PEO parameters to obtain corrosion-resistant coatings on AM50 alloy was carried out by Taguchi method [32]. It turned out that between variations of current density, time of electrolysis and electrolyte composition (KOH,  $\text{NaAlO}_2$ ), the concentration of alkali was of decisive importance. The optimal process values were found such as: current density  $1200 \text{ A.m}^{-2}$ , time of electrolysis 12 min, KOH and  $\text{NaAlO}_2$  concentrations 9 and  $15 \text{ g.L}^{-1}$  respectively.

#### 4. Sealing of PEO coatings

The main disadvantage of PEO coatings for anticorrosion ability is their porosity [33]. As usual, porous anodic films are sealed by soaking in hot water with additives of potassium dichromate [34]. This method is not applicable for PEO coatings because of their hydrophobicity. The nonequilibrium vitrified surface of films obtained under sparking followed by quenching in a cold electrolyte cannot be stabilized in hot water.

The best way to stabilize the nonequilibrium phases on the surface is to calcine the coatings, but the temperature regime should be carefully followed, taking into account the very complex mechanism of hydroxide dehydration and the relatively low melting temperature of the metal substrate ( $650^\circ\text{C}$ ). The thermal treatment of coatings in the range of  $50 - 250^\circ\text{C}$ , leading to the dehydration of  $\text{Mg(OH)}_2$  and  $\text{Al(OH)}_3$  and their transition to  $\text{MgO}$  and  $\text{Al}_2\text{O}_3$  oxides is quite effective. Calcination at  $150^\circ\text{C}$  followed by air cooling significantly increased the corrosion resistance of the AZ91D alloy in 3.5% NaCl [35].

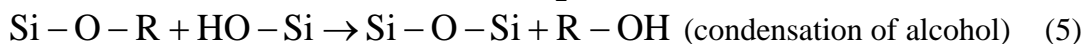
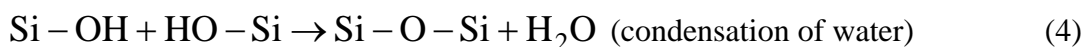
The method of filling PEO coatings on magnesium which used in commercial processes Magoxid-Coat® and Tagnite®, has been described in [36]. Immediately after oxidation in the aluminate-phosphate electrolyte, the samples were immersed for 5 min in an alkaline phosphate solution (12%  $\text{NaH}_2\text{PO}_4$ ) at  $60^\circ\text{C}$ , or for 15 min in a silicate solution (5%) at  $95^\circ\text{C}$ . The samples were then thoroughly washed and dried. As a result of this treatment, the overall thickness and porosity of the coatings were reduced. The silicate solution appeared to be more effective than the phosphate solution.

Dense corrosion-resistant coatings on the AM50B and AM60B alloys were obtained after sealing of PEO coatings with a sol-gel method. To prepare the sol-gel solution, 14 ml of tetraethylorthosilicate (TEOS) and 2% by weight of methyltriethoxysilane (MTES) were dissolved in 2 ml of high purity ethanol. The solution was hydrolysed by adding  $\text{H}_2\text{O}$  (2.5 ml) acidified with 0.35 ml HCl and stirred for 1 hour. Hydrochloric acid served as a catalyst for hydrolysis and polycondensation reactions, and also prevented the agglomeration of particles. After electrolysis, the samples were immersed in the mixture for 1 minute, slowly removed, then held for 3 hours at  $160^\circ\text{C}$  and cooled in air. The procedure was repeated three times then samples were washed for 3 min by distilled water and dried 24 hours at room temperature.

The similar technology was used for filling PEO coatings on an AZ91D alloy [37]. The silica sol (0 – 30% by volume) was added to the silicate electrolyte (1M  $\text{Na}_2\text{SiO}_3$ ). The sol was prepared from tetraethoxysilane (TEOS), methyltriethoxysilane (MTES). Water ( $\text{pH} = 2$ , adjusted with  $0.1 \text{ mol.L}^{-1} \text{ H}_2\text{SO}_4$ ) and ethanol

were taken in molar ratios of 1:2:10:15, respectively. The components were mechanically stirred for 1 hour and held for 5 hours at 60°C.

The reactions underlying the formation of the gel are given below:



A significant improvement in the corrosion resistance of coatings was observed even at a sol concentration of 10% by volume.

The application of sol-gel over the PEO films obtained from the aluminate electrolyte was reported in [38]. The gel was prepared by mixing 3-methacryloxypropyl-trimethoxysilane (MEMO, 99.97%, 19.8 g), 3-mercaptopropyl trimethoxysilane (TPTMS, 95%, 0.8 g) and ethanol (95%, 0.8 g). Then, colloidal silica (9 g) was added dropwise to the mixture while stirring. After hydrolysis of the mixture, an oligomer (6.8 g) and a photo initiator (2-hydroxyl-2-methylpropiophene, 2 g) were added thereto. The sol was diluted with alcohol to obtain an appropriate viscosity and applied to the oxide by spraying (up to 5 layers). The samples were then irradiated with ultraviolet and thermally treated at 1500 ° C for 30 min. Optimal results in electrochemical corrosion tests in 3% NaCl were obtained by applying two sol-gel layers (15 µm each).

The application of tetrafluoroethylene should be considered as a productive method of sealing the PEO surface layer. The application of organic substance above PEO coating was described in [39]. Coatings were immersed in the solution for 1 min, followed by vulcanization at 50°C for 30 min. The thickness of the sealing layer with this treatment reached 2 µm. For qualitative filling of pores and defects, the process was repeated two to three times.

## 5. Conclusion

PEO technology is suitable for treatment of different Mg alloys to obtain oxide (MgO), hydroxide Mg(OH)<sub>2</sub>, and different chemical compounds sintered from the electrolyte (MgAl<sub>2</sub>O<sub>4</sub>, Mg<sub>2</sub>SiO<sub>4</sub>, Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>) in crystalline and amorphous forms. Today, the most qualitative and homogeneous coating can be formed in silicate electrolytes at the high frequency bipolar pulse mode but there are no clear evidences of significant advantages of any used technologies. The better results can be obtained by adding fluoride in the electrolyte. PEO coatings possess a coarse porous structure and relatively poor mechanical properties which can be partly eliminated by following filling.



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