Influence of Complex SiF$_6^{2-}$ Ions on the PEO Coatings Formed on Mg–Al6–Zn1 Alloy for Enhanced Wear and Corrosion Protection

Zeeshan Ur Rehman 1, Bon Heun Koo 2,* and Dongjin Choi 1,*

1 School of Materials Science and Engineering, Hongik University, Sejong-si 30016, Korea; Zeeshan.Physics@gmail.com
2 School of Materials Science and Engineering, Changwon National University, Changwon 642968, Korea
* Correspondence: bhkoo@changwon.ac.kr (B.H.K.); djchoi@hongik.ac.kr (D.C.)

Received: 30 December 2019; Accepted: 20 January 2020; Published: 22 January 2020

Abstract: The present study was carried out to explore the effect of SiF$_6^{2-}$ incorporation and concentration on the plasma electrolytic oxidation (PEO) coatings formed on AZ61 Mg alloy. The coatings were prepared using electrolyte solution with various concentration of Na$_2$SiF$_6$(0.0–0.7 g/L). Highly compact coatings with minimum porosity were obtained for an optimum concentration of Na$_2$SiF$_6$ ~0.3 g/L added into the electrolyte. The highest corrosion resistance, $\sim$2.04 × 10$^{-6}$ Ω·cm$^2$, was obtained for 0.3 g/L of Na$_2$SiF$_6$, in addition to its superior anti-wear properties. However, it was found from the scanning electron microscope (SEM) image analysis that increasing concentration above 0.3 g/L, could cause severe breakdown in the inner layers, and thus the said coatings could not withstand effectively against wear and corrosion.

Keywords: fluoride ions; SEM; PEO; corrosion; wear; hardness

1. Introduction

As researchers unveil the attractive and novel features of the plasma electrolytic oxidation coatings, its domain extends rapidly in terms of applications as well as experimentation. Using PEO process, hard ceramic coatings can be formed on various kinds of light metal alloys using appropriate solutions and additives such as alkaline silicates, phosphates, etc. Though the PEO coatings have comparable mechanical properties, due to porosity and defect issues, however, the coatings need further improvement in regards to corrosion protection, for long-term applications [1–7].

To solve this issue, various electrolyte compositions and concentrations were used by the researchers [8–10]. Alkaline silicate or phosphate electrolytes, with various fluoride precursors, are recently attracting the researchers, due to their enhanced mechanical and electrochemical protective properties [11,12]. Several advantages of the fluoride-based species in PEO electrolytic solution have been proposed earlier: formation of a protective barrier film, which offers resistance to pitting corrosion; [13–15] assisting the initiation of sparks during the plasma discharge; and improving the hardness of the coatings [12,13]. Though various fluoride species were used for the said purposes, the obtained results are still under examination stage. Additionally, fluoride species, such as K$_2$ZrF$_6$, upon adding to the silicate solution form precipitates with silica, which is slightly harmful for the uniform growth of the PEO coatings [16–18]. Therefore, new fluoride precursors and species are required with enhanced solubility and less hazard effects to be used as additive in the PEO electrolytes.

Na$_2$SiF$_6$ is a complex hexafluoroarsilicate, which has rarely been used in the PEO process, and thus also has comprehensive details [19,20]. An important property of Na$_2$SiF$_6$ relating to PEO experiment is its solubility, as, from the material safety data sheet of Na$_2$SiF$_6$, confirms its solubility as ~40 mg/L at 20 °C. Furthermore, adding Na$_2$SiF$_6$ to alkaline silicate solution, the precipitation or
agglomeration phenomenon cannot be observed. Thus, it is highly preferable for use as PEO additive for excellent coating properties. In this work, PEO coatings were formed on AZ61 alloy in a Na2SiF6-based electrolyte solution. Various concentration of Na2SiF6 was used in this experiment and the final properties such as microstructure, composition, corrosion, and wear were correlated with the concentration.

2. Experiment

2.1. PEO Process and Electrolytes

Commercial AZ61A (Al 6.1 wt.%, Zn 0.45 wt.%, Mn 0.27 wt.%, Fe ≤ 0.02 wt.%, others ≤ 0.01 wt.%, Mg balance) was cut into coupons of working area ~9.5 cm². Before the PEO process, samples were polished with SiC paper (up to grade 2000), followed by washing in deionized water and decreasing in ethanol. Composition of the electrolytes is given in Table 1. The PEO process was conducted by means of lab-made external hybrid power supply under constant voltage 200 alternating current (AC) and 260 direct current (DC) volts. During the PEO process, the temperature of the electrolyte solutions was maintained below 25 °C by adjusting a cool water flow.

Table 1. Composition and concentration of the PEO electrolyte.

<table>
<thead>
<tr>
<th>Sample Codes</th>
<th>Na2SiO3 (g/L)</th>
<th>NaOH (g/L)</th>
<th>Na2SiF6 (g/L)</th>
<th>Processing Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1</td>
<td>12</td>
<td>3.5</td>
<td>0.1</td>
<td>30</td>
</tr>
<tr>
<td>N2</td>
<td>–</td>
<td>–</td>
<td>0.3</td>
<td>–</td>
</tr>
<tr>
<td>N3</td>
<td>–</td>
<td>–</td>
<td>0.5</td>
<td>–</td>
</tr>
<tr>
<td>N4</td>
<td>–</td>
<td>–</td>
<td>0.7</td>
<td>–</td>
</tr>
</tbody>
</table>

2.2. Coating Characterization

Phase composition of the coatings was investigated by means of X-ray diffraction (XRD, MiniFlex II, Rigaku, Tokyo, Japan), using Cu Kα source. The microstructure of the surface and various portions of the cross sections of the samples was examined by scanning electron microscope (SEM, JSM-6510, Jeol, Tokyo, Japan). Micro-hardness of the coating was measured on 10 different places through the length as well as through thickness of the cross section by a VLPACK2000 Mitutoyo hardness test machine (Mitutoyo, Tokyo, Japan) using Vickers-type indenter under constant loading/unloading rates of 0.025 mN/s with holding time of 5 s at maximum load of 0.1 N. To perform the wear test, the samples were held against the stainless steel (GCr15) ball with diameter ~6 mm. A normal perpendicular force ~600 gf was applied as the steel ball rotated on the sample at a constant speed of 5 Hz in a 10 mm diameter trace. After a total of 3000 s of revolutions, the weight loss of samples was measured at a sophisticated electronic balance. Electrochemical corrosion test of the PEO-coated specimens was performed by an Electrochemical Testing System (1280B, Wonatech, Seoul, Korea) with a conventional three electrodes; saturated calomel electrode (SCE) electrode as reference and graphite as a counterelectrode. The coated specimens as working electrode were immersed into the electrolyte of 3.5 wt.% NaCl. Tafel curves were obtained from 4.0 V below the open circuit potential (OCP) to 2 V above the OCP at a scan rate of 1 mV/s. The exposed surface area of the coated specimens to the corrosion solution was ~0.75 cm². Corrosion potential and corrosion current density were obtained by curve fitting process of the obtained tafel curves using IVman software provided by the Wonatech Inc. (Seoul, Korea). All characterizations were carried out at Changwon National University (Changwon, Korea).

3. Results and Discussion

3.1. Microstructure of Coatings

Figure 1a–d shows the surface morphology of the PEO coatings for various concentration of Na2SiF6. It can be seen that coatings with lowest concentration of Na2SiF6 has irregular eruption
appeared on the surface. The resultant pancakes from the discharge eruption were therefore believed to have flat-tops, and raised to maximum height than the plan coating matrix as indicated by A. In addition, solids melts and perforated episodic discharge pancakes as indicated in panel B have bigger sizes in N1 coatings. As the concentration increases, the pores were blocked and relatively uniform coatings were obtained as shown for 0.3 g/L.

![Figure 1](image1.png)

**Figure 1.** (a–h) Illustrative SEM images of the coating surface and sections prepared at various concentration of Na$_2$SiF$_6$ (0-0.7 g/L).

The small white bulbs on the surface of the coating are believed to be amorphous silica, which produced in the low temperature zone of the discharge channels and could not crystallized due to the insufficient plasma sparking heat. The presence of amorphous silica was also confirmed by Kaseem et al [20]. It can be seen that as the concentration of Na$_2$SiF$_6$ increases up to 0.3 g/L, the pancakes grow in a well spherical shape. The spherical shape pancakes are formed from the solid melts as a result of physio-electrochemical reactions caused by the plasma discharges and their consequent quenching. Several mechanical and electrochemical forces simultaneously disrupt the growth of these melts into pancakes, as portrayed in Figure 2a. If all the forces are balanced (i.e., $F_x$ is balanced by $-F_x$ and $F_z$ is balanced by $-F_z$), a uniform cylindrical shape pancakes can be obtained with the energy as mentioned in the figure. In case of uniform growth, the solid melt is attracted to the center of the discharge thus pores are nearly blocked as shown in N2. The phenomenon of pancake formation can be correlated with the water inside spinning or high-pressure cyclone.

![Figure 2](image2.png)

**Figure 2.** (a) Cartesian model of the possible forces acting on the discharge melt in a single discharge channel and (b) XRD pattern of the coatings prepared at various Na$_2$SiF$_6$ concentration.
Further, amorphous bulbs, dents, or nodules cannot be seen on the surface of N2. The uniform growth, which yields the sealing feature to the coating, can be attributed to the catalytic role of the SiF$_6^{2-}$ ions. SiF$_6^{2-}$ ions are considered as aggressive and can be readily attracted to the anode, and thus increase the current flow by its two effects; first, an increase in its individual flow and, second, catalyzing the flow of SiO$_3^{2-}$ ions towards anode. The boundaries between any two consecutive pancakes as seen in Figure 1 are formed due to the difference in temperature caused by the quenching shots (earlier quenched or later quenched melts). Such boundaries are well cleared in N3 and N4 coatings due to the high catalytic role of SiF$_6^{2-}$ ions.

Cross-sectional morphologies of the coatings are shown in Figure 1e–h. It can be seen that thickness of the coating increases linearly with Na$_2$SiF$_6$ concentration as in Figure 3a. However, the inner layer defects significantly increased with concentration above 0.3 g/L. Moreover, the curvature of the outer layer suggests the high difference between the crest and trough. The crests are formed from the pancakes, whereas the trough represents the plan coating matrix. The defective structure for 0.7 g/L suggests the highly corrosive role of SiF$_6^{2-}$ ions. By measuring thickness of the crest and diameter of the pancake, the surface volume occupied by the pancakes can be calculated; however, due to maximum deviation in the diameter and shape values, the error chances could be maximum.

The interface layer between the substrate and the coating is compact for 0.3 g/L, however a damaged interface layer can be seen in case of N3 and N4 coatings. Through the entire cross section layer, two types of inner layer defect can be observed: surface connected (A) and surface-free (B) defects. The non-connected inner layer defect occurs due to the blasts caused by breakdown of localized gas packet and the ionized material present in the inner layers. The higher number of surface free defect in the N3 and N4 coating can be attributed to the maximum ionic flow, which provokes such inner layers defects.

![Figure 3. (a) Thickness and (b) texture relation with Na$_2$SiF$_6$ concentration.](image)

3.2. Compositional and Phase Analysis

XRD pattern of the coating is shown in Figure 2b. The major phases identified in the XRD pattern were MgO, Mg$_2$SiO$_4$, Mg, and MgF$_2$. The MgF$_2$ phase formed due to the presence of SiF$_6^{2-}$ in the electrolyte solution. SiF$_6^{2-}$ has octahedral structure and has $d^2sp^3$ hybridization. Such bond distribution is weak, and thus, due to the electrochemical effect, these ions are dissociated, which react with magnesium and form polycrystalline phases due to plasma sintering effect. In addition, the voluminous availability of Mg ions further boosts the formation of MgF$_2$. Additionally, intensity of the MgF$_2$ phases also increases with increasing its precursor concentration. These phases are sintered under high temperature and high pressure in the discharge channels. Mg$_2$SiO$_4$ is generated from the fact that SiO$_3^{2-}$ in the silicate electrolyte penetrates into the microdischarge channels. After SiO$_3^{2-}$ anions lose an atom of oxygen, the reaction between SiO$_2$ and O$_2$ occurs. The early formed MgO and SiO$_2$ could melt during the high temperature process and produce the Mg$_2$SiO$_4$, as shown
in Equations (1) and (2) [21,22]. Secondly, Mg\(^2+\) and SiO\(^{3-}\) ions can react directly react with each other to generate Mg\(_2\)SiO\(_4\) phase thorough the following sequential reactions.

\[
\text{SiO}_2^{3-} - 2e \rightarrow \text{SiO}_2 + 1/2O_2 \quad (1)
\]
\[
2\text{MgO} + \text{SiO}_2 \rightarrow \text{Mg}_2\text{SiO}_4 \quad (2)
\]
\[
2\text{Mg} + 2\text{SiO}_2^{3-} \rightarrow \text{Mg}_2\text{SiO}_4 + \text{SiO}_2 \quad (3)
\]
\[
\text{Na}_2\text{SiF}_6 = 2\text{Na}^+ + \text{SiF}_6^{2-} \quad (4)
\]

The texture coefficient trend of MgO and Mg\(_2\)SiO\(_4\) as shown in Figure 3b, further proves that the Mg\(_2\)SiO\(_4\) phase increases with Na\(_2\)SiF\(_6\) concentration. An increase in Mg\(_2\)SiO\(_4\) compared to MgO implies the increasing availability of SiO\(^{3-}\) with Na\(_2\)SiF\(_6\) concentration. As melting point of Mg\(_2\)SiO\(_4\) (forsterite) is ~2183 K, thus increment in the temperature of plasma discharge channels can be visualized with increasing concentration of Na\(_2\)SiF\(_6\).

### 3.3. Mechanical Properties

The hardness profile of the coatings is shown in Figure 4. It can be seen that hardness increase linearly with increasing concentration up to 0.3 g/L. Hardness is function of both intrinsic and extrinsic parameters. The hard phases, such as MgF\(_2\) and Mg\(_2\)SiO\(_4\), are responsible for the intrinsic higher hardness of N2 sample. Deviation in the hardness values increases significantly for N3 and N4 due to the damaged inner layers. Importantly, the compact and dense coating of N2, in addition to its highest hardness, showing the lowest deviation and scatter in the hardness values. As hardness is a localize property of the coating, in addition to the average hardness values, the deviation between the localized value is also of great importance for the exact identification of the mechanical strength of the coatings. Coating with minimum deviation and high average values can be assumed as best coatings. Hardness is localized property and one cannot rely totally on the hardness to predict wear properties of the coatings through the following relation [23],

\[
w = \frac{k}{LH} \quad (5)
\]

where \(w\) is the wear rate, \(k\) is the wear coefficient, \(L\) is the applied load, and \(H\) is the hardness of the material. Therefore, to examine the average response of the coating surface, wear analysis of the coating was carried out. It can be seen in Figure 5 that the wear rate is significantly higher for the bare AZ61 alloy ~11.85 mg\cdot N\(^{-1}\)\cdot m\(^{-1}\). However, this was reduced considerably by the coating process; the lowest wear rate was recorded for 0.3 g/L.

![Figure 4. Hardness profile of the coating prepared at various Na\(_2\)SiF\(_6\) concentration.](image)
The significant increase in the wear-resistance of the PEO coatings with addition of Na$_2$SiF$_6$ can be related to the excellent melting and fusing of the silicate and oxide species on the metal substrate surface in the presence of intensive sparks. Moreover, Nemcova et al. discussed, in detail, fluoride injection into the coatings to greatly improve the adhesion of the coating [24]. Thus, the combine effect of excellent adhesion and sintering in the case 0.3 g/L of Na$_2$SiF$_6$ contribute to the better wear protection of the coatings.

![Figure 5. Wear rate of the coatings for various Na$_2$SiF$_6$ concentration.](image)

3.4. Corrosion Analysis

Figure 6 shows potentiodynamic polarization curves of the coatings in 3.5 wt.% NaCl solutions. The corrosion potential (E$_{corr}$), corrosion current density (I$_{corr}$), and anodic/cathodic Tafel constant ($\beta_a$ and $\beta_c$) were derived using IVman software package for electrochemical experiments. All the resultant corrosion parameters are given in Table 2.

![Figure 6. Tafel curves for the coating obtained at various concentrations.](image)
Table 2. Corrosion parameters obtained from the tafel curve analysis.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$\beta_\mathrm{e}$ (V/decade)</th>
<th>$\beta_\mathrm{i}$ (V/decade)</th>
<th>$E_\text{corr}$ (V)</th>
<th>$I_\text{corr}$ (A/cm²)</th>
<th>$R_p$ (Ω·cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AZ61A</td>
<td>0.09</td>
<td>0.19</td>
<td>−1.31</td>
<td>$3.06 \times 10^{-4}$</td>
<td>$1.5 \times 10^4$</td>
</tr>
<tr>
<td>N1</td>
<td>0.37</td>
<td>0.18</td>
<td>−1.35</td>
<td>$5.70 \times 10^{-4}$</td>
<td>$3.82 \times 10^3$</td>
</tr>
<tr>
<td>N2</td>
<td>1.01</td>
<td>0.68</td>
<td>−0.28</td>
<td>$5.80 \times 10^{-7}$</td>
<td>$2.04 \times 10^5$</td>
</tr>
<tr>
<td>N3</td>
<td>0.88</td>
<td>1.59</td>
<td>−1.28</td>
<td>$6.40 \times 10^{-5}$</td>
<td>$1.77 \times 10^2$</td>
</tr>
<tr>
<td>N4</td>
<td>0.84</td>
<td>0.64</td>
<td>−0.85</td>
<td>$9.21 \times 10^{-6}$</td>
<td>$1.72 \times 10^4$</td>
</tr>
</tbody>
</table>

From the Tafel curves, all the coatings have different corrosion potentials as represented by the arrows. Corrosion potential, as can be seen from the tafel curves, increases up to 0.3 g/L of Na$_2$SiF$_6$ concentration reaching the highest potential of −0.28 V. However, further increase in the concentration caused a severe decrease in the corrosion potential. This increase can be attributed to the sealed surface of N2 coatings and uniform matrix that could prevent the corrosive solution form penetrating through the coating layers. The inner coating layer and the interface layer are the secondary resistive barriers to oppose the corrosive solution. It can be seen from the anodic parts that bare AZ61, N1, and N3 have lower resistance to the corrosive solution form the initial stage. Unlike N4, offers the highest resistance to the corrosive solution in the initial stage as seemed in Figure 6 (encircled part). However, due to the damaged inner layer of N4, as discussed in the earlier section, the resistance of the layers could not withstand for long time, and thus a trans-passive region on the anodized curve was obtained as mentioned by arrow (b). In N2, there is no complete passive region; however, the rate of corrosion is significantly lower and started at sufficiently higher potential and with slower rate (Table 2). Thus, the corrosion current that obtained for N2 has the lowest value: $5.80 \times 10^{-7}$ Ω·cm². Such a noble behavior can be attributed to the optimum concentration of fluoride additives that formed compact and hard layers. The noble properties also have a deep link with the phases present in the coatings. As reported earlier that presence of undissolved MgF$_2$ thin film formed in the initial stages of PEO could prevent the corrosion ions (Cl$^-$) penetrating through the PEO films to corrode the Mg substrate [7]. For comparison, the tafel curve of bare AZ61 can also be seen in Figure 6. Clearly, the corrosion resistance of the N2 is less than bare AZ61 up to 5 decades.

4. Conclusions

Various concentrations of Na$_2$SiF$_6$ were added to the PEO electrolyte, and the final properties of the PEO coatings were examined. With increasing concentration of Na$_2$SiF$_6$, uniform and steady process incremented stable phases, such as Mg$_2$SiO$_4$, in the coatings. At the same time, the undissolved phase MgF$_2$ was also obtained from the incorporation of Na$_2$SiF$_6$ into the PEO coatings. Due to increase in the Mg$_2$SiO$_4$ phase and presence of MgF$_2$ phase, a highly compact and poreless coating was obtained for 0.3 g/L of Na$_2$SiF$_6$ concentration with the highest corrosion resistance, $2.04 \times 10^6$ Ω·cm², and lowest wear rate. It was observed from the microstructure that further increase in Na$_2$SiF$_6$ concentration could damage the inner layer and initiate considerable surface defects. Therefore the use of 0.3 g/L could be recommended for further experimentation work in the relevant technology.

Author Contributions: Conceptualization, methodology, software, validation, formal analysis, investigation, data curation, writing—original draft preparation, writing—review and editing, Z.U.R.; visualization, resources, conceptualization, supervision, project administration, writing—review and editing, funding acquisition, B.H.K. and D.C. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Ministry of SMEs and Startups (S2779368) and by the new faculty research support fund, Hongik University.

Acknowledgments: The administrative and technical support, materials used and facilitation were provided by Hongik University and Changwon National University.

Conflicts of Interest: The authors declare no conflict of interest.

References


© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).