Effects of silica and Ag on the electrochemical behavior of titania-based nanocomposite coatings deposited on 2024 aluminum alloy by the sol-gel method

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ABSTRACT

To enhance the service lifetime and effectiveness of Al 2024-T4 in medical applications, the corrosion and wear characteristics can be improved by deposition of ceramic coatings. Herein, titania, titania-Ag and titania-silica-Ag nanocomposite coatings are deposited on 2024 aluminum substrate by the sol-gel and dip-coating techniques and the corrosion behavior is investigated in 0.05 M NaCl, 0.5 M NaCl, and Ringer’s solutions. The adhesion strength and thickness of the coatings decrease from 23 to 19 mN and 516 to 508 nm, respectively, with addition of Ag, but increase from 23 to 28 mN and 516–547 nm, respectively, when silica is added. Owing to the formation of favorable protective layers, the corrosion resistance of the titania-silica-Ag coating is better than that of the other two coatings. The presence of calcium and potassium ions leads to more rigorous reactions on the surface and formation of a protective compact oxide layer on 2024 aluminum substrate.

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1. Introduction

Owing to the large strength-to-weight ratio and good workability, aluminum alloys have many industrial applications [1] and in particular, Al 2024-T4 alloys can be good candidate for high-strength structural biomedical applications such as orthopedic braces [2]. The materials have good biocompatibility and do not release ions that may be cause cancer and allergy. In order to enhance the service lifetime and effectiveness in the physiological environment, the corrosion and wear characteristics must be improved and a viable approach is to deposit ceramic coatings composed of titania, silica, alumina, and zirconia [3]. Ceramic coatings are commonly deposited by chemical vapor deposition (CVD), physical vapor deposition (PVD), plasma-assisted CVD, and the sol–gel technique [4,5]. The sol gel method is especially attractive because of the low cost, versatility, simplicity, and good film adhesion [4,6]. Although the sol-gel technique can produce uniform and homogeneous composite coatings with thicknesses below 2 μm [7], sol-gel coatings are prone to surface cracking caused by solvent evaporation during drying and heat treatment. These cracks and other defects such as holes and pits allow aggressive corrosion media to penetrate the coating into the substrate exacerbating corrosion and methods such as drying at high humidity, low-rate heat treatment, and deposition of composite coatings. Composite coatings can also improve the mechanical and anticorrosive behavior of sol-gel coatings [4,8–12].

Titania-silica exists in bones and can serve as a barrier against corrosive ions such as chloride [13,14]. Doping titania-silica with silver can further improve the barrier properties, corrosion resistance, and bacterial resistance of the coatings bonding well for application to orthopedic implants and products [15–17]. The objective of this work is to prepare homogeneous and uniform titania-based nanocomposite coatings on Al 2024-T4 by the sol-gel method and investigate the effect of silica and silver (Ag) on the corrosion behavior of the coatings by electrochemical impedance spectroscopy (EIS) in three different media of 0.05 M NaCl, 0.5 M NaCl, and Ringer’s solutions.

2. Experimental details

As shown in Fig. 1, titania, titania-Ag and titania-silica-Ag solutions were prepared by using butyl orthotitanate, orthosilicate, and silver nitrate with 98% ethanol as the solvent,
Fig. 1. Schematic of preparation of Titania, Titania-Ag and Titania-silica-Ag sol.

Fig. 2. GIXRD patterns acquired at 5°: (a) Titania coating, (b) Titania-Ag nanocomposite coating, and (c) Titania-silica-Ag nanocomposite coating.
ethylacetoacetate, and 65% nitric acid. To start the hydrolysis re-
action, a small amount of deionized water was added to the solu-
tion drop wise and mixed for 30 min. To conduct the polymer
reactions, the solution was aged for 12 h.

The 2024 aluminum alloys (AA2024-T4) samples was ground
with 800–3000 SiC paper and 0.1–0.3 μm alumina pastes. The
polished samples were degreased ultrasonically in acetone, alcohol,
and distilled water and the coatings were deposited by the sol-gel
dip coating techniques at a rate of 18 mm/min. In order to
remove the remaining organic compounds and control the existing
defects and cracks, the samples were dried at 50 °C in an atmos-
phere containing 85% moisture for 60 min and then heated to
90 °C and 120 °C for 45 and 30 min, respectively, to control evap-
oration of the organic compounds with minimal stress and
cracking. Finally, the samples were heated to 300 °C for 60 min.

The crystal structure of the coatings was determined by grazing-
incidence X-ray diffraction (GIXRD) (Philips PW-1730 diffractom-
eter) in the continuous scanning mode using Cu Kα radiation
(λ = 0.154056 nm) from 10° to 80° and 0.1°/sec. The bonding in-
formation was obtained by the Fourier transform infrared spec-
troscopy (FTIR, Jasco v-550) and absorption spectrophotometry was
performed in the range of 400–4000 cm⁻¹. The surface
morphology, film uniformity, and homogeneity were studied by
field-emission scanning electron microscopy (FE-SEM, MIR-
A3TESTSCAN), elemental analysis was carried out by energy-
dispersive X-ray spectroscopy (EDS), and film thickness was
determined by ellipsometry. The adhesion strength was deter-
mined on a microscratch tester with a diamond tip (radius of
10 mm) at a sliding speed of 15 mm/s. The critical load L was
declared as the smallest load at which the coatings started to
delaminate from the Al 2024-T4 substrate and coating delamina-
tion was confirmed by optical microscopy.

The corrosion properties of the coatings were determined by
electrochemical impedance spectroscopy (EIS) in 0.05 M NaCl,
0.5 M NaCl, and Ringer’s solutions at room temperature for 1 and
12 h. Ringer’s solution contained 6.8 g/l NaCl, 0.41 g/l KCl, and
0.27 g/l CaCl₂ and the pH was 7.2. The standard electrochemical cell
consisted of three electrodes including the coated sample as the
working electrode, saturated calomel as the reference electrode,
and platinum net as the auxiliary electrode. EIS was performed
between 0.01 Hz and 100 kHz at the open circuit potential by using
a sinusoidal wave with an amplitude of 10 mV (CompactStat Ivium
Soft 1.805 Release IVIUM Technologies Netherlands). Inductively-
coupled plasma mass spectrometry (ICPMS, PerkinElmer Optima

### Table 1

Coating thickness, critical load, and elemental composition of the titania, titania-Ag,
and titania-silica-Ag coatings.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Titania nanostructured coating</th>
<th>Titania-Ag nanostructured coating</th>
<th>Titania-silica-Ag nanostructured coating</th>
</tr>
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<tbody>
<tr>
<td>Coating Thickness (nm)</td>
<td>516</td>
<td>508</td>
<td>547</td>
</tr>
<tr>
<td>Critical load (mN)</td>
<td>23</td>
<td>19</td>
<td>28</td>
</tr>
<tr>
<td>Ti (W%)</td>
<td>78.3</td>
<td>72.7</td>
<td>53.9</td>
</tr>
<tr>
<td>Si (W%)</td>
<td>–</td>
<td>–</td>
<td>18.4</td>
</tr>
<tr>
<td>Ag (W%)</td>
<td>–</td>
<td>2.8</td>
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</tr>
<tr>
<td>O (W%)</td>
<td>21.7</td>
<td>24.5</td>
<td>25.6</td>
</tr>
</tbody>
</table>

![Fig. 3. FTIR spectra](a) AA2024, (b) Titania nanostructured coating, (c) Titania-Ag nanocomposite coating, and (d) Titania-silica-Ag nanocomposite coating.)
2100 DV) was performed to measure the amounts of Al released to the solutions from the Al 2024, titania, titania-Ag, and titania-silica-Ag nanocomposite coatings after EIS test and immersion for 1 and 12 h.

3. Results and discussion

The GIXRD results in Fig. 2 are acquired at 5° to determine the phases in the titania, titania-Ag, and titania-silica-Ag nanocomposite coatings. The anatase phase is identified according to ICCC-JCPDS anatase titanium oxide No. 78-2486, ICCC-JCPDS silica No. 05-0492, and ICCC-JCPDS silver No. 04-0783. Silica delays formation of the anatase phase and peak widening suggests nanostructures and amorphous titania-silica-Ag coatings. The absence of Ag peaks may be due to the small amount of only 2.8% as determined by EDS (Table 1) [3].

The FTIR data in Fig. 3 reveal O-H functional groups (1660–1632 and 3400 to 3438 cm⁻¹) [3,18,19]. The Ti-O-Ti peaks in the range of 430–466 and 630 to 656 cm⁻¹, Si-O-Si peaks in the range of 793–802 and 1015 to 1098 cm⁻¹, and Ti-O-Si bond in the range of 925 cm⁻¹ are observed [3,18,19]. In the FTIR spectrum of the titania-silica-Ag coating, the peaks between 930 and 950 cm⁻¹ stem from polymerization of silicate compounds with titanium and those observed between 562 and 580 cm⁻¹ are related to Ag [3,18]. There is reduced dispersion due to Ag in the titania coating because Ag stabilize the titania coating and titanium bonds leading to the formation of a homogeneous coating on the Al 2024 substrate. However, it should be noted that identification of bonds related to Ag by FTIR curve is quite difficult [3,18–21].

Fig. 4 shows the FE-SEM image of the titania, titania-Ag, titania-silica-Ag nanocomposite coatings revealing good homogeneity, uniformity and nano-structure. The agglomeration phenomenon
and white islands are observed from the titania-Ag coating. The morphology of the coating becomes coarser with addition of Ag (titania-Ag coating) compared to the titania coating, but the islands and agglomerates disappear from the titania-silica-Ag coating which shows a more homogenous and finer morphology than the titania-Ag coating. During calcination, silver ions migrate to the surface from the bulk and settle on the surface of the particles. In general, the coating homogeneity plays an important role in self-cleaning, corrosion resistance, and bacterial resistance \[3,13,22\]. The radius of silver ions (126 pm) is bigger than those of titania (68 pm) and silica (40 pm) and also silver ions cannot easily enter the network of the anatase phase and silica leading the formation of a nano-composite on the titania and silica particles.

Table 1 compares the thickness and critical loads of the coatings. The presence of silica increases the thickness from 508 to 547 nm and critical loads from 19 to 28 mN compared to the titania-Ag nanocomposite coating. The adhesion strength and thickness of the titania coating decreases with the addition of Ag possibility due to formation of islands and agglomerated particles but increase with addition of silica creating a uniform distribution and preventing the formation of agglomerated particles.

Fig. 5 shows the Nyquist, Bode, and Bode-phase curves of the coatings after immersion for 1 and 12 h in 0.05 M NaCl, 0.5 M NaCl, and Ringer’s solutions. The Nyquist diameter is an indicator of the overall resistance and the capacitor is simulated by a constant phase element (CPE) using Eq. (1) \[23,24\]:

\[
\text{CPE} = \frac{Y_0(\omega)^{n-1}}{}
\]

where \(Y_0\) and \(\omega\) are constants being the angular frequency of maximum imaginary impedance and power of CPE, respectively. And also \(n\) is heterogeneity parameter of coating (\(n\) value is between 0 and 1), when \(n\) is equal to 1, the CPE behaves like an ideal capacitor. An impedance spectrum is simulated using the
equivalent electrical circuits as shown in Fig. 6 and the results of EIS curves are summarized in Tables 2–4. \( C_P E_{coat} \), \( C_P E_{pro} \), and \( C_P E_{dl} \) explain the semi-capacitor behavior of the absorbed ions in the coating, corrosion products and double layer, respectively. \( R_{sol} \), \( R_{coat} \), \( R_{pro} \), and \( R_{ct} \) are used for the solution, coating, corrosion products, and charge transfer resistance, respectively. The circuits are consistent with the EIS curves and represent the physical features of the electrode surface, e.g., electrical double layer and monotonic film of surface.

According to Fig. 5a–b, the Nyquist plot shows that the resistance of the coating at high frequencies is almost the same for the titania and titania-Ag coatings. With addition of silica, the first ring of the Nyquist plot expands, indicating increased resistance of the coating against corrosive ions. According to the bode-phase plot, the titania coating has a capacitive behavior because the permeability of the titania coating during 1-h immersion is less than that of the other coatings. According to GIXRD and FE-SEM, silica in the coating prevents crystallization of titania. However, the titania-silica-Ag coating is amorphous and nano-structured giving rise to the dominance of uniform corrosion over localized corrosion in the silica-containing coating compared to the other coatings.

According to Fig. 5c–d, with decreasing amounts of chloride ions in the solutions and presence of calcium and potassium in Ringer’s solution, the coating ring at high frequencies increases for the titania-Ag coating indicating increased corrosion resistance compared to the other coatings. The reason may be the reactions between potassium and calcium ions and Ti-O and Si-O compounds. Agglomeration of silver ions on the surface leads to the formation of a protective layer resulting from the corrosion products. The reactions on the titania-silica-Ag coating require a longer time and the incomplete process increases localized corrosion. Although the amounts corrosive ions in Ringer’s solution are
smaller, incomplete formation of the layer gives rise to localized corrosion in lieu of uniform corrosion. In addition, the Bode-phase plot confirms the capacitive behavior and high resistance of the titania-Ag coating compared to the other coatings. In fact, the high resistance of the titania-Ag coating leads to movement of the electrons from the capacitive path. All in all, improved corrosion resistance is observed according to the following changes in the Nyquist and Bode-phase plots [3,4,25]:

1. Increased diameter of the rings and expanding rings especially at high frequencies.
2. Increased number of time constants implying the formation of obstacles in the movement path and penetration of the corrosive ions into the layer.

As shown in Fig. 5e–f, the titania-silica-Ag coating has a higher corrosion resistance than the other coatings in 0.05 M NaCl.

**Table 2**

<table>
<thead>
<tr>
<th>Time period (h)</th>
<th>Samples</th>
<th>$R_{\text{sol}}$ ($\Omega \cdot \text{cm}^2$)</th>
<th>$R_{\text{coat}}$ ($\Omega \cdot \text{cm}^2$)</th>
<th>$C_{\text{PEcoat}}$ ($\mu \text{F} \cdot \text{cm}^{-2} \cdot \text{s}^{-1/2} \cdot \text{m}^{-1}$)</th>
<th>$n_{\text{coat}}$</th>
<th>$R_{\text{pro}}$ ($\Omega \cdot \text{cm}^2$)</th>
<th>$C_{\text{PEpro}}$ ($\mu \text{F} \cdot \text{cm}^{-2} \cdot \text{s}^{-1/2} \cdot \text{m}^{-1}$)</th>
<th>$n_{\text{pro}}$</th>
<th>$R_{\text{ct}}$ ($\Omega \cdot \text{cm}^2$)</th>
<th>$C_{\text{PEdl}}$ ($\mu \text{F} \cdot \text{cm}^{-2} \cdot \text{s}^{-1/2} \cdot \text{m}^{-1}$)</th>
<th>$n_{\text{dl}}$</th>
<th>Chi-squared</th>
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<td>45</td>
<td>8956</td>
<td>13.31</td>
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<td>--</td>
<td>--</td>
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<td>7375</td>
<td>34.63</td>
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<td>--</td>
<td>--</td>
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<td>--</td>
<td>--</td>
<td>--</td>
<td>35640</td>
<td>233.3</td>
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<tr>
<td>12 h</td>
<td>Al 2024</td>
<td>38</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>9933</td>
<td>70.96</td>
<td>0.89</td>
<td>3952</td>
<td>553.7</td>
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<td>0.0061</td>
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<td>16283</td>
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<td>--</td>
<td>--</td>
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<td>6539</td>
<td>267.5</td>
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<td>370.2</td>
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**Table 3**

<table>
<thead>
<tr>
<th>Time period (h)</th>
<th>Samples</th>
<th>$R_{\text{sol}}$ ($\Omega \cdot \text{cm}^2$)</th>
<th>$R_{\text{coat}}$ ($\Omega \cdot \text{cm}^2$)</th>
<th>$C_{\text{PEcoat}}$ ($\mu \text{F} \cdot \text{cm}^{-2} \cdot \text{s}^{-1/2} \cdot \text{m}^{-1}$)</th>
<th>$n_{\text{coat}}$</th>
<th>$R_{\text{pro}}$ ($\Omega \cdot \text{cm}^2$)</th>
<th>$C_{\text{PEpro}}$ ($\mu \text{F} \cdot \text{cm}^{-2} \cdot \text{s}^{-1/2} \cdot \text{m}^{-1}$)</th>
<th>$n_{\text{pro}}$</th>
<th>$R_{\text{ct}}$ ($\Omega \cdot \text{cm}^2$)</th>
<th>$C_{\text{PEdl}}$ ($\mu \text{F} \cdot \text{cm}^{-2} \cdot \text{s}^{-1/2} \cdot \text{m}^{-1}$)</th>
<th>$n_{\text{dl}}$</th>
<th>Chi-squared</th>
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<tr>
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<td>--</td>
<td>--</td>
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<td>--</td>
<td>--</td>
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Table 4
EIS analysis parameters after immersion for 1 and 12 h in 0.05 M NaCl.

<table>
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<tr>
<th>Time period (h)</th>
<th>Samples</th>
<th>$R_{\text{tel}}$ (Ω cm$^2$)</th>
<th>$R_{\text{coat}}$ (Ω cm$^2$)</th>
<th>$\text{CPE}_{\text{coat}}$ (µF cm$^{-2}$ s$^{-1}$)</th>
<th>$n_{\text{coat}}$</th>
<th>$R_{\text{ps}}$ (Ω cm$^2$)</th>
<th>$\text{CPE}_{\text{ps}}$ (µF cm$^{-2}$ s$^{-1}$)</th>
<th>$n_{\text{ps}}$</th>
<th>$R_{\text{ct}}$ (Ω cm$^2$)</th>
<th>$\text{CPE}_{\text{dl}}$ (µF cm$^{-2}$ s$^{-1}$)</th>
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<th>Chi-squared</th>
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<tr>
<td>1 h</td>
<td>Al 2024</td>
<td>78</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>9522</td>
<td>561.43</td>
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<td>0.0013</td>
<td></td>
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<td>12 h</td>
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<td>-</td>
<td>-</td>
<td>-</td>
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</tbody>
</table>

corrosion resistance of the titania-Ag coating and titania coating is similar and is about 3 times in 0.5 M NaCl. Based on the Bode-phase plot, less absorption of water and penetration of chloride ions in 0.05 M NaCl produce the capacitive behavior on the titania-Ag and titania-silica-Ag coatings compared to the titania coating. In the three solutions, formation of protective layers from the corrosion products gives rise to larger corrosion resistance on the titania-silica-Ag coatings compared to the titania coating. In the time constants at low frequencies for immersion time of 1 and 12 h indicating the stability of the corrosion mechanism. The negative charges on the coating leads to more intense reactions with calcium and potassium compounds and formation of a protective oxide layer on aluminum. This behavior leads to higher corrosion resistance on all three coatings in Ringer's solution with more chloride ions than 0.05 M NaCl.

Table 5
Released Al (mg/l-cm$^2$) from the coatings after EIS at 1 and 12 h immersion in the three different solutions.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Immersion time (h)</th>
<th>Al 2024 Titania nanostructured coating</th>
<th>Titania-Ag nanostructured coating</th>
<th>Titania- Silica- Ag nanostructured coating</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 M NaCl</td>
<td>1 h</td>
<td>1.7482 0.0042</td>
<td>0.0038</td>
<td>0.0021</td>
</tr>
<tr>
<td></td>
<td>0.05 M NaCl</td>
<td>0.9541 0.0021</td>
<td>0.0016</td>
<td>0.0008</td>
</tr>
<tr>
<td>Ringer’s solution</td>
<td>0.5 M NaCl</td>
<td>3.1926 0.0193</td>
<td>0.0082</td>
<td>0.0075</td>
</tr>
<tr>
<td></td>
<td>0.05 M NaCl</td>
<td>2.5418 0.0098</td>
<td>0.0041</td>
<td>0.0048</td>
</tr>
<tr>
<td>Ringer’s solution</td>
<td></td>
<td>2.9527 0.00125</td>
<td>0.0064</td>
<td>0.0036</td>
</tr>
</tbody>
</table>

Table 6
Critical loads of coatings after immersion for 1 and 12 h in three different solutions.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Immersion time (h)</th>
<th>Titania nanostructured coating</th>
<th>Titania-Ag nanostructured coating</th>
<th>Titania- Silica- Ag nanostructured coating</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 M NaCl</td>
<td>1</td>
<td>17</td>
<td>15</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>Failed</td>
<td>Failed</td>
<td>16</td>
</tr>
<tr>
<td>Ringer’s solution</td>
<td>1</td>
<td>18</td>
<td>17</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>14</td>
<td>16</td>
<td>23</td>
</tr>
<tr>
<td>0.05 M NaCl</td>
<td>1</td>
<td>17</td>
<td>18</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>15</td>
<td>14</td>
<td>19</td>
</tr>
</tbody>
</table>

Si – $\text{O} - \text{H} + \text{OH}^- \rightarrow \text{O} - \text{Si} - \text{O} + \text{H}_2$  (2)

Si – $\text{O}^- + \text{H}_2\text{O} \rightarrow \text{SiO}_2 + \text{OH}^-$  (3)

2 The presence of composites with negative charges on the surface prevents penetration of chloride ions by creating a repellent leading to improved corrosion resistance.

In Ringer’s solution, calcium and potassium ions activate the mechanisms during the first hour of immersion. There is no change in the time constants at low frequencies for immersion time of 1 and 12 h indicating the stability of the corrosion mechanism. The...
4. Conclusion

The corrosion behavior of titania, titania-Ag, and titania-silica-Ag deposited on Al 2024 by the sol-gel method is investigated by EIS in 0.05 M NaCl, 0.5 M NaCl, and Ringer’s solutions. The morphology of the coating becomes coarser with addition of Ag and addition of potassium ions expedite the formation of a protective layer during the first hour of immersion. Less penetration of corrosive chloride ions and less absorption of water reduce access of the solution to the substrate giving rise to smaller release of Al ions, for instance, decreasing adhesion due to formation of corrosion products at the interface between the coating and substrate is clearly observed from the titania and titania-Ag coatings and the adhesion strength decreases by about 100% especially in 0.5 M NaCl.

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References