Investigation of the corrosion resistance of composite ZrO_2–Al_2O_3–Sm_2O_3 films obtained by sol-gel method on aluminum alloy A356

Angel Velikov, Stancho Yordanov, Vladimir Petkov, Shaban Uzun, Boiko Krastev,
Institute of Metal Science, Equipment, and Technologies “Acad. A. Balevski” with Center for Hydro- and Aerodynamics at the Bulgarian Academy of Sciences, 67 "Shipchenski prohod" str., 1574 Sofia, Bulgaria
e-mail: stancho14@abv.bg

Abstract: *Corrosion remains a major limitation for the long-term use of aluminum alloys such as A356, particularly in chloride-rich environments. Although traditional chromate coatings provide effective protection, their toxicity necessitates environmentally friendly alternatives. In this study, a composite ZrO_2–Al_2O_3–Sm_2O_3 coating was synthesized via a sol-gel method and deposited on A356 alloy using dip-coating. The precursor system was formulated from zirconyl chloride, samarium oxide, and aluminum oxide, stabilized with acetylacetone and acetic acid at pH 0.5 to ensure homogeneous film formation. The coated samples were thermally treated at 400 °C to obtain dense oxide layers. Corrosion resistance was assessed under neutral salt spray conditions (5% NaCl, 35 °C, 648 h) according to BDS EN ISO 9227:2023. Comparison between uncoated A356, binary Al–Zr (ADZ), and ternary Sm–Al–Zr (SADZ) coatings demonstrated a clear performance improvement with increasing film complexity. While ADZ coatings reduced surface damage relative to the bare alloy, the SADZ films exhibited the lowest amount of corrosion products, minimal surface darkening, and significantly reduced pitting. The enhanced performance is attributed to the synergistic effect of the three oxides: ZrO_2 provides chemical stability, Al_2O_3 increases layer density, and Sm_2O_3 contributes active corrosion inhibition.*

Overall, the ZrO_2–Al_2O_3–Sm_2O_3 composite film offers a promising non-chromate protective system for improving the long-term corrosion resistance of A356 aluminum alloy.

***Keywords**: CORROSION RESISTANCE, A356, SOL-GEL, ZrO_2–Al_2O_3–Sm_2O_3*

1. Introduction

Corrosion of aluminum alloys remains a key challenge in their industrial application, especially in environments with high concentrations of chloride ions. Aluminum alloys such as A356 are preferred materials in the automotive and aerospace industries due to their low density, good castability, and acceptable strength. However, their natural corrosion resistance is insufficient for long-term operation in aggressive environments, which necessitates the use of protective coatings. Traditional chromate coatings demonstrate high efficiency, but their toxicity and the restrictions imposed by environmental regulations require the search for non-toxic and sustainable alternatives [1,2,3]. One of the most promising approaches for protecting aluminum alloys is the deposition of oxide coatings using the sol-gel method. This technology allows precise control over the chemical composition, morphology, and thickness of the layer, while also enabling the incorporation of additional protective compounds. Sol-gel films can form dense, porous, or self-healing barrier layers that effectively reduce the contact of the metal surface with corrosion-active ions [4,5]. The ability of sol-gel coatings to be chemically and structurally modified makes them particularly suitable for the creation of multilayer and composite systems with high corrosion resistance [4,5,7].

Zirconium oxides (ZrO_2) are among the most attractive materials for corrosion protection due to their chemical stability, low solubility, and excellent barrier properties. Studies on aluminum alloys such as AA2024 show that ZrO_2 films deposited via sol-gel significantly reduce the corrosion current with an increasing number of layers [4,6]. When ZrO_2 is combined with Al_2O_3, an additional decrease in porosity and an increase in layer density are observed, forming a strong and compact surface network with high adhesion to the metallic substrate [5,6]. Aluminum oxide (Al_2O_3) provides additional structural stability and durability to the coating by “sealing the pores” and reducing the penetration of corrosion-active ions. Multilayer systems containing Al_2O_3 and ZrO_2 exhibit high impedance resistance when exposed to NaCl solutions and significantly improved corrosion resistance [5,6,7]. This combination provides both barrier and mechanical protection while also creating a suitable base for the incorporation of active corrosion inhibitors.

The rare-earth element samarium (Sm) is an active corrosion inhibitor capable of forming insoluble oxides or hydroxides that passivate cathodic sites. Multicomponent layers including Sm and SiO_2, deposited on aluminum alloys such as AA3003, demonstrate significant reduction in corrosion current and improved long-term protection [8,9]. Furthermore, rare-earth salts, including Sm acetates, show inhibitory effects on the corrosion of alloys such as AA7075 in the presence of NaCl [10]. Classic studies confirm that Sm^{3+} reduces the corrosion current through the formation of an oxide/hydroxide coating [11], while modern research indicates that rare-earth elements can act both as a barrier layer and as an active inhibitor, enabling self-healing of the protective film [12].

Despite extensive research on ZrO_2- and Al_2O_3-based coatings and separate studies on active protection using Sm, the combination of these three components (ZrO_2–Al_2O_3–Sm_2O_3) remains insufficiently explored. Such a trilayer composite film could unite the barrier protection of ZrO_2, the density and structural stability of Al_2O_3, and the active self-healing effect of Sm_2O_3, providing significantly improved and long-lasting corrosion resistance for aluminum alloys such as A356.

The present study focuses on evaluating the behavior of a composite ZrO_2–Al_2O_3–Sm_2O_3film deposited via the sol-gel method on A356 aluminum alloy. The analysis includes the chemical composition of the layer and its ability to provide corrosion protection, considering it as a potential environmentally friendly alternative to traditional chromate coatings. The combination of ZrO_2, Al_2O_3, and Sm_2O_3 in a single composite film enables simultaneous barrier, structural, and active protection of the metal surface. ZrO_2 provides mechanical strength and chemical resistance, Al_2O_3 contributes thermal stability and additional corrosion protection, while Sm_2O_3 may participate in active corrosion-inhibiting processes. The integration of these components into a single layer has the potential to significantly enhance the durability and corrosion resistance of the A356 aluminum alloy.

2. Experimental procedure

For the synthesis, zirconyl chloride octahydrate ($ZrOCl_2 \cdot 8H_2O$), samarium oxide (Sm_2O_3), nitric acid (HNO_3), acetic acid (CH_3COOH), and distilled water were used. All reagents were of analytical grade and were used without further purification. $ZrOCl_2.8H_2O$ (8.048 g) was dissolved in 35 mL of absolute ethanol C_2H_5OH (99.9%). The solution was homogenized under magnetic stirring for 1 h and then left to rest for an additional 2 h to ensure complete dissolution and stabilization at room temperature.

Sm_2O_3 (0.527 g) was added to 15 mL of deionized water. To the suspension, 2.5 mL of concentrated HNO_3 was added, ensuring its complete dissolution through the conversion of Sm_2O_3 into $Sm(NO_3)_3$, resulting in a clear solution. The obtained transparent solution was used without further processing.

Al_2O_3 (0.255 g) was dispersed in 15 mL of deionized water, followed by the addition of 2.5 mL of HNO_3. The acid treatment improved the surface activity of the particles, facilitating the formation of a stable aqueous dispersion.

The precursors were combined in the following sequence: the $ZrOCl_2$ solution was successively mixed with the nitrate solution of Sm and the Al_2O_3 dispersion under continuous stirring. To the resulting mixture, 3 mL of acetylacetone (AcAc) was added as a stabilizing agent and 2.5 mL of glacial acetic acid (AcOH) to adjust acidity and stabilize the metal complexes. The final pH of the system was adjusted to 0.5, which prevented hydrolysis and precipitation of the highly charged metal ions and ensured a stable, homogeneous precursor. All processes were carried out at room temperature. The resulting homogeneous mixture was left to age for 20 hours before use.

Samples of aluminum alloy A356 were cleaned in an ultrasonic bath with 99.9% ethyl alcohol for 15 minutes and acetone for 15 minutes, and then dried. The prepared sol-gel was deposited onto the A356 samples using a dip-coating technique at a withdrawal speed of 8 cm/min and a 30-second dwell time. After deposition, the wet films were dried at 100°C for 50 minutes to remove residual solvents. The coating process was repeated for 1–3 layers to achieve the desired thickness. The coated samples were subsequently heat-treated in air at 400°C for 1 hour and 50 minutes.

3. Results and Discussion

The corrosion resistance of composite ZrO_2– Al_2O_3–Sm_2O_3 films on A356 aluminum alloy was evaluated under neutral salt spray conditions according to BDS EN ISO 9227:2023. Six coated samples and one uncoated reference sample were tested. The samples were coded as follows:

- **0-Al** – uncoated A356 alloy
- **1-ADZ, 2-ADZ, 3-ADZ** – Al–Zr coated samples
- **1-SADZ, 2-SADZ, 3-SADZ** – Sm–Al–Zr coated samples

Testing was performed in a Q-FOG CCT1100 chamber (USA) in a neutral 5% NaCl solution (pH 6.5–7.2) at 35.0 °C for 648 h. Visual inspections of the sample surfaces were performed before testing and at 180, 312, and 648 h (Appendix 1). After the exposure, a qualitative assessment of the coatings was performed according to BDS EN ISO 10289:2006.

3.1. Visual Observations

- **0-Al (uncoated)**: Dense white to gray corrosion products formed on the surface. After removal of corrosion products, more than 50% of the surface exhibited darkening and moderate pitting / Figure 1/.

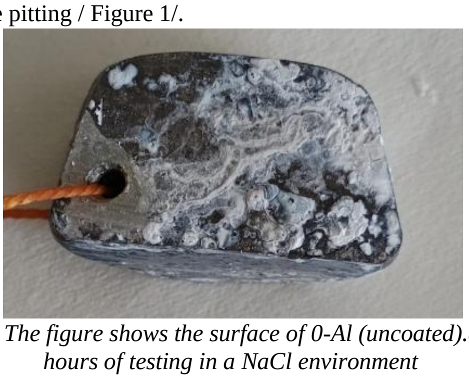

Figure 1. *The figure shows the surface of 0-Al (uncoated).after 648 hours of testing in a NaCl environment*

- **ADZ-coated samples**:
  - *1-ADZ*: Sparse white/gray corrosion products; minor surface darkening, shallow pitting, and few star-shaped defects. / Figure 2/
  - *2-ADZ*: Dense white/gray corrosion products; moderate color change, minor surface pitting, and few star-shaped defects.
  - *3-ADZ*: Dense white/gray corrosion products; slight surface darkening, very minor pitting, and few star-shaped defects.

Figure 2. *The figure shows the surface of 1-ADZ after 648 hours of testing in a NaCl environment*

- **SADZ-coated samples**:
  - *1-SADZ*: Small white/gray corrosion products; moderate surface darkening, very minor pitting. /Figure 3/
  - *2-SADZ*: Very thin white corrosion layer; moderate surface darkening, moderate pitting, very few star-shaped defects.
  - *3-SADZ*: Negligible white corrosion products; very minor surface darkening, moderate surface pitting.

The degree of surface degradation was assessed according to BDS EN ISO 10289:2006 using Rp and RA scales:

Figure 3. *The figure shows the surface of 1-SADZ.after 648 hours of testing in a NaCl environment*

3.2. Discussion

The results indicate that all coatings improved the corrosion resistance of A356 compared to the uncoated alloy. ADZ coatings reduced the amount of corrosion products and surface degradation, but some moderate pitting and defects were still observed.

SADZ coatings, containing Sm in addition to Al and Zr, demonstrated the best performance. They exhibited minimal corrosion product formation, very limited surface darkening, and fewer pitting defects. This improvement suggests that the incorporation of Sm into the Al–Zr matrix enhances the barrier properties of the films, likely by increasing their chemical stability and adhesion to the substrate.

The visual observations correlate with the protective mechanism of ternary oxide coatings: denser and more uniform layers act as effective physical barriers to chloride ion penetration, slowing the corrosion processes. The differences between ADZ and SADZ films highlight the beneficial effect of rare-earth oxide (Sm_2O_3) addition in enhancing corrosion resistance.

Overall, the study confirms that Sm–Al–Zr sol-gel coatings provide superior protection for A356 aluminum alloy under neutral salt spray conditions, making them promising candidates for applications requiring enhanced corrosion resistance.

4. Conclusion

The present study demonstrates that composite ZrO_2–Al_2O_3–Sm_2O_3 films synthesized via the sol-gel method provide a significant improvement in the corrosion resistance of A356 aluminum alloy when exposed to an aggressive chloride environment. Neutral salt spray testing for 648 h revealed that all coated samples outperform the uncoated alloy; however, the protective efficiency strongly depends on the film composition.

Binary Al–Zr (ADZ) coatings offer a noticeable reduction in surface corrosion, limiting the formation of white/gray corrosion products and decreasing the severity of pitting. Nevertheless, localized defects and moderate surface darkening remain visible, indicating that barrier protection alone is insufficient for long-term performance.

The ternary Sm–Al–Zr (SADZ) films exhibit the highest corrosion resistance. These coatings show minimal accumulation of corrosion products, reduced darkening, and substantially less pitting damage. The enhanced behavior is attributed to the synergistic effect of the three oxides: ZrO_2 provides chemical and mechanical stability, Al_2O_3 increases compactness and reduces porosity, while Sm_2O_3 contributes active corrosion inhibition through the formation of insoluble samarium compounds at cathodic sites. This combination results in a dense, adherent, and partially self-healing protective layer.

Overall, the results confirm that ZrO_2–Al_2O_3–Sm_2O_3 sol-gel coatings represent a promising non-chromate alternative for the long-term protection of A356 aluminum alloy. Their multifunctional protective action—combining barrier, structural, and active inhibition mechanisms—makes them suitable for applications where aluminum components are exposed to chloride-rich environments and strict environmental regulations limit the use of chromate-based treatments.

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