Electrochemical and Salt Spray Testing of Hybrid Coatings Based on Si and Zr Deposited on Aluminum and Its Alloys

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While aluminum has good corrosion resistance in seawater, its high-strength alloys in the 2xxx (Al-Cu-Mg) and 7xxx series (Al-Zn-Mg) are normally not recommended for use under these conditions. Since there is an ongoing need for lightweight, high-strength materials, the possibility of using alloys other than those of the series 5xxx (Al-Mg-Mn), 6xxx (Al-Mg-Si) normally recommended for sea-coast applications has to be considered.

Aluminum and its alloys are highly susceptible to oxidation, resulting in the passivation of the surface by a 0.01 to 10 μm thick oxide layer when exposed to air. This naturally formed oxide protects aluminum under atmospheric conditions. Passivation of the alloys is, however, less effective. Due to the presence of unevenly distributed intermetallic particles (IMPs), the passive film is, overall, thinner and less uniform. IMPs such as Al2CuMg, Al-Cu-Mn-Fe, Al3Cu, Al2Fe, MgSi2, MgZn2, create local galvanic cells that promote corrosion on the surface. Al2O3 is a good insulator but, when containing IMPs, is a semiconductor that allows limited passage of electrons. High concentrations of chloride ions allow localized breakdown of the aluminum oxide film, most commonly observed as pitting, crevice or intergranular corrosion.

Al alloys have been protected for decades using chromate conversion coatings. In the last decade these coatings have been widely prohibited within and outside the EU due to the fact that hexavalent chromium is a toxic, carcinogenic and environmentally hazardous compound. Other environmentally hazardous compounds, such as volatile organic compounds (VOCs) used, for example, in the painting industry, have also been subject to stricter regulations. The need therefore exists for non-toxic, environmentally friendly surface treatments capable of providing corrosion protection.

Sol-gel systems are one of the options for replacing chromate-based pre-treatments and reducing the use of VOCs. The sol-gel process is convenient for synthesising oxide films from alkoxysilyl containing materials via continuous reaction steps of hydrolysis and (poly)condensation. The sol-gel process allows incorporation of organic molecules inside the inorganic network, thereby forming organic-inorganic hybrid materials. These have several advantages such as curing at relatively low temperatures of less than 200 C, and the fact that the process is inexpensive and easy, especially when compared to deposition techniques involving vacuum. Low temperature curing of the coating is important also for the underlying substrate which undergoes artificial ageing at temperatures between 100 and 200°C.

Sol-gel coatings based specifically on the precursors tetraethyl orthosilicate (TEOS) and 3-methacryloxypropyl trimethoxysilane (MAPTMS) show good corrosion protection. Their anti-corrosion properties can be improved by adding non-silicon, metal alkoxides such as zirconium tetrapropoxide and methacrylic acid were added. Short- and long-term electrochemical behavior was assessed. The degree of protection was dependent on the sol composition, ageing time and curing temperature. A coating containing Zr/Si ratio of 0.41, aged for 48 h and cured at 100°C exhibited the best combination of resistance towards general and localized corrosion. Electrochemical parameters obtained under polarization (corrosion current density of 4.4 nanA/cm² and stability up to 7 V), and under open circuit conditions (impedance in the few tens of Mohm cm² after one week immersion) proved that the protection was high. At other conditions, such as higher Zr/Si ratios, shorter ageing time or curing at room temperature, protection was excellent after early immersion but then lessened rapidly. Coatings prepared under optimal conditions provided a high degree of protection over 500 hours salt spray testing, especially on aluminum metal. These coatings have the potential to provide good protection in chloride environments.

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and for increasing the ZTP/MAA ratio that determines the degree of chelation. In order to test the possibilities for the use of these hybrid coatings we continue the study, using the same type of Si and Zr hybrid coatings, but expanding their composition and ageing/curing conditions and examining other substrates and another solution. In the present study the coatings were deposited on aluminum and two alloys, AA2024-T3 and AA7075-T6, and studied electrochemically in 0.5 M NaCl solution as an approximation to seawater conditions. All coatings were aged under daylight to enable UV-induced polymerization. The effects of ZTP and MAAN contents, ageing time and curing temperature were studied. In addition to electrochemical potentiodynamic measurements and electrochemical impedance spectroscopy (EIS), salt spray chamber testing was employed to assess the long-term stability to 500 h exposure.

### Experimental

**Chemicals.—** The chemicals used in sol-gel synthesis were tetraethyl orthosilicate (TEOS: Si(OCH3)4, 99.9%, Aldrich), 3-methacryloxypropyl trimethoxysilane (MAPTMS: H2C=CH2(C2H5)OCH2Si(OCH3)3, ≥ 98% Sigma), zirconium tetrapropoxide (ZTP: Zr(OC2H5)4, 70 wt. %, in 1-propanol, Aldrich), methacrylic acid (MAA: H2C=CH2(COOH, 99.0% Aldrich), deionized water Milli-Q Direct, resistivity 18.2 MΩ cm at 25°C, (Millipore, Billerica, MA) and hydrochloric acid (HCl: > 37%, AppliChem). Chemicals sodium chloride (NaCl), sodium hydroxide (NaOH) and HCl used for electrochemical and salt spray experiments were of p.a. quality and supplied by AppliChem (Darmstadt, Germany).

**Synthesis of sols and deposition of coatings.—** Organic-inorganic hybrid coatings were synthesized according to previous studies, by combining two, separately prepared, alkoxide sols (Sol 1 and Sol 2). Sol 1 is a mixture of TEOS and MAPTMS hydrolysed under acid conditions. Sol 2 is a mixture of ZTP and MAAN. Sol 1 and Sol 2 were combined to give a hybrid sol-gel solution denoted as TMZ (TEOS, MAPTMS and ZTP). Compositions of TMZ sols are summarized in Table I.

**Substrate materials.—** Aluminum (99.0 wt. %) was supplied in the form of 1.0 mm thick sheets (GoodFellow Cambridge Ltd., UK). Aluminum alloys 2024-T3 (AA2024-T3) and 7075-T6 (AA7075-T6) were supplied in the form of 0.5 mm thick sheets (Kaiser Aluminum, USA). The certified compositions of these alloys are given in Table II.

Discs of diameter 14 mm were cut from the sheets, then ground successively with 2400- and 4000-grit SiC emery papers (Stuers, United Kingdom), rinsed thoroughly with deionized water and cleaned ultrasonically in ethanol for 10 minutes.

**Deposition and curing of the coatings.—** After synthesis the TMZ sols were aged, applied in the form of coating on the substrate using a spin coater (Laurell WS-650-23NPP/LITE/IND) and then cured as described. Different ageing and curing treatments were used (Table I). Sols TMZ-1 to TMZ-5 were aged for 48 h before application in the form of coating and cured at 100°C for 1 h. Curing at room temperature was also examined (TMZ-5*). TMZ-6a differed from other sols in that the ageing time was only 1 h and samples were cured at 100°C (TMZ-6a) or room temperature (TMZ-6a*). For the sake of comparison, the TMZ-5 coating was aged for 1 h and cured at room temperature (TMZ-5a) or at 100°C on a preheated hot plate (TMZ-5a*). All coatings were cured under daylight to stimulate polymerization and densification due to presence of UV component compared to curing in the dark.

**Electrochemical measurements.—** A three-electrode standard corrosion cell (Corrosion Cell Kit, model K0047, volume 1 L, EG&G) was used, at 25°C, for electrochemical measurements. The working electrode was embedded in a Teflon holder (model K0105 Flat Specimen Holder Kit, EG&G), leaving an area of 0.95 cm² exposed to the solution. A saturated calomel electrode (SCE, 0.241 V vs. Saturated Hydrogen Electrode), placed in a Luggin capillary, was used as reference electrode. All potentials in the text refer to the SCE scale. Carbon rods served as counter electrode. Electrochemical experiments were carried out with an Autolab PGSTAT 12 (Metrohm Autolab, Utrecht, The Netherlands) potentiostat/galvanostat controlled by Nova 1.10 software.

The electrochemical measurements were made in 0.5 M NaCl, pH = 5.9 prepared using Milli-Q Direct water.

**Linear polarization and potentiodynamic polarization measurements.—** Prior to measurements, samples were allowed to stabilize under open circuit conditions for approximately 1 hour to bring them to equilibrium. During that time, the open circuit potential (Eoc) was measured as a function of time. Electrochemical measurements were carried out following stabilization.

### Table I. The concentrations of zirconium tetrapropoxide (ZTP) and methacrylic acid (MAA), and the ratios ZTP/MAA and Zr/Si (ZTP/MAPTMS + TEOS) used in the synthesis of TMZ hybrid sol-gel solutions. The concentrations of silicon precursors TEOS and MAPTMS were constant (0.18 and 1 mol). Sols were aged for 1 h or 48 h before application to the substrate. After application the coatings were cured at room temperature or 100°C.

| Name   | ZTP [mol] | MAA [mol] | ZTP/MAA | Zr/Si | Ageing [h] | Curing [°C] |
|--------|-----------|-----------|---------|-------|------------|-------------|
| TMZ-1  | 0.06      | 0.12      | 0.5     | 0.05  | 48         | 100         |
| TMZ-2  | 0.12      | 0.12      | 1       | 0.10  | 48         | 100         |
| TMZ-3  | 0.48      | 0.12      | 4       | 0.41  | 48         | 100         |
| TMZ-4  | 0.48      | 0.48      | 1       | 0.41  | 48         | 100         |
| TMZ-5  | 0.48      | 0.96      | 0.5     | 0.41  | 48         | 100         |
| TMZ-5* | 0.48      | 0.96      | 0.5     | 0.41  | 48         | room T      |
| TMZ-5a | 0.48      | 0.96      | 0.5     | 0.41  | 1          | 100         |
| TMZ-6a | 0.06      | 1.92      | 0.5     | 0.81  | 1          | 100         |
| TMZ-6a*| 0.06      | 1.92      | 0.5     | 0.81  | 1          | room T      |

### Table II. Certified composition of aluminum alloy substrates.

| Alloy     | Si  | Fe  | Cu  | Mg  | Mn  | Zn  | Cr  | other | Al  |
|-----------|-----|-----|-----|-----|-----|-----|-----|-------|-----|
| AA2024-T3 | 0.09| 0.25| 4.35| 1.33| 0.53| 0.1 | -   | -     | 93.28|
| AA7075-T6 | -   | 0.21| 1.67| 2.55| -   | 5.81| 0.19| 0.08  | 89.41|
Table III. Electrochemical corrosion parameters measured in 0.5 M NaCl for uncoated aluminum and coated with TMZ coatings after 1 h stabilization at the open circuit potential: polarization resistance ($R_p$), corrosion current density ($i_{corr}$), cathodic and anodic Tafel slopes ($\beta_c$, $\beta_a$), corrosion potential ($E_{corr}$), pitting potential ($E_{p pit}$) and difference in potentials ($\Delta E = E_{p pit} - E_{corr}$). Results are presented as mean value ± standard deviation. Composition of the coatings and conditions of ageing and curing are given in Table I.

| Substrate | $R_p$ [MΩ cm²] | $i_{corr}$ [nA/cm²] | $\beta_c$ [mV/dec] | $\beta_a$ [mV/dec] | $E_{corr}$ [V] | $E_{p pit}$ [V] | $\Delta E$ [V] |
|-----------|----------------|---------------------|-------------------|-------------------|---------------|----------------|--------------|
| Al        | 0.008 ± 0.001  | 351.3 ± 30.5        | 55 ± 5            | 64 ± 4            | −0.78 ± 0.01  | −0.70          | 0.08         |
| TMZ-1     | 6.9 ± 1.6      | 5.7 ± 0.4           | 270 ± 33          | 308 ± 28          | −0.73 ± 0.02  | /              | > 7.9        |
| TMZ-2     | 9.7 ± 1.8      | 3.2 ± 0.2           | 240 ± 35          | 239 ± 21          | −0.60 ± 0.03  | /              | > 7.9        |
| TMZ-3     | 9.0 ± 2.0      | 4.4 ± 0.2           | 274 ± 26          | 304 ± 22          | −0.71 ± 0.02  | /              | > 7.9        |
| TMZ-4     | 10.1 ± 3.1     | 3.8 ± 0.4           | 250 ± 34          | 256 ± 34          | −0.71 ± 0.05  | 0.28           | 0.99         |
| TMZ-5     | 17.4 ± 2.9     | 1.8 ± 0.1           | 185 ± 16          | 197 ± 21          | −0.70 ± 0.03  | 0.29           | 0.99         |
| TMZ-5*    | 24.5 ± 1.6     | 1.5 ± 0.1           | 184 ± 15          | 133 ± 8           | −0.74 ± 0.02  | /              | > 7.9        |
| TMZ-5a    | 6.2 ± 2.2      | 4.7 ± 0.2           | 207 ± 15          | 210 ± 19          | −0.81 ± 0.03  | 0.04           | 0.85         |
| TMZ-5a*   | 15.2 ± 1.8     | 1.5 ± 0.1           | 130 ± 9           | 126 ± 14          | −0.74 ± 0.04  | −0.55          | 0.19         |
| TMZ-6a    | 99.9 ± 5.8     | 0.2 ± 0.08          | 105 ± 12          | 109 ± 12          | −0.75 ± 0.03  | −0.21          | 0.54         |
| TMZ-6a*   | 258.4 ± 20.8   | 0.1 ± 0.05          | 153 ± 8           | 151 ± 13          | −0.60 ± 0.06  | −0.05          | 0.55         |

Results

The corrosion protection of aluminum and its two alloys, AA2024-T3 and AA7075-T6, was examined in terms of coating composition, ageing and curing conditions aiming to explore the use of these materials in chloride environment.

Electrochemical potentiodynamic measurements on aluminum.— The effect of composition of the coating.— The values of $R_p$ of only a few kΩ cm² and of $i_{corr}$ in the range of several hundreds of nA cm⁻² for uncoated aluminum confirm its poor corrosion resistance (Table III). At potentials more positive than $E_{corr}$ a constant increase in current density was observed indicating pitting of aluminum (Fig. 1). The aluminum surface is thus not stable and requires additional corrosion protection. First, coatings containing different amounts of ZTP (0.06, 0.12 and 0.48 mol) at constant MAA content (0.12 mol) were considered (TMZ-1, TMZ-2 and TMZ-3). The coatings were prepared from aged sols and cured for 1 h at 100 °C. Coated samples exhibited $R_p$ values three orders of magnitude greater than that for uncoated aluminum, reaching between 6.9 and 9.6 MΩ cm². The shape of the polarization curves (Fig. 1) of coated samples shows that the coatings act as a barrier substrate and chloride medium, with values of $i_{corr}$ smaller by four orders of magnitude (from 3.25 to 5.75 nA cm⁻²).

Salt spray test.— Selected samples, i.e. TMZ-3 and TMZ 6a*, deposited on aluminum and aluminum alloys substrates were tested by salt spray testing. The salt spray chamber had 0.17 m³ capacity (ASCOTT, Staffs, Great Britain) and was operated according to the standard. The pH of NaCl solution (50 ± 1% g/L) was set between 6.0 and 6.5 at room temperature to give values of pH between 6.5 and 7.2 after heating the solution to 35 °C. pH was adjusted with 0.1 M NaOH or HCl solutions.

The device for spraying the salt solution comprised a supply of clean air of controlled pressure and humidity, a reservoir to contain the solution to be sprayed and a single sprayer. The compressed air was passed through a filter to remove all traces of oil or solid matter. The temperature of the hot water in the saturation tower was 46 °C and the overpressure 85 kPa. The temperature in the salt spray chamber was set to 35 °C ± 2 °C. Each test lasted for 21 days.

The samples were taken from the chamber every 24 hours and photographed (Canon digital camera).
Effects of ageing time and curing temperature.—The effects of ageing time and curing temperature on the corrosion properties of coated aluminum substrates were investigated. Coatings were aged for 48 h and then cured at 100 °C (TMZ-5) or at room temperature (TMZ-5a), and for only 1 h and then cured at 100 °C (TMZ-5a) or at room temperature (TMZ-5a*) (Table III and Fig. 3). A longer ageing time is shown to be essential to achieving good protection, especially for curing at room temperature, at which the best results, i.e. the largest $R_p$ value and smallest values of $i_{corr}$ and $E_{pit}$ > 7.9 V, were achieved (TMZ-5). Curing at 100 °C exhibited only slightly poorer $R_p$ and $i_{corr}$ values but the coating started to break down already at 0.29 V (TMZ-5). Coatings prepared from fresh sol (TMZ-5a and TMZ-5a*) both exhibited results that were poorer than those from aged sols; the values of current density being greater and breakdown of the coating appearing earlier at 0.04 V and -0.55 V. These results underline that the ageing process is very important for effective anti-corrosion characteristics of these hybrid coatings in chloride solution. Similar behavior was observed in Harrison’s solution for AA7075-T6 coated with TMZ-5 coating.32 Optimal results were obtained by longer ageing times at room temperature; coatings aged for shorter times could not compete with coatings aged longer times regardless of the curing temperature.

The effect of larger amounts of ZTP and MAA (sol TMZ-6a).—In order to decrease the time of preparation of the coating, ageing of the sol was accelerated by adding larger amounts of ZTP and MAA (sol TMZ-6a). TMZ-6a was aged for only 1 h as opposed to the 48 h used for sols TMZ-1 to TMZ-5. The relative effectiveness of corrosion protection of the coatings TMZ-5a, TMZ-5a*, TMZ-6a and TMZ-6a* was determined from the effects of ageing time (1 h and 48 h) and curing temperature (room temperature and 100 °C) (Table III, Fig. 4). For the coatings cured at 100 °C and aged 1 h, increased contents of ZTP and MAA compared to 351.3 nA cm$^{-2}$ for uncoated substrate (Table III). At the same time the value of $E_{corr}$ did not change significantly (Fig. 1). At potentials more positive than the Tafel range, the current density plateau was established at approximately 10$^{-6}$ A cm$^{-2}$. It remained independent of potential up to the high electrode potential of 7 V. This behavior was observed for all three coatings. Coatings TMZ-1 to TMZ-3 thus provide excellent protection of aluminum in chloride solution. The differences between the coatings are small and almost insignificant when compared to that from the uncoated substrate. The behavior is comparable to that observed for corrosion protection of AA7075-T6 in Harrison’s solution.32

The effect of different amounts of MAA (0.12, 0.48 and 0.96 mol) was investigated at constant content of ZTP (n = 0.48 mol) in coatings TMZ-3, TMZ-4 and TMZ-5 respectively. The coatings were prepared from aged sols and then cured for 1 h at 100 °C after deposition. Coated samples exhibited $R_p$ values from 9 to 17.4 MΩ cm$^2$, the value approximately doubling as the content of MAA was increased (Table III). The value of $i_{corr}$ was lower for larger amounts of MAA (Fig. 2). At the same time the $E_{corr}$ value shifted to slightly more positive potentials. The most significant difference between these coatings is the breakdown potential, $E_{pit}$. While the TMZ-3 coating remained stable up to 7 V, coatings TMZ-4 and TMZ-5 exhibited localized breakdown, resulting in $E_{pit}$ values of about 0.3 V (Fig. 2). Thus, despite larger $R_p$ value and a smaller $i_{corr}$ value, increased amounts of MAA led to coatings inferior to that of TMZ-3, due to their susceptibility to localized breakdown.

Effects of ageing time and curing temperature.—The effects of ageing time and curing temperature on the corrosion properties of coated aluminum substrates were investigated. Coatings were aged for 48 h and then cured at 100 °C (TMZ-5) or at room temperature (TMZ-5a), and for only 1 h and then cured at 100 °C (TMZ-5a) or at room temperature (TMZ-5a*) (Table III and Fig. 3). A longer ageing time is shown to be essential to achieving good protection, especially for curing at room temperature, at which the best results, i.e. the largest $R_p$ value and smallest values of $i_{corr}$ and $E_{pit} > 7.9$ V, were achieved (TMZ-5). Curing at 100 °C exhibited only slightly poorer $R_p$ and $i_{corr}$ values but the coating started to break down already at 0.29 V (TMZ-5). Coatings prepared from fresh sol (TMZ-5a and TMZ-5a*) both exhibited results that were poorer than those from aged sols; the values of current density being greater and breakdown of the coating appearing earlier at 0.04 V and -0.55 V. These results underline that the ageing process is very important for effective anti-corrosion
resulted in values of \( R_p \) from 6.2 MΩ cm\(^2\) (TMZ-5a) to \( \approx 100 \) MΩ cm\(^2\) (TMZ-6a) (Table III). The values of \( i_{corr} \) were accordingly smaller. However, the breakdown potential for the TMZ-6a coatings occurred at \(-0.21\ V\), \( \approx 200\ \text{mV} \) more negative than for TMZ-5a. Further improvement in \( R_p \) and \( i_{corr} \) values was observed for the coatings cured at room temperature and aged 1 h, TMZ-5a* and TMZ-6a*. For TMZ-6a*, extreme values of almost 260 MΩ cm\(^2\) and 0.1 nA cm\(^2\) were observed. At the same time the value of \( E_{pit} \) shifted in a more positive direction compared to values obtained after curing at 100 °C (\(-0.21\ V\) for TMZ-6a) and for coatings containing smaller amounts of ZTP and MAA and cured at room temperature (\(-0.55\ V\) for TMZ-5a*).

However, none of the coatings prepared from sols aged for only 1 h (TMZ-5a, TMZ-5a*, TMZ-6a, TMZ-6a*) achieved the stability of coatings prepared from sols aged for 48 h (TMZ-5, TMZ-5*, TMZ-6). This is due to the high electrode potential of 7 V and the current density remained below \( 10^{-6}\ \text{A/cm}^2\). The hybrid coatings described here achieve better corrosion protection of AA2024-T3 than other hybrid sol-gel coatings containing ZrO\(_2\).\(^{19,34}\)

Curing of coatings containing larger ZTP content (TMZ-5*) was also optimal at room temperature for corrosion protection of AA2024-T3 substrate, a high \( R_p \) value in the vicinity of \( E_{corr} \) along with the broad range of stability at high electrode potentials being achieved (Table IV, Fig. 5). Compared to TMZ-5*, TMZ-6a and TMZ-6a* coatings exhibit even larger values of \( R_p \) and smaller \( i_{corr} \) values, but were susceptible to localized breakdown already at \( -0.37\ V\). As with aluminum, TMZ-6a on AA2024-T3 substrate is highly resistant to general corrosion in the vicinity of \( E_{corr} \) but susceptible to breakdown once polarized to anodic potentials.

The TMZ coatings deposited on AA7075-T6 substrates exhibit similar behavior as on AA2024-T3 substrate, except for the TMZ-6a (aged 1 h and cured at 100 °C) and TMZ-6a* (aged 1 h and cured at room temperature) coatings (Table V, Fig. 6). In contrast to aluminum and AA2024-T3 substrates, where extremely high values of \( R_p \) (100–200 MΩ cm\(^2\)) were achieved, the TMZ-6 coatings exhibit values of 0.24 and 1.8 MΩ cm\(^2\) for TMZ-6a and TMZ-6a*, respectively. The shape of the potentiodynamic curves follows that of uncoated substrate.

The presented results show that the TMZ coatings offer barrier protection not only on aluminum but also on two alloys. Comparable performance to coated aluminum is achieved for the 2024-T3 and 7075-T6 alloys coated with TMZ-2, TMZ-3 and, especially, TMZ-5* coatings. It seems therefore that the effect of substrate is largely suppressed due to the good protection properties of the coatings, mainly based on homogeneous coverage of the metal surface and small porosity averaging only 2.3 \( \times \) \( 10^{-5}\%)\).\(^{35}\) Metal inclusions therefore do not affect significantly the effectiveness of the corrosion protection of the TMZ-1–TMZ-5 coatings. For the TMZ-6a coating, which is less stable upon polarization, the influence of substrate is more pronounced.

**Electrochemical potentiodynamic measurements on aluminum.**— EIS was used to study the time dependence of the coating protective performance during long-term immersion of aluminum in the corrosive chloride medium. Coatings were selected to reflect different synthesis and curing conditions, i.e. composition, ageing time and curing temperature. The effectiveness of the coatings on aluminum substrate immersed in chloride solution was followed after 1 hour, and 1, 2, 3 and 7 days of immersion. Bode plots of the impedance, \( Z \), and phase angle, \( \phi \), are presented for the coatings TMZ-3, TMZ-5* and TMZ-6a* (Figs. 7, 8 and 9). At frequencies \( f \) between \( 10^3 \) and \( 10^5\ \text{Hz} \), log \( |Z| \) for the TMZ-3 coating increased linearly as \( f \) decreased, with a slope close to 1 (Fig. 7). The maximum value of \( \phi \) of almost \(-90\)° spanned over a broad range of frequencies indicates the highly capacitive character of the coating. In the range between \( 10^3 \) and \( 10^5\ \text{Hz} \), the impedance reached a plateau. Within one week of immersion the magnitude of this plateau decreased from \( 10^7 \) to \( 2 \times 10^6\ \Omega\ \text{cm}^2\) and \( \phi \) shifted to higher frequencies. These changes indicate the progressive development of a corrosion process through the pores of the coating and at the coating/metal interface. The latter process may be related to the increase observed in the Bode \( \phi \) vs. \( f \) curve in the range between 1 and 100 Hz.

**Table IV.** Electrochemical corrosion parameters measured in 0.5 M NaCl for uncoated AA2024-T3 and coated with TMZ coatings after 1 h stabilization at the open circuit potential: polarization resistance \( (R_p) \), corrosion current density \( (i_{corr}) \), cathodic and anodic Tafel slopes \( (\beta_c, \beta_a) \), corrosion potential \( (E_{corr}) \), pitting potential \( (E_{pit}) \) and difference in potentials \( (\Delta E = E_{pit} - E_{corr}) \). Results are presented as mean value ± standard deviation. Composition of the coatings and conditions of ageing and curing are given in Table 1.

| Substrate  | \( R_p \) [MΩ cm\(^2\)] | \( i_{corr} \) [mA/cm\(^2\)] | \( \beta_c \) [mV/dec] | \( \beta_a \) [mV/dec] | \( E_{corr} \) [V] | \( E_{pit} \) [V] | \( \Delta E \) [V] |
|------------|------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| AA2024-T3  | 0.010 ± 0.002    | 317.3 ± 60.5    | 27 ± 2          | 112 ± 12        | -0.72 ± 0.02    | -0.71           | 0.10            |
| TMZ-2      | 9.7 ± 1.7        | 4.2 ± 0.2       | 254 ± 21        | 255 ± 31        | -0.72 ± 0.03    | /               | > 7.9           |
| TMZ-3      | 5.7 ± 1.3        | 5.6 ± 0.1       | 241 ± 18        | 248 ± 21        | -0.73 ± 0.02    | /               | > 7.9           |
| TMZ-5*a    | 17.9 ± 2.4       | 3.1 ± 0.5       | 329 ± 25        | 314 ± 24        | -0.50 ± 0.01    | /               | > 7.9           |
| TMZ-6a     | 97.2 ± 5.3       | 0.3 ± 0.1       | 161 ± 21        | 170 ± 16        | -0.02 ± 0.03    | /               | > 7.9           |
| TMZ-6a*    | 78.4 ± 3.2       | 0.2 ± 0.05      | 94 ± 8          | 102 ± 7         | -0.88 ± 0.03    | -0.38           | 0.50            |
Table V. Electrochemical corrosion parameters measured in 0.5 M NaCl for uncoated AA7075-T6 and coated with TMZ coatings after 1 h stabilization at the open circuit potential: polarization resistance ($R_p$), corrosion current density ($i_{corr}$), cathodic and anodic Tafel slopes ($\beta_c$, $\beta_a$), corrosion potential ($E_{corr}$), pitting potential ($E_{pit}$) and difference in potentials ($\Delta E = E_{pit} - E_{corr}$). Results are presented as mean value ± standard deviation. Composition of the coatings and conditions of ageing and curing are given in Table I.

| Substrate    | $R_p$ [MΩ cm$^2$] | $i_{corr}$ [nA/cm$^2$] | $\beta_c$ [mV/dec] | $\beta_a$ [mV/dec] | $E_{corr}$ [V] | $E_{pit}$ [V] | $\Delta E$ [V] |
|--------------|-------------------|-------------------------|-------------------|-------------------|----------------|----------------|----------------|
| AA7075-T6    | 0.001 ± 0.001     | 1862 ± 220              | 758 ± 70          | 17 ± 5            | -0.75 ± 0.04   | -0.71          | 0.10           |
| TMZ-2        | 9.7 ± 1.8         | 3.0 ± 0.3               | 284 ± 25          | 188 ± 16          | -0.40 ± 0.03   | /              | > 7.9          |
| TMZ-3        | 19.2 ± 2.1        | 1.0 ± 0.1               | 129 ± 14          | 123 ± 11          | -0.69 ± 0.02   | /              | > 7.9          |
| TMZ-5$^*$    | 34.2 ± 3.8        | 0.8 ± 0.1               | 192 ± 21          | 176 ± 15          | -0.63 ± 0.03   | 3.76           | 4.39           |
| TMZ-6a       | 0.24 ± 0.3        | 35.8 ± 2.4              | 68 ± 5            | 5 ± 3             | -0.71 ± 0.04   | -0.71         | 0              |
| TMZ-6a$^*$   | 1.8 ± 0.8         | 4.7 ± 0.3               | 359 ± 31          | 18 ± 5            | -0.75 ± 0.02   | -0.75         | 0              |

Figure 6. Potentiodynamic polarization curves for uncoated AA7075-T6, and for AA7075-T6 coated with TMZ-2 coating (aged 48 h aged and cured 1 h at 100°C), TMZ-5$^*$ coating (aged 48 h and cured 1 h at room temperature), and TMZ-6a$^*$ coating (aged 1 h and cured 1 h at room temperature). Samples were cured under daylight. dE/dt = 1 mV/s.

and $10^{-2}$ Hz. It is notable, however, that the extent of the impedance plateau remained unchanged, indicating that the corrosion process did not significantly affect the coating structure. Thus, despite signs of slow deterioration of the coating the impedance value still remained in the MΩ cm$^2$ range after one week of immersion.

Figure 7. Bode impedance and Bode phase plots in 0.5 M NaCl for aluminum coated with TMZ-3 coating measured after various immersion times of up to 1 week.

The general shape of the Bode plots of the coating TMZ-5$^*$ was similar to that for the TMZ-3 coating (Fig. 8). However, after already 2 days, the Z values decreased below $10^6$ Ω cm$^2$ and decreased further. The $\phi$ shifted to higher frequencies and the shape of the $\phi$ vs. $f$ curve changed, indicating the progressive deterioration of the coating. At short immersion time, i.e. after 1 h, the TMZ-6a$^*$ exhibited Z values higher by more than one order of magnitude (Fig. 9) compared to TMZ-3 and TMZ-5$^*$ coatings. The maximum $\phi$ of almost $-90^\circ$ spanned over an even broader range of frequencies compared to the TMZ-3, up to $10^5$ Hz. With increasing immersion time the value

Figure 8. Bode impedance and Bode phase plots in 0.5 M NaCl for aluminum coated with TMZ-5$^*$ coating measured after various immersion times of up to 3 days.

Figure 9. Bode impedance and Bode phase plots in 0.5 M NaCl for aluminum coated with TMZ-6a$^*$ coating measured after immersion for times up to 2 days.
of impedance decreased and \( \phi \) shifted to higher frequencies. Despite these changes, after 1 day of immersion was still more than \( 10^7 \, \Omega \, \text{cm}^2 \), i.e. slightly higher than for the TMZ-3 coating (Fig. 7). After one day, however, \( Z \) dropped to values below \( 10^6 \, \Omega \, \text{cm}^2 \), and the shape of the \( \phi \) vs. \( f \) curve changed, indicating the beginning of the corrosion process. Therefore, despite extremely high values of impedance, the coating with high ZTP and MAA contents deteriorated faster than that with smaller ZTP and MAA contents. Typically, coatings with initial resistance above \( 10^7 \, \Omega \, \text{cm}^2 \) provide excellent corrosion protection, while those with resistance lower than \( 10^6 \, \Omega \, \text{cm}^2 \) provide poor corrosion protection.37,38

The porosity of the coatings based on Si and Zr is very low32 and its effect on the coating degradation with immersion time is relatively small. In addition to the coating porosity, another parameter involved in the degradation of the sol-gel coating may be the hydrolysis of the polysiloxane network. For example, coatings containing higher concentration of TEOS were hydrophilic and degraded faster due to the formation of Si(OH)\(_4\) as a product of hydrolysis of SiO\(_2\).39 In the present work this process has been minimized due to high degree of chelation and polymerization, as well as the hydrophobic character of the coating.33,39

**Schematic presentation of the network formation.**— Optimal conditions are shown to exist that ensure the highest resistance towards both general and localized corrosion. While increased contents of ZTP and MAA and shorter ageing times (TMZ-6a) resulted in high stability to general corrosion, the coating, once polarized, was more susceptible to localized breakdown, regardless of the curing temperature (Fig. 4).

Similar results are obtained by EIS measurements under open circuit conditions after only 2 days immersion (Fig. 9). At smaller contents of ZTP and MAA and longer ageing time, the coating cured at room temperature (TMZ-5\(^*\)) exhibited good stability under polarization (Figs. 3, 5 and 6) but deteriorated rapidly during long-term immersion (Fig. 8). The optimal conditions are achieved for coatings with Zr/Si ratio of 0.41, longer ageing time and curing at 100\(^\circ\)C (TMZ-3), both under polarization (Figs. 1 and 2) and long-term immersion conditions (Fig. 7).

The reason for this behavior may be found in the nature of the processes taking place at different temperatures. MAA is involved in three important steps: chelation of ZTP, polymerization of the acrylic group between MAA–MAA or MAA–MAPTMS and passivation of the metal surface by formation of the protective complex.21,32 ZTP affects both inorganic network structure with Si–O–Si and Si–O–Zr bonds, as well as organic structure through coordination with methacrylic acid. Steps of hydrolysis, condensation and network formation including polymerization were explained and schematically presented in our previous study.21 The scheme of formed network is taken herein as a starting point for explanation of role of zirconium in the process of radical polymerization (Fig. 10).

Molecular oxygen acts as an inhibitor of free-radical polymerization. It scavenges the radicals formed during the initiation of polymerization, leading to peroxyl radicals, ROO\(^*\), that are unreactive towards double bonds and thus inhibit the polymerization. Conventional routes to overcoming oxygen inhibition include the use of irradiation, inert gases or special oxygen scavengers. It was reported that ZTP constitutes an alternative to the conventional routes taken to overcome \( O_2 \)
ZTP reacts with peroxyl radicals $\text{ROO}^*$ (Fig. 10) to give a pentavalent alkoxide $(\text{ROO}^*\text{Zr(OR)}_4)$.\textsuperscript{24} In the succeeding step, $\text{ROO}^*$ are converted to propoxyl radical $\text{PrO}^*$, which are the initiating species of radical polymerization.\textsuperscript{31} The reason why the degree of protection varies with Zr/Si content and curing temperature lies in the variation of network formation. Coatings with large ZTP and MAA contents (TMZ-6a, TMZ-6*a) undergo radical polymerization at room temperature, which occurs mainly through polymerization of acrylic group (Fig. 10). However, these coatings readily degrade once exposed to chloride solution. In contrast, coatings with smaller ZTP and MAA contents require higher curing temperatures (TMZ-3) to induce polymerization, which proceeds mainly by condensation where the formation of $\text{Si}−\text{O}−\text{Si}$ and $\text{Si}−\text{O}−\text{Zr}$ bonds are dominant. When coatings with smaller ZTP and MAA contents cured at room temperature (TMZ-5*) the polymerization of organic network again prevails over condensation of inorganic network leading to worse protective properties during longer immersion in chloride solution.

Salt spray testing on aluminum and alloys AA2024-T3 and AA7075-T6.— AA2024-T3 (Fig. 12) and AA7075-T6 (Fig. 13) alloys, bare and coated with TMZ-3 and TMZ-6a*, were compared with aluminum (Fig. 11) after different periods of time in a salt spray chamber. The coatings TMZ-3 and TMZ-6a* are chosen as two extremes in curing and ageing conditions.

Aluminum corroded very rapidly and, after only 16 h, corrosion products were clearly observed on the metal surface. The corrosion process continued, resulting in increasing amounts of corrosion products. On the other hand, aluminum coated with TMZ-3 coating was protected against corrosion, even after 21 days (Fig. 11). No corrosion products were observed, thus confirming good corrosion resistance of the sol-gel coating. The protection of aluminum by TMZ-6a* coating is less effective. The protection is stable up to 7 days but, at longer exposure times, corrosion products were formed on the metal substrate. Therefore, despite good electrochemical results (Table III), protection gradually decreased at longer exposure times, probably due
to dissolution of the coating through the pores, as confirmed by EIS (Fig. 9). Nonetheless, after 7 days the surface appearance of the substrate coated with TMZ-6a coating is comparable to the appearance of uncoated substrate after 16 h exposure, which accounts for the reasonable substrate protection.

AA2024-T3 is poorly resistant to chloride containing media and corroded fast in the salt spray chamber (Fig. 12). Corrosion products were observed after only a few hours and, after 16 h, covered almost the whole surface. In contrast, AA2024-T3 coated with TMZ-3 coating was protected, even after 21 days. Corrosion products were not observed, demonstrating that the sol-gel coating provided good corrosion protection in the salt spray environment. As for Al, the TMZ-6a coating was less effective than the TMZ-3 coating.

AA7075-T6 alloy was even more susceptible to corrosion in chloride media than AA2024-T3 being visibly corroded after only 2 h, with corrosion progressing with time (Fig. 13). The TMZ-3 coating protected the substrate though showing some corrosion defects after 21 days. The TMZ-6a coating was less effective, with corrosion products seen after only one day’s exposure.

Conclusions

The corrosion protection of aluminum-based materials by the hybrid sol-gel coatings is affected by the composition of the sol, as well by the conditions of ageing and curing temperature. For constant conditions of 48 h ageing and curing at 100 °C, the greatest degree of protection was achieved at a Zr/Si ratio of 0.41 (TMZ-3).

When curing at 100 °C, ageing improved the corrosion protection but the effect was much more important for curing at room temperature. Under these conditions the best short-term results for Al and both alloys were obtained for coatings prepared from aged sols (TMZ-5). However, coatings cured at room temperature cannot withstand longer immersion in chloride solution.

The addition of larger amounts of ZTP and MAA (TMZ-6a) is of interest due to the shortening of ageing time to only 1 h. However, the protective ability deteriorates rapidly, the coating showing poorer long-term performance than coatings prepared with smaller ZTP contents, longer ageing and cured at 100 °C. The presented results show that differences in the process of network formation have an important impact on corrosion properties. Condensation resulting in the formation of inorganic network of Si−O−Si and Si−O−Zr bonds and increased cross-linking and polymerization produced by MAA which affects the coating density are both essential for good short- and long-term protection. In terms of $R_p$ and $I_{corr}$ values, the degree of coating protection achieved by hybrid coatings on Al, AA2024-T3 and AA7075-T6 in 0.5 M NaCl is comparable to protection on AA7075-T6 in Harrison’s solution, even though that chloride solution is a more aggressive medium.

Salt spray testing showed aluminum and AA2024-T3, both coated with TMZ-3 coating, to be resistant to corrosion for 500 h operating service. When deposited on AA7075-T6 somewhat poorer results were obtained but still much better than for the uncoated alloy. Overall it has been demonstrated that the described hybrid coatings are applicable for the use of aluminum-based materials in chloride environments.

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