

CORROSION AND CORROSION PROTECTION
OF ALUMINIUM ALLOYS BY ZIRCONIUM
CONVERSION COATINGS

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Doctoral Dissertation
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MEDNARODNA PODIPLOMSKA ŠOLA JOŽEFA STEFANA
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KOROZIJA IN PROTIKOROZIJSKA ZAŠČITA
ALUMINIJEVIH ZLITIN S KONVERZIJSKIMI
PREVLEKAMI NA OSNOVI CIRKONIJA

Doktorska disertacija

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...To my dearest sister Sanja and brother Saša...

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Abstract

The subject of this doctoral dissertation is the corrosion protection of aluminium alloys. Aluminium alloys are important technological materials with excellent mechanical properties but prone to corrosion in chloride and other aggressive environments which may provoke the localized or uniform dissolution of the alloy surface. The susceptibility to corrosion originates from the microstructure of aluminium alloys which contain intermetallic particles added to improve aluminium's mechanical properties; however, the presence of these particles stimulates the corrosion due to the difference in their electrochemical activity. Understanding the corrosion mechanism of aluminium alloys is important as it serves as a basis for postulating the subsequent methodology of their protection in aggressive environments. This dissertation was devoted to the (i) study of corrosion of aluminium alloys in a chloride environment with and without added sulphide as a pollutant, and the (ii) development and study of zirconium conversion coatings as a contemporary protection method for aluminium alloys. The methodology was versatile, including electrochemical measurements in 0.5 M NaCl solution and microstructural and surface analysis carried out using SEM-EDXS, TEM, XPS, ToF-SIMS, XRD and digital imaging technique.

Aluminium alloys containing silicon are suitable for the use in the marine environment. Under such conditions not only chloride ions are provoking corrosion; other pollutants may be aggressive as well. For example sulphide ions which are known to promote the corrosion of copper- and steel-based alloys. The behaviour of aluminium alloys in the presence of sulphide has not been investigated in detail. In this dissertation, the corrosion behaviour of AlSi7Mg0.3 cast alloy (A356.0) was studied in artificial seawater with and without added sodium sulphide. It simulated sulphide which can form as a product of decaying of a biological compound as a result of the action of sulphate-reducing bacteria. The addition of Na₂S to artificial seawater was studied for concentrations from 20 to 100 ppm in the period of 40 days. Low sulphide concentration (<50 ppm) in seawater improved the corrosion resistance of the substrate which was ascribed to the slower kinetics of oxide formation leading to a more dense, crystalline and compact aluminium-based oxide layer. At higher concentrations, the surface layers formed were thicker and contained an increased content of magnesium hydroxide. These layers initially provided increased protection but became porous with immersion time. Therefore, in terms of corrosion protection, most compact layers were formed in the presence of lower sulphide concentrations in seawater.

In order to outperform traditional corrosion protection based on chromate conversion coatings, contemporary methods have to be as efficient but environmentally friendly. An example of the contemporary coatings are zirconium conversion coatings (ZrCCs). Their formation was investigated as a parameter of a conversion bath: concentration of hexafluoric acid and conversion time. Appropriate conversion conditions were determined for different aluminium alloys. It was reported herein for the first time that ZrCCs applied on aluminium alloys show a self-sealing/active corrosion effect during immersion in 0.5 M NaCl resulting in improved corrosion resistance with time. This effect was ascribed to the leaching of fluorine out from the ZrCC, which leads to the transformation of ZrF_4 / ZrO_xF_y into $\text{ZrO}_2 \cdot x\text{H}_2\text{O}$ and the formation of aluminium oxide/hydroxide; the latter also reacts with major elements from the substrate, i.e. Mn and Si. These changes resulted in the closing of nanopores in ZrCC and reinforced the coating/substrate interface against dissolution. The self-sealing effect depends on conversion time and the type of aluminium alloy substrate, i.e. the major alloying elements in the alloy. At appropriate conversion time, the self-sealing effect was most pronounced for AA3005 (Mn-containing alloy) followed by AA356.0 (Si-containing alloy) and AA5754 (Mg-containing alloy). In contrast, corrosion resistance of ZrCC applied on AA2024 (Cu-containing alloy), and AA7075 (Zn-containing alloy) decreased during immersion in 0.5 M NaCl solution. Therefore, self-sealing zirconium conversion coatings provide excellent corrosion protection of aluminium alloys containing manganese and good protection for those containing silicon and magnesium. The same coatings provide only poor protection of aluminium alloys containing copper and zinc.

Povzetek

Predmet doktorske disertacije je protikorozijska zaščita aluminijevih zlitin. Aluminijeve zlitine so pomembni tehnološki materiali z odličnimi mehanskimi lastnostmi, vendar so nagnjeni k koroziji v kloridnih in drugih agresivnih okoljih, kar lahko izzove lokalizirano ali enakomerno raztapljanje površine zlitine. Dovzetnost za korozijo izvira iz mikrostrukture aluminijevih zlitin, ki vsebujejo intermetalne delce, dodane za izboljšanje mehanskih lastnosti aluminija, vendar pa prisotnost teh delcev spodbuja korozijo zaradi razlike v njihovi elektrokemijski aktivnosti. Razumevanje korozijskega mehanizma aluminijevih zlitin je pomembno, saj je podlaga za določanje metodologije njihove zaščite v agresivnih okoljih. Ta disertacija je bila namenjena (a) preučevanju korozije aluminijevih zlitin v kloridnem okolju z in brez dodanega sulfida kot onesnaževalca ter (b) razvoju in preučevanju cirkonijevih konverzijskih prevlek kot sodobne zaščitne metode za aluminijeve zlitine. Metodologija je bila vsestranska, vključno z elektrokemijskimi meritvami v 0,5 M raztopini NaCl ter mikrostrukturno in površinsko analizo, izvedeno s pomočjo SEM-EDXS, TEM, XPS, ToF-SIMS, XRD in digitalne tehnike slikanja.

Aluminijeve zlitine, ki vsebujejo silicij, so primerne za uporabo v morskem okolju. V takšnih pogojih so poleg kloridnih ionov tudi druga onesnaževala lahko agresivna in povzročajo korozijo. Eden od njih so sulfidni ioni, za katere je znano, da spodbujajo korozijo zlitin na osnovi bakra in jekla, njihov vpliv na aluminijeve zlitine pa ni bil podrobno raziskan. V tej disertaciji smo proučevali korozijsko vedenje zlitine AlSi7Mg0,3 (A356.0) v umetni morski vodi z in brez dodanega natrijevega sulfida. Slednji je simuliral sulfid, ki se lahko tvori kot produkt razpada bioloških spojin kot posledica delovanja bakterij, ki reducirajo sulfat. Študija je preučevala korozijsko vedenje zlitine AlSi7Mg0,3 v obdobju 40 dni v umetnem morju z in brez dodanega Na₂S v razponu koncentracij od 20 do 100 ppm. Nizka koncentracija sulfida (<50 ppm) v morski vodi je izboljšala korozijsko odpornost podlage, ki je bila posledica počasnejše kinetike tvorbe oksida, kar je vodilo do bolj goste, kristalinične in kompaktne oksidne plasti. Pri višjih koncentracijah so bile tvorjene površinske plasti debelejšje in so vsebovale povečano vsebnost magnezijevega hidroksida. Te plasti so sprva zagotavljale večjo zaščito, vendar so postale porozne s časom potopitve. Glede na protikorozijsko zaščito se je ob prisotnosti nižjih koncentracij sulfida v morski vodi oblikovala bolj kompaktna in zaščitna oksidna plast.

Da bi presegli tradicionalno protikorozijsko zaščito na osnovi pretvornih kromatnih prevlek, morajo biti sodobne metode enako učinkovite, a okolju prijazne. Cirkonijeve konverzijske prevleke (CKP) so sodobna, okolju prijazna različica kromatnih pretvornih prevlek. Prvi korak je bil raziskati lastnosti konverzijskih prevlek v odvisnosti od parametrov pretvorbene kopeli: koncentracije heksafluorne kisline in časa konverzije. Za različne aluminijeve zlitine so bili določeni ustrezni pogoji konverzije. V tej disertaciji smo prvič poročali, da CKP, nanesene na aluminijeve zlitine, izkazujejo samotesnjenje ali aktivno korozijsko zaščito med potapljanjem v 0,5 M NaCl, kar se izkazuje kot izboljšanje protikorozijske odpornosti s časom. Ta učinek je bil pripisan izločanju fluora iz CKP, kar vodi k pretvorbi ZrF_4 / ZrO_xF_y v $\text{ZrO}_2 \cdot x\text{H}_2\text{O}$ in tvorbi aluminijevega oksida / hidroksida; slednji reagira tudi z glavnimi elementi iz podlage, kot sta Mn in Si. Te spremembe povzročijo zapiranje nanopor v prevleki in dodatno zaščitijo vmesno plast med prevleko in podlaga zoper raztapljanje. Učinek samotesnjenja je odvisen od časa pretvorbe in vrste aluminijeve zlitine, to je glavnih legirnih elementov v zlitini. Ob ustreznem času pretvorbe je bil učinek samotesnjenja najbolj izrazit za AA3005 (zlitina, ki vsebuje Mn), nato AA356.0 (zlitina, ki vsebuje Si) in AA5754 (zlitina, ki vsebuje Mg). Nasprotno pa se je med potopitvijo v 0,5 M raztopino NaCl korozijska odpornost CPP slabšala na zlitinah AA2024 (zlitina, ki vsebuje Cu) in AA7075 (zlitina, ki vsebuje Zn). Torej cirkonijeve konverzijske prevleke zagotavljajo odlično protikorozijsko zaščito aluminijevih zlitin, ki vsebujejo mangan, in dobro zaščito za tiste, ki vsebujejo silicij in magnezij. Enake prevleke zagotavljajo le slabo zaščito aluminijevih zlitin, ki vsebujejo baker in cink.

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Abbreviations

AA		Aluminium alloy
IMP		Intermetallic particle
ZrCC		Zirconium conversion coating
CCC		Chromate conversion coating
HER		Hydrogen evolution reaction
OER		Oxygen evolution reaction
SCE		Saturated calomel electrode
SHE		Standard hydrogen electrode
SRB		Sulphate reducing bacteria
TCP		Trivalent chromium process
OCP		Open circuit potential
LPR		Linear polarization resistance
PD		Potentiodynamic
EIS		Electrochemical impedance spectroscopy
NSST		Natural salt spray test
ASTM		American Society for Testing and Materials
XPS		X-ray photoelectron spectroscopy
XRD		X-ray diffraction
ToF-SIMS		Time of flight secondary ion mass spectroscopy
SEM		Scanning electron microscopy
TEM		Transmission electron microscopy
FIB		Focus ion beam
EDS		Energy-dispersive X-ray spectroscopy
SE		Secondary electrons
BSE		Backscattered electrons
MP		Mechanically pre-treated
CP		Chemically pre-treated
at		Atomic
wt		Weight
SD		Standard deviation
ppm		Parts per million

Symbols

J_{corr}		Corrosion current density
E_{corr}		Corrosion potential
E_{pit}		Pitting potential
ΔE		$ E_{\text{pit}} - E_{\text{corr}} $
β_a		Anodic Tafel slope
β_c		Cathodic Tafel slope
R_p		Polarization resistance
$ Z _{3\text{mHz}}$		Impedance module at the frequency of 3 mHz
t		Time
d		Day

Chapter 1

Introduction

1.1 Aluminium and Aluminium Alloys

Aluminium alloys (AAs) are the most important lightweight construction materials. Aluminium is a metal with unique properties: density of 2.7 kg/m^3 , non-magnetic, excellent electrical and thermal conductivity, good ductility [1]. Another advantage of aluminium is its excellent corrosion resistance due to spontaneous passivation and formation of 10 nm thick aluminium oxide passive film when being exposed to air [2]. On the other hand, aluminium is a soft metal and lacks strength and hardness required in many applications.

Aluminium is mainly present as bauxite ore in the earth crust. With 8 wt. %, it is the third most abundant element in general and most abundant metal in the earth crust. It is produced by electrolysis from molten salt of aluminium oxide in cryolite (Hall-Héroult process), where aluminium oxide is pre-obtained from bauxite ore in the Bayer process [3]. Alloying of aluminium with other elements improves its hardness, strength, ductility, machinability and other properties. Cu, Mn, Si, Mg, Zn are added in aluminium alloys up to 10% (major alloying elements) while Cr, Ni, Zr, V, Ti, Pb, Sb, Ca, Ce up to 1% (minor alloying elements). Some aluminium alloys can reach and even exceed the strength of steel (yield strengths $\geq 500 \text{ MPa}$, AA 7xxx series). Thanks to their unique properties, aluminium alloys are used in: aerospace industry, transportation industry, automotive industry, architectural and construction industry, food packaging, shipbuilding, marine construction and many other industries [4]. In transportation, automotive and shipbuilding industries, the trend is to replace traditional construction materials, such as iron, steel and galvanized steel, with lightweight materials such as aluminium and magnesium to reduce gasoline consumption and CO_2 emission. In the aerospace industry, aluminium alloys are the primary construction material since 1910 (duraluminium) and especially since the discovery of AA 7xxx series in the 1930s. However, even in the aerospace industry, the trend is to replace heavy construction materials used in engine construction with novel aluminium alloys. Due to this trend, the production of aluminium was tripled since 2000 and reached 63.7 million tonnes annual production of primary aluminium in 2019 with a tendency for further growth (Figure 1.1). Another advantage of aluminium is that it could be readily recycled. In 2019, approximately 12 million tonnes (15.9 % of the global market) of aluminium were recycled. To summarize, the total global demand for aluminium reached 75.7 million tonnes in 2019. World's most significant producer of aluminium is China, with 55% of the annual production of primary aluminium in 2019 [5]. Expectations are that global demand for aluminium will further increase in years to come.

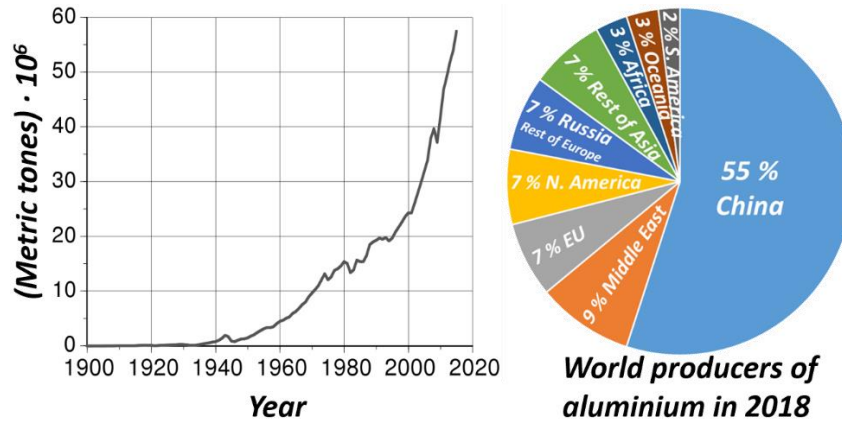


Figure 1.1: Annual production of aluminium for the period 1900-2020 with the most significant world producers of aluminium in 2018 [5].

1.1.1 Classification, designation and application

Aluminium alloys are divided into two main categories based on their production process: wrought alloys and cast alloys. Further differentiation is based on the mechanism of property development. An aluminium alloy that responds to different thermal treatments based on phase solubility is referred to as heat-treatable alloys. Another group of aluminium alloys are non-heat treatable and develop properties by work hardening through mechanical reduction, usually in combination with various annealing procedures. There are more than 400 wrought alloys and more than 200 cast alloys currently on the market. Proper designation and classification of aluminium alloys are crucial. The most recognized and used nomenclature system is the one developed by the Aluminium Association in the United States [4, 6].

Wrought alloys are designated with a 4-digit nomenclature system (xxxx) while cast alloys are designated with a 3-digit with one decimal place system (xxx.xX). Designation of aluminium alloy series, hardening method and application are presented in Table 1.1. In the wrought designation system (**X**xxx), the first digit identifies the principal alloying element, the second digit identifies the modification of alloy from the primary alloy in that series (**x**Xxx) and the last two digits (xx**XX**) define the exact alloy composition. Example: alloy 7175-T6: the first digit (7175-T6) means that the principal alloying element is Zn, the second digit (7175-T6) implies that it first modification from primary alloy 7075 and the last two digits (7175-T6) identify the exact alloy composition. The letter at the end (7175-T6) identifies the property development treatment. The only exception from this rule is the aluminium alloy series 1000 where the last two digits show the minimum aluminium percentage above 99%, for example, the last two digits in AA1050 mean that these alloys contain minimum 99.50% aluminium.

In the cast alloy designation system, the first digit (**X**xx.x) identifies the principal alloying element, the second and third digits (**xx**.x) are arbitrary numbers given to recognise a specific alloy in the series. The digit following the decimal point indicates whether the alloy is a casting (.0) or an ingot (.1 or .2). The capital letter prefix indicates a modification to a specific alloy.

Example: alloy A356.0: the capital A (Axxx.x) indicates a modification of alloy 356.0. The number 3 (A3xx.x) indicates that it is of the silicon plus copper and/or magnesium series. 56 (Ax56.0) identifies the alloy within the 3xx.x series, and .0 (Axxx.0) indicates that it is a final shape casting and not an ingot.

The temper designation system is used for all product forms (both wrought and cast), except for ingot (Table 1.2). The system is based on the sequences of mechanical or thermal treatments, or both, used to produce various tempers. The temper designation follows the alloy designation and is separated from it by a hyphen.

Table 1.1: Wrought and cast aluminium alloy series with the principal alloying element, strengthening method and application areas [4].

Aluminium alloy	Principal alloying element	Strengthening method	Application
Wrought alloys			
1xxx	≥ 99.000 % of Al	Cold-work	Electrical and chemical industries
2xxx	Cu	Heat-treat	Aerospace industry <i>Yield strength of ≈ 450 MPa</i>
3xxx	Mn	Cold-work	Architectural and general applications
4xxx	Si	Cold-work / some heat-treat	Welding rods and brazing sheet
5xxx	Mg	Cold-work	Boat hulls, gangplanks and other marine applications
6xxx	Si + Mg	Heat-treat	Architectural extrusions and automotive industry
7xxx	Zn	Heat-treat	Aerospace industry <i>the strongest aluminium alloy, Yield strength ≥ 550 MPa</i>
8xxx	Sn, Li and/or Fe	Heat-treat	
9xxx	Reserved for future use	/	/
Cast alloys			
1xx.x	≥ 99.000 % of Al	Cold-work	Electrical rotors
2xx.x	Cu	Heat-treat	Automotive and aerospace industry <i>pumps, pistons, cylinders, aircraft generator housing</i>

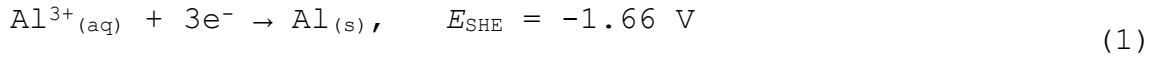
3xx.x	Si + Cu and/or Mg	Cold-work	Automotive and aerospace industry <i>impellers, aircraft wheels, gasoline and oil tanks, airframe, machine parts, pump bodies, jet engine compressor cases</i>
4xx.x	Si	Cold-work / some heat-treat	Architectural, food packaging, dental equipment, marine industry, etc.
5xx.x	Mg	Cold-work	Architectural, automotive and marine industries
6xx.x	Unused	Heat-treat	/
7xx.x	Zn	Heat-treat	General-purpose casting that requires subsequent brazing, automotive parts, pumps, mining equipment
8xx.x	Sn	Heat-treat	Bushings and journal bearings for railroads
9xx.x	Reserved for future use	/	/

Table 1.2: Temper designation for aluminium alloys [4].

Symbol	Meaning
F	As-fabricated - applies to products of a forming process in which no special control over thermal or strain hardening conditions is employed.
O	Annealed - applies to a product which has been heated to produce the lowest strength condition to improve ductility and dimensional stability.
H	Strain-Hardened - applies to products which are strengthened through cold-working. The strain hardening may be followed by additional thermal treatment, which produces some reduction in strength. The "H" is always followed by two or more digits.
W	Solution Heat-Treated - an unstable temper applicable only to alloys which age spontaneously at room temperature after solution heat-treatment.
T	Thermally Treated - applies to a product which has been heat-treated, sometimes with supplementary strain-hardening, to produce a stable temper. The "T" is always followed by one or more digits.
Subdivision of H tempers	
H1	Strain-Hardened Only.
H2	Strain-Hardened and Partially Annealed.
H3	Strain-Hardened and Stabilized.
H4	Strain-Hardened and Lacquered or Painted.
HX2	Quarter Hard
HX4	Half Hard
HX6	Three-Quarters Hard
HX8	Full Hard
HX9	Extra hard
HXx - The first digit after the H indicates a basic operation. HxX - The second digit after the H indicates the degree of strain hardening.	
Subdivision of T tempers	
T1	Naturally aged after cooling from an elevated temperature shaping process, such as extruding.
T2	Cold-worked after cooling from an elevated temperature shaping process and then naturally aged.
T3	Solution heat-treated, cold-worked and naturally aged.
T4	Solution heat-treated and naturally aged.
T5	Artificially aged after cooling from an elevated temperature shaping process.
T6	Solution heat-treated and artificially aged.
T7	Solution heat-treated and stabilized (overaged).
T8	Solution heat-treated, cold-worked and artificially aged.
T9	Solution heat-treated, artificially aged and cold-worked.
T10	Cold-worked after cooling from an elevated temperature shaping process and then artificially aged.
Additional digits indicate stress relief: TX51 - Stress-relieved by stretching. TX52 - Stress-relieved by compressing.	

1.2 Corrosion Behaviour of Aluminium and Aluminium Alloys

Aluminium should spontaneously dissolve in aqueous solution according to electrode potential for the electrochemical reaction of aluminium oxidation:



Among construction metals, only Be and Mg are more reactive than aluminium according to electromotive force series for metals. However, aluminium is thermodynamically stable in air environment due to the formation of 10 nm thick passive film of Al_2O_3 [4, 7]. This aluminium oxide film is spontaneously formed in a few seconds when pure Al is exposed to the air environment. Thanks to this, aluminium has excellent corrosion resistance and can be used without maintaining service for many years. Even if the surface of aluminium is damaged, Al_2O_3 film will self-repair in a few seconds and continue to protect aluminium from corrosion. These aluminium oxides consist of an inner barrier layer 3-5 nm thick and an outer porous layer 5-7 nm thick (Figure 1.2).

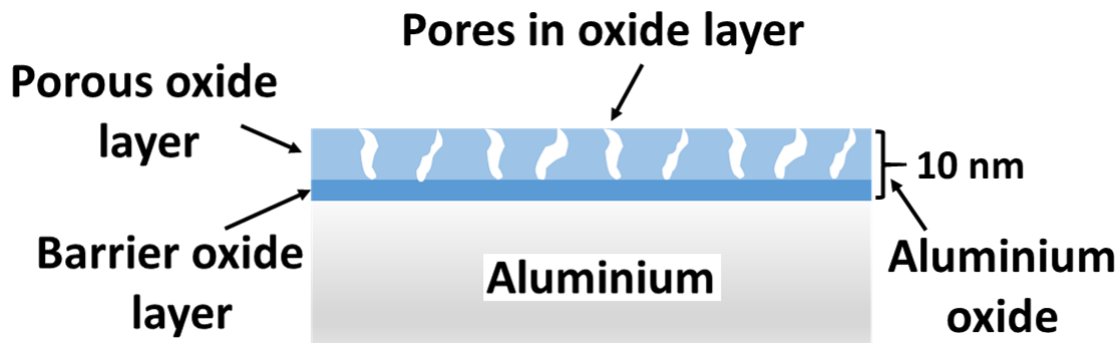


Figure 1.2: Natural aluminium oxide formed on the surface of aluminium in the air.

During exposure to water, it will slowly corrode and form an outer porous aluminium oxide film, 20-200 nm thick, that will together with the inner barrier Al_2O_3 protect aluminium from further corrosion. Depending on environmental conditions, this outer-amorphous aluminium oxide film could be bayerite / $\alpha\text{-Al}(\text{OH})_3$, gibbsite / $\gamma\text{-Al}(\text{OH})_3$, hydragite / $\text{Al}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$ or boehmite / $\gamma\text{-AlO}(\text{OH})$ [2]. To summarize, when exposed to water aluminium it will be protected by the formation of a thicker aluminium oxide film that is thermodynamically stable in $4 \leq \text{pH} \leq 8.5$ (Figure 1.3). Aluminium will corrode outside of this pH range or even in this pH range if Cl^- ions are present in accordance with the following electrochemical reactions:

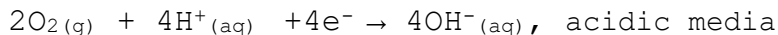
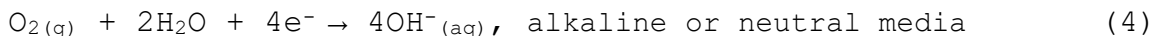
Oxidation of Al:



Reduction of hydrogen:



or the reduction of O_2 :



In excess of OH^- ions, the formation of amorphous aluminium oxide will occur:

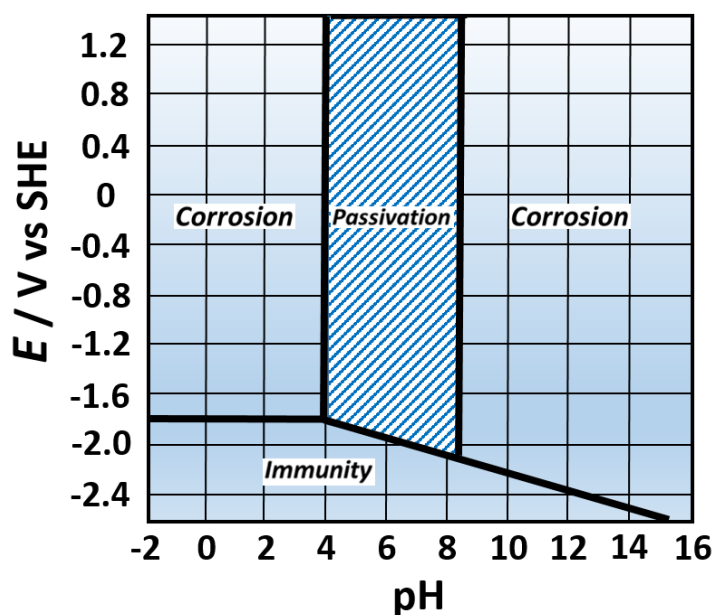


Figure 1.3: Electrode potential vs. pH (so-called Pourbaix) diagram for aluminium [2, 8].

However, aluminium and aluminium alloys are susceptible to localized corrosion when exposed to water, even in a thermodynamically stable range [2]. Corrosion rate and corrosion mechanism depend on the alloy type. The localized form of corrosion is mainly in the form of pitting, but intergranular corrosion, exfoliation corrosion and stress corrosion cracking could occur depending on the alloy type and environmental conditions. Ultra-pure 99.99% Al has the best resistance to corrosion. However, the presence of little contamination in the alloy or environment speeds up the corrosion rate and causes pitting. Localized corrosion of aluminium alloys is caused by the presence of alloying elements in the aluminium matrix. These alloying elements could be completely dissolved in aluminium or form the second phase in the form of intermetallic particles (IMPs) [9-13]. By the size, IMPs can be divided into small - dispersoids (0.05 to 0.5 μm), medium ($\approx 1 \mu m$), large (1-10 μm). Intermetallic particles improve the mechanical properties of aluminium alloys, resistance to corrosion stress cracking, wear resistance, and so forth, but decrease the corrosion resistance of aluminium alloys. IMPs are made of aluminium and one or more alloying elements and form binary, ternary or quaternary second phases. All metals are nobler than Al except Zn and Mg.

The general rule is that metals nobler than Al create cathodic IMPs while Zn and Mg create anodic IMPs. Corrosion potentials of most common IMPs found in aluminium alloys are given in Table 1.3.

Dispersoids are small particles comprising alloying elements that are highly insoluble in aluminium. Dispersoid sizes typically range from 0.05 to 0.5 μm . Cr, Ti, Zr, and Mn are standard dispersoid formers. With the possible exception of Mn, the alloying elements concentrated in dispersoids are entirely passive in environments where Al alloys are regularly used. These particles form at high temperatures and are present to control grain-size and recrystallization behaviour, hence are homogeneously dispersed. Typical examples include Al_3Ti , Al_6Mn , $\text{Al}_{20}\text{Cu}_2\text{Mn}_3$, and Al_3Zr .

On the other hand, larger IMPs have the determinative role on the corrosion behaviour of aluminium alloys. Intermetallic particles induce weak spots in aluminium oxide, where the corrosion process is initiated. The reason for this is the difference in Volta potential between the aluminium matrix and intermetallic particles. This potential difference produces a current flow (micro-galvanic cell) in a conductive environment and causes a local breakdown of the passive film. By electrochemical activity, intermetallic particles could be divided into [9]:

- Noble particles with high electrochemical activity, e.g., Al_2Cu , $\text{Al}_7\text{Cu}_2\text{Fe}$. $E_{\text{corr}} \geq E_{\text{corr}}$ of alloy, with the ability to sustain a large cathodic current.
- Noble particles with low electrochemical activity, e.g., Al_3Zr . $E_{\text{corr}} \geq E_{\text{corr}}$ of alloy, however, these particles do not sustain large cathodic currents and may be too small to impact corrosion kinetics adversely. Pitting is not often associated with these intermetallics.
- Active particles with high self-dissolution rates, e.g., MgZn_2 . $E_{\text{corr}} \leq E_{\text{corr}}$ of alloy, with the ability to undergo anodic dissolution at high rates.
- Active particles with low self-dissolution rates, e.g., Mg_2Al_3 .
- Active particles with a noble elemental component, e.g., Al_2CuMg . Dealloying and incongruent dissolution may lead to polarity reversal. These particles could be selectively dissolved or lead to peripheral pitting.

Most intermetallic particles are nobler than the aluminium matrix and act as local cathodes for hydrogen reduction reaction (HER) or oxygen reduction reaction (ORR). In contrast, the surrounding aluminium matrix acts as a local anode where aluminium is dissolved. Some of the intermetallic particles are anodic with respect to the surrounding aluminium matrix and will dissolve. Some intermetallic particles can change the polarity of the micro-galvanic cell during corrosion. The typical example of this case is S-phase (Al_2CuMg) in AA 2024. S-phase first acts as a local anode where Mg is dissolved; when all Mg has dissolved, the potential of IMPs is changed from anodic (less noble) to cathodic (more noble) due to the presence of an excess of the Cu [11, 14, 15].

Table 1.3: Corrosion potentials of most common intermetallic particles and metals in 0.5 M NaCl solution [4, 16].

Intermetallic particle	Phase	E_{corr} , (V vs SCE)
Al ₃ Fe	β	-0.566
Al ₂ Cu	θ	-0.695
Al ₃ Zr	β	-0.801
Al ₆ Mn		-0.913
Al ₃ Ti	β	-0.799
Al ₃₃ Zn ₄₉	T'	-1.063
Mg ₂ Al ₃	β	-1.162
MgZn ₂	M, η	-1.095
Mg ₂ Si	β	-1.536
Al ₇ Cu ₂ Fe		-0.654
Mg (AlCu)		-0.936
Al ₂ CuMg	S	-1.061
Al ₂₀ Cu ₂ Mn ₃		-0.617
Al ₁₂ Mn ₃ Si		-0.858
Al		-0.849
Cu		-0.220
Si	α	-0.452
Mg		-1.688
Mn		-1.318
Cr		-0.571
Zn		-1.028
Al-2%Cu	α	-0.744
Al-4%Cu	α	-0.642
1050		-0.84
2024		-0.69
3003		-0.83
356.0		-0.82
380.0		-0.63
5754		-0.77
6063		-0.83
7075		-0.83

1.2.1 The mechanism of pitting corrosion in aluminium alloys

Pitting is the most common type of corrosion in aluminium alloys. All other types of corrosion in the aluminium, such as intergranular and exfoliation corrosion, start with pitting and breakdown of the aluminium oxide passive layer [2, 17-23]. Understanding the mechanism of pitting corrosion (Figure 1.4) is of paramount importance for understanding the corrosion behaviour of aluminium alloys and their protection [17, 22, 23].

Pitting occurs in 2 stages:

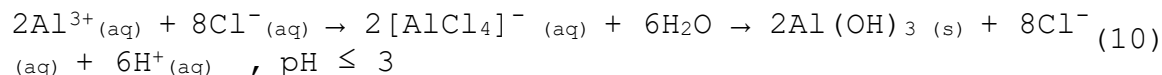
- Pit initiation
- Pit propagation



Deposition of aluminium hydroxide at the pit opening:



Formation and hydrolysis of aluminium chloride complex at the bottom of the pit:



For years, there has been debate over question **"what step is crucial in the pitting?"**: a passive film breakdown or a pit growth [20, 24–27]. According to a novel unified theory of pitting, in a more aggressive environment, the passive film breakdown and the pit initiation will be determining the step, while in a less aggressive environment the pit growth will be determining the step (Table 1.4). The susceptibility to pitting corrosion, intergranular corrosion and exfoliation corrosion of aluminium alloy series is given in Table 1.5.

Table 1.4: The rate-controlling step in the pitting.

Environment	Passive film breakdown	Metastable pitting	Pit growth
More aggressive	Slow (rate-controlling)	Fast	Fast
Less aggressive	Fast	Fast	Slow (rate-controlling)

Table 1.5: The susceptibility of aluminium alloys to pitting corrosion, intergranular corrosion and exfoliation corrosion [4].

Pitting susceptibility		Intergranular corrosion	Exfoliation corrosion
Low	1xxx	No	No
↓	5xxx	Yes (if alloy contains $\geq 3\% \text{ Mg}$)	No
	3xxx	No	No
	6xxx	Yes	No
	7xxx	Yes	Yes
High	2xxx	Yes	Yes

1.2.2 Corrosion of aluminium alloys in seawater with increased concentration of sulfides

Aluminium alloys have excellent corrosion resistance when exposed to air or natural freshwater. However, in a coastal region or seawater, they are susceptible to pitting corrosion due to the presence of NaCl [17, 28]. Aluminium wrought alloy series 3xxx, 5xxx, 6xxx and cast alloys 3xx.x, 5xx.x have excellent corrosion resistance even in seawater [4, 29, 30]. Thanks to superior mechanical strength/weight ratio, thermal conductivity and excellent corrosion resistance they are used in desalination plants, off-shore oil and gas industries, shipbuilding, off-shore platforms and other marine applications. Nowadays, military and police patrol boats that require high speed are entirely made from

aluminium alloys. Considering the composition of aluminium alloys, magnesium provides better re-passivation of pits than manganese. Still, when the content of magnesium is higher than 3%, aluminium alloys are prone to intergranular corrosion. Environmental parameters of seawater: pH [31], temperature [32], salinity, the concentration of organic compounds, the concentration of dissolved CO_2 [33], the concentration of dissolved O_2 , biofouling and pollution have a significant influence on the corrosion rate of aluminium alloys in seawater [34-36]. The most corrosive combination is low pH, low temperature and high concentrations of dissolved oxygen. Sulphides are one of the most common pollutants in natural seawaters [36-39]. The concentration of sulphides in harbours, near coastal power plants, off-shore oil platforms, shipyards can reach and exceed 50 ppm [37, 39]. Sulphides could originate from the natural sulphur cycle where sulphur species with higher oxidation states are reduced to sulphide by the action of sulphate-reducing bacteria [38]. Some researchers proposed that sulphides are responsible for microbiological induced corrosion of aluminium alloys caused by the action of sulphate-reducing bacteria (Figure 1.5) [38, 40].

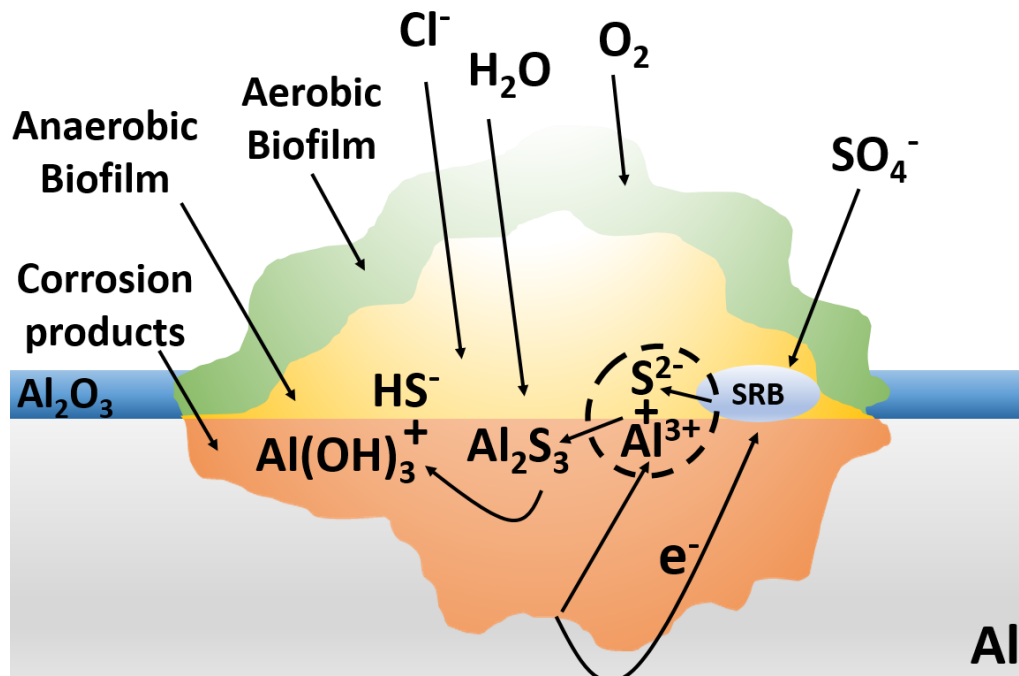


Figure 1.5: Mechanism of microbiologically induced corrosion of aluminium and aluminium alloys by sulphate-reducing bacteria (SRB) [38, 40].

Sulphides are highly corrosive for most metals and their alloys: Fe, Cu, Ni, Cr, stainless steel, mild steel, carbon steel, copper-nickel alloy, aluminium bronze, and so forth [41-47]. Contrary to steels and copper-based alloys, sulphides and H_2S have a beneficial effect on corrosion resistance of aluminium alloys in various environments (water-oil mixtures, oil, dry and moist environment, fresh, natural water and natural sea waters). It is believed that sulphides improve passivation and barrier properties of the aluminium oxide film [48-51]. The concentration of sulphur species and sulphides is especially increased in oil and gas explanation facilities and plants. There are only a few articles about this topic in the scientific literature probably because these studies are closely correlated with the oil and gas industry and confidential.

1.3 Corrosion Protection of Aluminium and Aluminium Alloys

As shown in previous chapters, aluminium alloys are susceptible to localized corrosion in the natural environment, and they require additional corrosion protection. They are protected by the application of organic paints and the use of corrosion inhibitors. Corrosion inhibitors are used in a closed system like re-boilers, condensers, evaporators, pipes, etc. In open systems like aircraft, car bodies, architectural constructions, etc., organic paints are applied. Full paint system is complex [52] (Figure 1.6) and consists of:

- conversion treatment or anodization or cladding
- primer
- topcoat

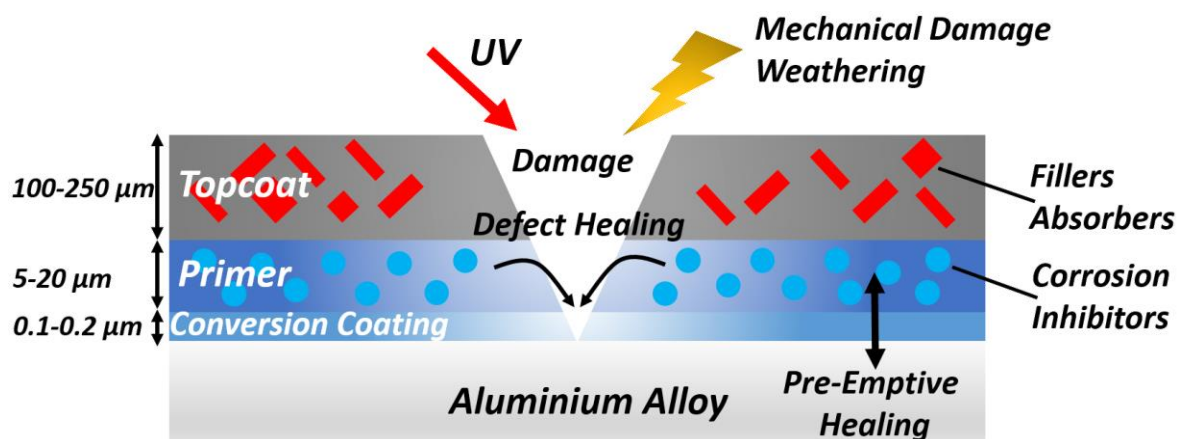


Figure 1.6: Scheme of a complete coat system applied on an aluminium alloy.

Each part of this system has a different role in corrosion protection. Conversion coatings provide essential corrosion protection, preferably active corrosion protection. However, the primary purpose of conversion coating is to improve adhesion of primers/organic coatings [53]. In some cases, when better corrosion resistance is required, the anodization process of aluminium is employed. Anodization is electrochemical oxidation of aluminium where a thick protective anodic oxide film is formed [54]. Anodic oxide film consists of an inner barrier oxide layer and an outer porous aluminium oxide layer. Post-treatment that seals the porous aluminium oxide layer is often applied when excellent corrosion resistance is required. Sealed anodic oxide coating provides better corrosion protection in comparison with conversion coatings. Sometimes, instead of anodization cladding of aluminium alloys, 2xxx and 7xxx with pure aluminium is applied. It combines excellent mechanical properties of core 2xxx, 7xxx alloys and superior corrosion resistance of outer coating of pure aluminium. The primer has a role in providing active corrosion protection and improves the adhesion of the topcoat.

For many years, the organic primer with strontium chromate corrosion inhibitor pigments has been used [55]. When damage in the coating happens, chromates will leach inside the damaged area and inhibit corrosion. Due to carcinogenicity and toxicity of chromates, strontium chromate is being replaced on the market with green corrosion pigments [16]. The most promising and already commercialized primer technology for aluminium alloys is lithium leaching primer technology [56, 57] and magnesium-rich primer

technology [58-60]. There is a broad spectrum of potential replacements for chromate-based primers like organic or sol-gel coating filled with corrosion inhibitor based on cerium salts [61, 62], layer-double hydroxides pigments doped with organic/inorganic inhibitors [63], etc. The thickness of the primer is usually from few μm to 20 μm . On top of the primer, the topcoat is applied, which should provide excellent barrier protection to prevent diffusion of water, oxygen and Cl^- ions towards the substrate.

Additionally, it should provide excellent resistance against UV radiation and weathering. The topcoat is usually 100–250 μm thick and is based on epoxy, urethane, ester or alkyds polymers. This complex paint system should work as a good team and also provide a synergistic effect. Sometimes every single coating can meet the corrosion protection requirement but once joined in the whole system, it may not necessarily provide proper corrosion protection.

1.4 Zirconium Conversion Coatings

Chemical conversion coating is applied before the application of primers or organic coatings. It should provide essential corrosion protection for a metal substrate and improve the adhesion of topcoats [53]. Chemical conversion coatings are mainly applied by immersion in conversion baths. It is also possible to apply them by spraying. Contemporary chemical conversion coating process should meet the next requirements:

- green process
- economical process
- short conversion time ($\tau \leq 10$ minutes)
- multi-metal process
- provide active corrosion protection and improve adhesion of topcoats.

Schematic presentation of a typical conversion coating process is presented in Figure 1.7.

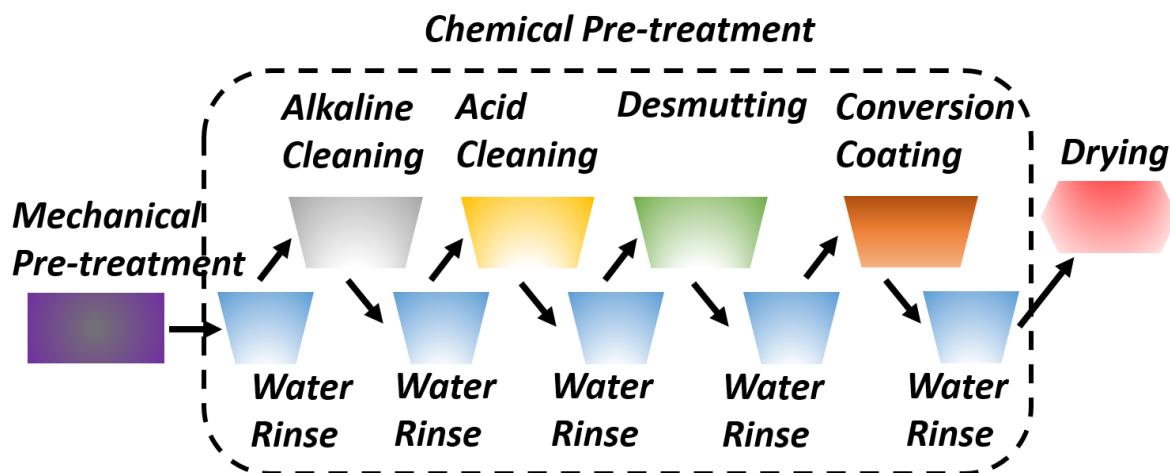


Figure 1.7: Scheme of pre-treatment of a metal surface.

Before the application of conversion coating, the metal substrate has to be pre-treated. Surface pre-treatments consist of mechanical and chemical pre-treatments [64-68]. In the industry, usually, only chemical pre-treatment is applied. Chemical pre-treatment typically consists of alkaline cleaning, acid cleaning/pickling and desmutting. After each of these steps, the substrate has to be properly rinsed in water. Mechanical pre-treatment is applied to remove old paint / severe corrosion damage and could be: grinding,

polishing, pin-shooting, dry-ice shooting, sandblasting, etc. Mild alkaline cleaners with pH=8.5-10 are employed to degrease and clean the surface of aluminium alloys, while strong alkaline cleaners will etch it since they contain alkaline active components such as sodium silicate, sodium hydroxide, potassium hydroxide, ammonium hydroxide, phosphates and specific corrosion inhibitor. Acid cleaners etch the surface of the aluminium to remove individual intermetallic particles and modify the surface composition and morphology. They contain some acids as an active component: HF, H₂SO₄, HNO₃, HCl alone or in combination. De-smutters have a role in removing surface products of acid cleaning and etching; most of them are based on a mixture of HF and H₂SO₄.

For the last 80 years, chromate conversion coatings (CCCs) were state-of-the-art in corrosion protection of aluminium alloys and light metals [16, 55]. For corrosion protection of iron, steel and galvanized steel, phosphate conversion coatings were used [69, 70]. CCCs are banned in the EU and USA since 2019 due to their carcinogenicity and toxicity of compounds used for their production. They are allowed to be used only in military and space industries with a special allowance. Phosphate conversion coatings are being replaced in the industry due to the ban of the use of heavy metals, eutrophication caused by the presence of P in wastewaters and high economic cost. Phosphate conversion bath operates at temperatures of 60-80 °C and requires additional cost for wastewater treatments and disposal of heavy metals.

During the last 30 years, there are considerable efforts in the scientific community and industry to find an equivalent replacement for CCCs [16]. Zirconium conversion coatings (ZrCCs) [53] and trivalent chromium process (TCP) [71-74] are the most promising alternatives. Trivalent chromium process is zirconium conversion coating loaded with Cr(III) salts as active corrosion protection agents, while zirconium conversion coatings are a completely chromium-free conversion coating. When better corrosion protection is required, TCP is used in aerospace and military industry. However, cases were reported when ZrCC painted with topcoat system performed equally as TCP conversion coatings painted with the same topcoat system [75-78]. Zirconium conversion coating is typically used in automotive, transportation, construction and other similar industries. The reason why ZrCC is a preferable choice in the automotive industry is that it works for all metals - "*multi-metal*" conversion coating [53, 79-81]. Thanks to that, the whole car and truck bodies could be coated with ZrCC in a single step.

Early works on ZrCC started in the beginning of the 1990s and resulted in the commercialization of the 1st generation ZrCC technology in 2004 in the automotive industry [82-86]. In 2010, the 2nd generation of ZrCC was introduced on the market. It had better uniformity, improved corrosion resistance and shorter conversion time in comparison with the 1st generation of ZrCC [80, 81, 87, 88]. In the last 30 years, there were more than 100 scientific papers published about ZrCC. Zirconium conversion coatings meet all the requirements for excellent conversion coating except active corrosion protection. Currently, there are a lot of efforts and studies on the development of a 3rd generation of ZrCC in the industry and scientific community. The 3rd generation of ZrCC should pose active corrosion protection ability and performance at the same or better level as chromate conversion coatings.

Zirconium conversion baths contain H₂ZrF₆ as an active component and minor addition of accelerators and/or organic additives [53, 89, 90]. The coatings are applied on the substrate by immersion in ZrCC baths or by spraying. Optimal ZrCC process parameters for protection of aluminium alloys are: T= 25-40 °C, concentration of 0.1 M H₂ZrF₆, pH = 4.5-4.8 and stirring speed of 450 rpm. One of the most important ZrCC process parameters is conversion time, and it

has to be tuned for each aluminium alloy or metal [91]. The optimal conversion time will provide the best performance of ZrCC. Process time depends on other process parameters and bath composition. The higher concentration of H_2ZrF_6 or the presence of accelerator will require shorter optimal conversion time. Kinetics of ZrCC process could be monitored by measuring the open circuit potential (OCP) of the substrate during conversion coating formation (Figure 1.8) [91–93]. Process of ZrCC formation has three steps:

- activation of the substrate surface
- conversion coating formation
- conversion coating overgrowth.

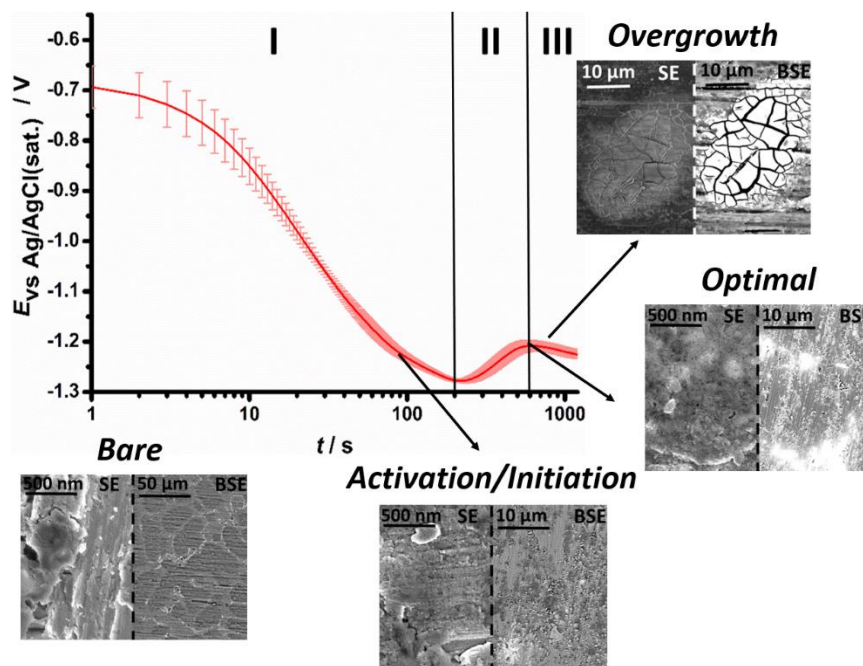
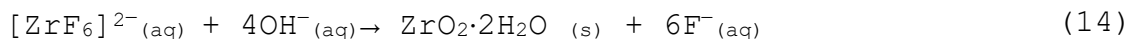
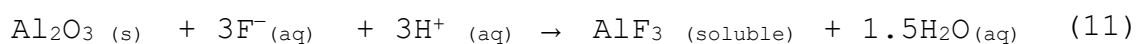


Figure 1.8: Open circuit potential and SEM images of aluminium alloy A365.0 during immersion in H_2ZrF_6 conversion bath.



In the activation step, natural aluminium oxide/metal oxide is removed by the free fluoride ions (reaction 11), allowing the formation of the zirconium conversion coating [94, 95]. In essence, this step corresponds to a negative shift of OCP (region I, Figure 1.8). After activation, HER and ORR occur at IMPs (reaction 12–13), causing high local alkalization ($\text{pH}=8.5$) [96]. In the alkaline environment, ZrF_6^{2-} ions are precipitated into $\text{ZrO}_2 \cdot x\text{H}_2\text{O}$ at IMPs (reaction 14); this is reflected in a positive shift of OCP (region II, Figure 1.8). Together with zirconium oxide aluminium oxy-fluoride is formed, especially in the inner part of the coating. Optimal conversion time is marked as maximum/plateau in OCP diagram. At this point, the conversion coating is fully formed. After this point, coating continues to grow further, but internal stress will cause cracks in the coating (region III, Figure 1.8)

and coating will lose its barrier protection properties [91, 97, 98].

Formation of zirconium conversion coatings is the electrochemical process and is caused by the difference in Volta potential between the aluminium matrix and intermetallic particles [93]. The coating formation will be initiated at IMPs or grain boundaries with higher Volta potential [91, 93, 99, 100]. In these spots, HER and ORR will occur, causing high local alkalization at/in the proximity of IMPs and precipitation of ZrCC in these areas. ZrCC will grow in a lateral direction from initiation sites covering the alloy matrix. When the whole surface is covered by the coating, the difference in Volta potential will disappear. Due to the nature of this process, ZrCC will be significantly thicker at IMPs/initiation sites [91, 92]. However, the formation of ZrCC is a dynamic process, balancing between the coating formation and coating dissolution due to the presence of free fluoride ions.

After the complete formation of ZrCC, H^+ and F^- ions will be able to migrate towards the substrate and HER together with coating overgrowth will continue. This will lead to cracking due to internal stress in the coating and evolution of H_2 microbubbles. In order to increase the speed and uniformity of ZrCC formation, accelerators are often added to bath formulations. A small addition of non-hazardous Cu or some other particle nobler than aluminium/or metal substrate will deposit on aluminium matrix surface introducing new cathodic sites [90, 101, 102]. These cathodic sites will be uniformly spread across the substrate surface, increasing the speed of ZrCC process and producing more uniform ZrCC. Increasing the concentration of free fluoride ions by adding HF will only increase the speed of the conversion coating process. Surface pre-treatments are very important for ZrCC formation, and final performance, e.g. the most hydroxylated surface will provide ZrCC with the best final properties [103].

ZrCC usually has a 2-layer/3-layer structure where the outer layer is mainly composed of $ZrO_2 \cdot xH_2O$, and the inner layers contain a higher concentration of aluminium oxyfluoride and aluminium oxide (Figure 1.9) [91, 92, 104].

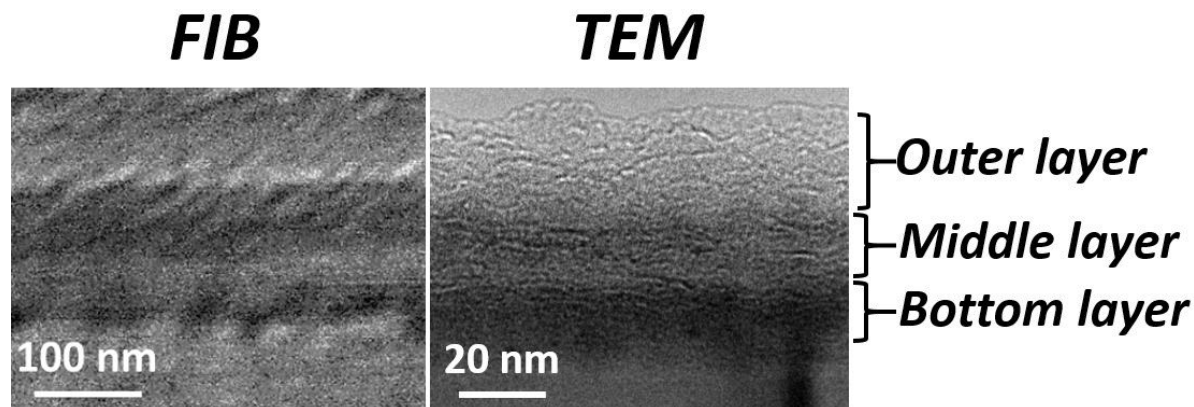


Figure 1.9: SEM and TEM images of the cross-section of ZrCC applied on AA 3005.

Average thickness of ZrCC on aluminium alloys is between 30 and 100 nm and depends on bath conditions, process parameters and the type of aluminium alloy substrate. Zirconium conversion coatings provide barrier corrosion protection for substrates and improve adhesion of topcoats [53, 78, 105, 106]. Recent studies showed that ZrCC possesses self-sealing/active corrosion protection properties on certain aluminium alloys [91, 92, 107, 108].

1.4.1 Testing performance of conversion coatings

The corrosion resistance of conversion coating should be evaluated by performing the following electrochemical measurements in 0.5 M NaCl:

- Potentiodynamic polarization measurements after a 1-h and at least 24-hour immersion.
- Electrochemical impedance spectroscopy measurements (from 10^5 kHz to 5 mHz) for at least two days, preferably for five days to obtain a trend of polarization resistance.

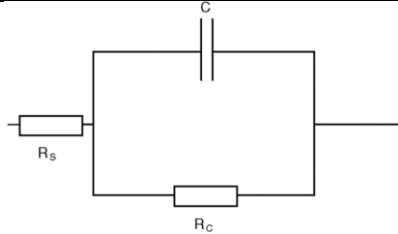
If corrosion current density decreases, and polarization resistance increases after a 24-h immersion in 0.5 M NaCl solution compared to a 1-h immersion, the conversion coating should be further evaluated with:

- Neutral Salt Spray Test
- Dry and Wet Adhesion Test.

Corrosion resistance, self-sealing effect and active corrosion protection of zirconium conversion coatings can be estimated with impedance modulus at low frequencies (1 mHz) which is approximately equal to total polarization resistance ($|Z|_{1\text{mHz}} \approx R_p$) [109, 110].

Experimental data obtained from EIS measurements can be used to estimate the natural salt spray test results. Buchheit et al. developed a statistical model for the approximation of natural salt spray test results [111]. In this model, they used a simplified equivalent electrical circuit $R_s(R_pC)$ to fit EIS data measured from 10^{-2} Hz to 10^4 Hz. R_c is defined as apparent integrated pitting resistance. Impedance module at low frequencies is approximately equal to integrated pitting resistance ($R_c \approx |Z|_{1\text{mHz}} \approx R_{p,1\text{mHz}}$). In this model parameter, R_{80} is defined as a threshold value that determines whether the coated material will pass the 168 h mark in natural salt spray (NSS) test; its range is listed in Table 1.6 for different aluminium alloys. If the coated metal after a 24-h immersion in 0.5 M NaCl exhibits the $R_{p,1\text{mHz}}$ within this range, it has the probability of >80% to pass the 168 h mark in NSS test (Table 1.6) [52].

Table 1.6: Threshold polarization resistance values for 80% cumulative passing frequency of natural salt spray test for conversion coatings applied on aluminium alloys and immersed in 0.5 M NaCl for 24 h. (R_c is defined as apparent integrated pitting resistance integrated pitting resistance in simplified equivalent electrical circuit $R_s(R_cC)$ used to fit EIS data) [52].

Alloy	80% CPF Threshold ($\Omega \cdot \text{cm}^2$)	95% Prediction interval at the R_{80} Threshold ($\Omega \cdot \text{cm}^2$)
AA 2024-T3	$2.4 \cdot 10^6$	$1.4 \cdot 10^6 \leq R_{80} \leq 4.1 \cdot 10^6$
AA 356	$4.6 \cdot 10^6$	$1.5 \cdot 10^6 \leq R_{80} \leq 1.5 \cdot 10^7$
AA 3003	$2.3 \cdot 10^7$	$1.1 \cdot 10^7 \leq R_{80} \leq 4.8 \cdot 10^7$
AA 6061-T6	$3.4 \cdot 10^6$	$2.0 \cdot 10^6 \leq R_{80} \leq 6.7 \cdot 10^6$
AA 7075-T6	$1.5 \cdot 10^7$	$3.6 \cdot 10^6 \leq R_{80} \leq 3.9 \cdot 10^7$
 Equivalent electric circuit model used to fit R_p values down to the frequency of 1 mHz.		

1.5 Purpose of the Dissertation

The primary purpose of this dissertation was to study the formation, and electrochemical behaviour of zirconium conversion coatings applied on aluminium alloys 2024, 3005, A365.0, 380.0, 5754 and 7075 in 0.5 M NaCl. Another purpose was to study the influence of Na_2S on corrosion behaviour of AA 365.0 in artificial seawater. The final goal was to obtain scientific data that will help to understand the corrosion process and to develop conversion coatings capable of replacing toxic chromate conversion coatings.

1.6 Objectives of the Dissertation

The objectives of this doctoral dissertation are the following:

- 1) To study the influence of Na_2S on the corrosion behaviour of AlSi7Mg0.3 aluminium alloy in artificial seawater.
- 2) To systematically study and obtain scientific data about the formation and electrochemical behaviour of zirconium conversion coatings applied on aluminium alloys: 1050, 2024, 380.0, 3005, A356.0, 5754, 7075.

1.7 Hypotheses of the Dissertation

This doctoral dissertation builds on the following hypotheses:

- Specific concentrations of sodium sulphide have a beneficial effect on corrosion behaviour of AlSi7Mg0.3 aluminium alloy in chloride-containing environments such as a solution of sodium chloride or artificial seawater.
- Zirconium conversion coatings applied to aluminium alloys are able to achieve self-sealing characteristics.
- Novel, optimized zirconium conversion coatings can reach the performance to the level similar to chromate conversion coatings.

1.8 Scientific Contribution

The results and findings of the research work presented within this doctoral dissertation contribute to the field of pre-treatment of aluminium alloys and corrosion protection of aluminium alloys. The original scientific contributions are as follows.

The effect of sodium sulphide on corrosion behaviour of aluminium alloy AlSi7Mg0.3 in artificial seawater.

Published in: G. Šekularac and I. Milošev, "Corrosion of aluminium alloy AlSi7Mg0.3 in artificial seawater with added sodium sulphide". *Corrosion Science*, vol. 144, pp. 54-73, 2018

Influence of sodium sulphide on the corrosion behaviour of aluminium alloy AlSi7Mg0.3 in artificial seawater was systematically studied. The novelty of this paper is that the addition of sodium sulphide has a beneficial effect on the corrosion protection of aluminium alloy AlSi7Mg0.3 exposed to the artificial seawater. The addition of a small concentration of sodium sulphide up to 50 ppm allowed the formation of a thicker and denser natural aluminium oxide, while a higher concentration of sodium sulphide induced incorporation of Mg^{2+} ions into a protective oxide layer and provided additional protection for aluminium alloy AlSi7Mg0.3.

The formation and self-sealing behaviour of zirconium conversion coating applied to AA 3005.

Published in: G. Šekularac and I. Milošev, "Electrochemical Behavior and Self-Sealing Ability of Zirconium Conversion Coating Applied on Aluminum Alloy 3005 in 0.5 M NaCl Solution", *Journal of The Electrochemical Society*, vol. 167, No. 2, pp. 021509-1-16, 2020

Corrosion behaviour of zirconium conversion coating applied to AA 3005 in 0.5 M NaCl solution was studied in this work. The most significant novelty of this work is that for the first time zirconium conversion coatings applied on any aluminium alloy improved corrosion resistance with immersion time in 0.5 M NaCl solution. We named this effect "**self-sealing**".

The formation and electrochemical behaviour of zirconium conversion coating applied to AA AlSi7Mg0.3.

Published in: G. Šekularac, J. Kovač and I. Milošev, "Prolonged protection of AlSi7Mg0.3 aluminium alloy in chloride solution by zirconium conversion coatings". *Corrosion Science*, vol. 169, pp. 108615-1-18, 2020

The formation of zirconium conversion coating applied to aluminium, alloy AlSi7Mg0.3, was systematically studied. A novelty in this work is that the processing time depends on the concentration of H_2ZrF_6 in conversion bath. Optimally prepared zirconium conversion coating applied to aluminium alloy AlSi7Mg0.3 showed self-sealing

behaviour and active corrosion protection when exposed to 0.5 M NaCl solution. Another novelty is the detection of Zn-rich spots in aluminium alloy AlSi7Mg0.3 for the first time. Pitting of ZrCC was initiated at Zn-rich areas.

The comparison of electrochemical behaviour and self-sealing effect of zirconium conversion coatings applied to aluminium alloys 1050, 2024, 380.0, 3005, A356.0, 5754, 7075.

To be published:

In this work, the formation of zirconium conversion coatings applied to aluminium alloys 1050, 2024, 380.0, 3005, A356.0, 5754, 7075 was studied. Electrochemical behaviour and self-sealing effect of optimally formed zirconium conversion coatings were evaluated and compared. Based on their performance, alloys suitable for this kind of protection were differentiated.

1.9 Methodology

Chemicals used for synthetic procedures are commercially available (reagent grade or better) from well-known suppliers (Sigma-Aldrich, Merck, Across Chemicals, and so forth.)

The following aluminium alloys were used as substrates:

- (1) **1050A-O / EN AW¹-1050A / EN AW-A199.5 UNS²-A91050** with nominal composition (Al 99.50 wt.%, Fe 0-0.4 wt.%, Si 0-0.25 wt.%, Zn 0-0.07 wt.%, Mn 0-0.05 wt.%, Ti 0-0.05 wt.%, Cu 0-0.05 wt.%, Mg 0-0.05 wt.%) produced by Impol 2000 d.d. (Slovenska Bistrica, Slovenia) in the form of a 1.5 mm thick sheet. Samples used in experiments were cut in a rectangular shape with dimensions 3 cm × 3 cm
- (2) **2024-T3 / EN AW-2024 / EN AW-AlCu4Mg1 / UNS-A92024** with a nominal composition (Cu 4.35 wt.%, Mg 1.33 wt.%, Fe 0.25 wt.%, Mn 0.53 wt.%, Zn 0.1 wt.%, other 0.07 wt.%, Al remaining) produced by Kaiser Aluminum in the form of 1 mm thick sheet.
- (3) **3005-O / EN AW-3005 / EN AW-AlMn1Mg0.5 / UNS-A93005** with nominal composition (Mn 1-1.5 wt.%, Mg 0.2-0.6 wt.%, Fe 0-0.7 wt.%, Si 0-0.6 wt.%, Cu 0-0.3, Zn 0-0.25 wt.%, Cr 0-0.1 wt.%, Ti 0-0.1 wt.%, residuals 0.15 wt.%) in the form of foil (thickness 70 microns) produced by Impol 2000 d.d. (Slovenska Bistrica, Slovenia) was used as a substrate. The composition given is provided by the supplier. Samples used in experiments were cut in a rectangular shape with dimensions 3 cm × 3 cm.
- (4) **A356.0-T6 / EN AC³ 42100 / EN AC AlSi7Mg0.3 / UNS-A13560** with nominal composition (Si 6.5-7.5 wt.%, Fe 0.15 wt.%, Cu 0.03 wt.%, Mn 0.10 wt.%, Mg 0.30-0.45 wt.%, Zn 0.07 wt.%, Ti 0.18 wt.%) produced by TALUM d.d. (Kidričevo, Slovenia) was used as a substrate. This is the alloy used for castings and corresponds to the following standards: International ISO⁴-A356.0, Germany-3.2371, UNS-A13560, A356.0 and USA-A356.0. Samples used in experiments were cut in a rectangular shape with dimensions 2.5 cm × 4 cm × 0.3 cm.

¹ EN AW = European standard (Euronorm) aluminium wrought

² UNS = Unified numbering system

³ EN AC = European standard (Euronorm) aluminium cast

- (5) **380.0-T6 / EN AC 46000 / EN AC AlSi9Cu3 / UNS-A03800** with nominal composition (Si 8.0–11.0 wt.%, Cu 2.0–4.0 wt.%, Fe 0.6–1.1 wt.%, Zn 1.2 wt.%, Mn 0.55 wt.%, Mg 0.15–0.55 wt.%, Cr 0.15 wt.%, Ni 0.55 wt.%, Pb 0.35 wt.%, Sn 0.25 wt.%, Ti 0.20 wt.%) produced by TALUM d.d. (Kidričevo, Slovenia) was used as a substrate. Samples used in experiments were cut in a rectangular shape with dimensions 2.5 cm × 4 cm × 0.3 cm.
- (6) **5754-H18 / EN AW-5754 / EN AW-AlMg3 / UNS-A95754** with nominal composition (Mg 2.6–3.6 wt.%, Mn 0–0.5 wt.%, Si 0–0.4 wt.%, Fe 0–0.4 wt.%, Cr 0–0.3 wt.%, Zn 0–0.2 wt.%, Ti 0–0.15 wt.%, Cu 0–0.1 wt.%) produced by Impol 2000 d.d. (Slovenska Bistrica, Slovenia) in the form of a 1.5 mm thick sheet. Samples used in experiments were cut in a rectangular shape with dimensions 3 cm × 3 cm
- (7) **7075-T6 / EN AW-7075 / EN AW-AlZn5,5MgCu / UNS-A97075** with a nominal composition (Zn 5.81 wt.%, Mg 2.55 wt.%, Fe 0.21 wt.%, Si 0.08 wt.%, Cu 1.67 wt.%, Al remaining) produced by Kaiser Aluminum in the form of a 1 mm thick sheet. Samples used in experiments were cut in a rectangular shape with dimensions 3 cm × 3 cm.

Throughout the doctoral dissertation, the following methods were used:

- Methods for surface/microstructural analysis of coatings and aluminium alloys: scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS), high-resolution transmission electron microscopy (HRTEM), focus ion beam microscopy (FIB), X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectroscopy (ToF-SIMS), digital imaging.
- Methods for electrochemical characterization: open circuit potential (OCP) vs. time curves, linear polarization resistance (LPR), potentiodynamic polarization curves (PD), electrochemical impedance spectroscopy (EIS).
- Other methods: immersion test.

1.10 Structure of the Dissertation

The doctoral dissertation is organized as follows:

- Chapter 2 describes the corrosion behaviour of AlSi7Mg0.3 aluminium alloy (A356.0) in artificial seawater with the addition of sodium sulphide.
- Chapter 3 presents the electrochemical behaviour and self-sealing ability of zirconium conversion coating applied to aluminium alloy 3005 in 0.5 M NaCl.
- Chapter 4 describes the formation and self-sealing ability of zirconium conversion coating applied to aluminium alloy AlSi7Mg0.3 (A356.0) in 0.5 M NaCl.
- Chapter 5 compares the electrochemical behaviour, and self-sealing ability of zirconium conversion coating applied on aluminium alloys 1050, 2024, 380.0, 3005, A356.0, 5754 and 7075 in 0.5 M NaCl

Chapter 1

Corrosion of Aluminium Alloy AlSi7Mg0.3 in Artificial Seawater with Added Sodium Sulphide

This chapter presents the study of the influence of Na₂S addition on the corrosion behaviour of AlSi7Mg0.3 aluminium alloy in artificial seawater. Corrosion behaviour was studied using electrochemical techniques: open circuit potential vs. time curves, potentiodynamic polarization curves, linear polarization resistance and electrochemical impedance spectroscopy. The microstructure of samples was analysed with FIB-SEM-EDS microscopy, XRD spectroscopy and digital imaging. The main result is that the addition of Na₂S up to 100 ppm improved corrosion resistance of AlSi7Mg0.3 in artificial seawater. The mechanism of formation of protection layers in the presence of sulphides was proposed.

This chapter addresses thesis Objective 1) from Chapter 1, Section 1.6.

Regarding my contribution: I made a literature overview of the topic, planned and performed the experiments and jointly prepared the manuscript with co-authors.



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Corrosion of aluminium alloy AlSi7Mg0.3 in artificial sea water with added sodium sulphide

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ABSTRACT

The corrosion behaviour of aluminium alloy AlSi7Mg0.3 in artificial sea water with added 0, 20, 50 and 100 ppm of Na₂S was investigated over the course of immersion of 42 days. Samples were taken at various times and their electrochemical and microstructural properties characterized. The corrosion current densities in all immersion solutions was very low, in the range of 10^{-7} – 10^{-9} A cm⁻². The structure, composition and protectiveness of the so formed oxide layers were dependent on the Na₂S concentration and immersion time. The presence of low sulphide concentration (< 50 ppm) is beneficial for the corrosion protection of AlSi7Mg0.3 alloy.

1. Introduction

Aluminium and aluminium alloys (AAs) have many applications due to their excellent mechanical, electrical and thermal properties coupled with lightness and high corrosion resistance in the pH range 4–9 [1]. Aluminium and AAs are protected by a spontaneously formed thin aluminium-oxide film that protects the underlying metal against corrosion [2]. However, in chloride containing environments, aluminium and AAs are susceptible to corrosion and pitting due to the presence of the intermetallic particles (IMPs) added to improve aluminium's mechanical properties [3]. The mechanical properties of AAs nowadays reach, or even exceed, those of carbon steels and of the copper-nickel and aluminium bronze alloys that have been traditionally used in sea water (SW) applications [4]. Consequently, interest in the application of AAs in SW and coastal environments has increased continuously from the mid 1970s, especially in recent years when AAs are increasingly used in the transportation industry in general, including also marine applications. This has promoted numerous studies devoted to the mechanism of corrosion of AAs in sea water [5–21].

AA series 5000 and 6000 showed the best corrosion resistance in SW [17] which, together with their good mechanical properties, made them suitable for marine and off-shore constructions, crafting of process equipment in desalination plants, ship-building, off-shore oil and gas industries, coastal power plants, etc. Bonewitz [5,6] investigated the corrosion of AAs 1100, 3003, 3004, 5052 and 6063 in artificial sea water (ASW) over the range 25–150 °C to check their suitability for use in desalination plants. The alloys exhibited corrosion rates of less than 1

mpy. AA3003 and AA3004 are suitable for use in ASW up to 150 °C, while AA5052 and AA6063 can be safely used up to 125 °C.

Considering the composition, alloying aluminium with magnesium improves the repassivation of pits more than manganese. Magnesium and manganese did not reduce general corrosion rate at 25 °C but, at higher temperatures, they shifted the potential to more active values and improved the resistance of alloys to corrosion and pitting. Experimental pH potential diagrams constructed for AA5086 in 3% NaCl showed that the passivity area lies between –863 and –1175 mV vs. saturated calomel electrode in the pH range 1–9 and only exists within the pH zone where the oxide is slightly soluble [7]. Anodic pitting exists only for the pH values where the oxide is insoluble and produces crystallographic pits. Above this region, uniform anodic attack occurs. Cathodic pitting occurs below –1175 mV and results in semi-spherical pits. These results are interpreted on the basis of local pH evolution during polarization, i.e., acidification generated by anodic polarization, and alkalization produced by cathodic polarization.

Parameters such as temperature, pH, salinity, pollution, sea depth, concentration of organic compounds and nutrients affect carbon dioxide system equilibria which, in natural sea water, were shown to have a significant influence on the corrosion behaviour of aluminium and AA5052 [9] and AA5053 [8]. The most corrosive combination was low pH, low temperature and high concentrations of dissolved oxygen. Another parameter worth investigating is the presence of sulphur-based species. There have been numerous studies on corrosion induced by sulphides on different metals used in SW and coastal applications. Sulphides are highly corrosive towards most metals: carbon steel

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[22–25], mild steel [26], stainless steel [27–29], copper-nickel alloys (Cu-Ni) [25,30–39], aluminium bronze [40,41], etc. Sulphides are one of the most common pollutants in natural sea water (NSW) and may reach levels of 50 ppm or more in severely polluted coastal or harbour water [42]. In unpolluted natural sea water sulphide concentration of 2–7 ppm was reported [43]. Its levels can rise during the decaying of biological compounds, during the natural sulphur cycle by the action of sulphate reducing bacteria (SRB) and from anthropological sources of pollution [42–45]. Increased concentrations of sulphides are detected in coastal regions, in harbours, near off-shore oil platforms, ship-yards, coastal power plants and geothermal sources, while lower concentrations are expected in the open sea. A 35 ppm sulphide concentration was reported as an average concentration of biogenic sulphide produced by the *D. desulfuricans* [46]. Marcus published a comprehensive review of the mechanism of corrosion induced by sulphur and its compounds [47]. Sulphur species originating from the environment, i.e. $\text{SO}_{2(g)}$, $\text{H}_2\text{S}_{(g)}$ or $\text{H}_2\text{S}_{(aq)}$, HS^- , H_2SO_3^- , $\text{S}_2\text{O}_3^{2-}$, etc., arrive to the metal surface by diffusion in aqueous solution and then the detrimental effect on the passivity of metals proceeds by several mechanisms: (i) sulphur can be adsorbed on metal surfaces, weakening the metal-metal bond and acting catalytically on the dissolution of metal, (ii) adsorbed sulphur blocks or retards the passivation by blocking the sites of adsorption of hydroxyl ions that are precursors for passive oxide formation, and (iii) nucleation of the sulphide, which may form when monolayer formation is exceeded. The latter may be responsible for local breakdown of the film and for pitting. Sulphur-assisted corrosion mechanisms are valid for Fe, Ni, Cr, Cu and their alloys [47].

In general it is believed that AA are resistive towards corrosion induced by H_2S and sulphides, but there are only few studies in the open literature on this topic [18–20,48]. H_2S and sulphides can actually have a beneficial effect and increase the corrosion resistance of aluminium alloys. Sinyavskii and Kalinin wrote a comprehensive review of studies carried out in the Russian academic community about marine corrosion and protection of aluminium alloys, including the influence of H_2S on corrosion in natural sea water, marine atmosphere, natural gas and the oil industry [18]. H_2S has a beneficial effect on all types of corrosion of AAs in various environments (dry and moist environments, mineralized water, oil mixtures) due to passivation, improvement of barrier properties of oxide film, and increasing resistance to pitting by shifting pitting and corrosion potential towards more positive values. Increased partial pressure of H_2S could promote removal of cathodic centres and shift a corrosion mechanism from localised towards more uniform corrosion. Antipodal corrosion behaviour of carbon steel and AAs in H_2S -bearing media was correlated with different semiconducting properties of Fe-oxide and Al-oxide layer, respectively [48]. Interaction of H_2S as electron donor with surface oxide causes a corrosion of n-type Fe-oxide and inhibition of p-type Al-oxide.

On the other hand, AAs are assigned an increased susceptibility to exfoliation corrosion and pitting when tested at a great depth in the Black Sea, due to increased concentrations of H_2S . At great depths anoxic conditions are established due to density gradient separation limiting the supply of dissolved oxygen to the deep water and the bacterial sulphate reduction then leads to formation of H_2S . It was proposed that H_2S decreased biofouling and thus reduced the coverage of AA with an aerobic biofilm which otherwise inhibits exfoliation corrosion.

Copper, in contact with aluminium alloys, acts adversely on corrosion resistance [20]. The greatest corrosion in the form of pitting, especially at 80 °C, was observed in the presence of Cu^{2+} and the absence of H_2S . H_2S has a role as a corrosion inhibitor by acting as a scavenger for Cu^{2+} ions and leading to deposition of insoluble CuS. This process prevents the formation of copper deposits which otherwise serve as sites for cathodic reduction of oxygen and leads to increased corrosion rate.

Despite these few studies there is still a lack of information about the effect of sulphides on the mechanism of corrosion of aluminium alloys in sea water and coastal applications. To tackle this issue in more

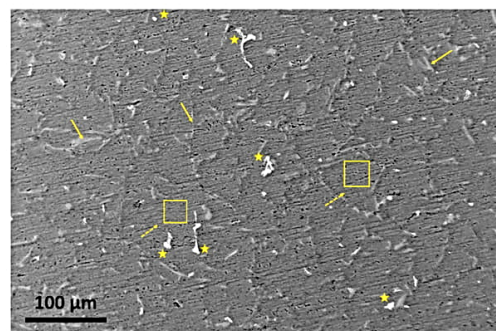


Fig. 1. SEM image of bare aluminium alloy AlSi7Mg0.3. Yellow marks denote the sites where EDS analysis was performed (Table 1): α -aluminium matrix (squares), silicon crystals (arrows) and intermetallic particles (stars). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

Table 1

Chemical composition of bare AlSi7Mg0.3 obtained by EDS analysis. Sites of analysis are denoted in SEM image (Fig. 1). Values of ΔE from literature data are given together with references.

Phases/Intermetallic particles	Elements/at. %						$\Delta E/mV$
	Al	Si	Mg	Fe	Mn	O	
α -Al solid solution	98	2	/	/	/	/	0 [67]
Crystallites of Si	3	97	/	/	/	/	260–280 [67]
Al(FeMn)Si	78.2	10.6	/	7.9	3	/	300–600 (2 μm –6 μm) [89] 100–300 (0.5–2 μm)
π -AlFeSiMg ("chinese script")	71.3	11.2	11.7	5.8	/	/	120–140 [67]
Al(FeMn)SiMg ; (Mg > Mn)	58.3	25.1	11.8	6.2	0.8	/	
Al(FeMn)SiMg ; (Mn $\approx$ Mg)	64.8	18.8	4.2	8.7	3.5	/	

detail, we have investigated the behaviour of AA AlSi7Mg0.3 in artificial sea water, with and without the addition of inorganic sulphide, Na_2S , during immersion for 42 days. Samples immersed for different periods of time were analysed in terms of their corrosion properties using electrochemical potentiodynamic measurements and electrochemical impedance spectroscopy (EIS) and, in terms of structure, composition and morphology of corrosion products using scanning electron microscopy with chemical analysis (SEM/EDS) and X-ray diffraction (XRD) techniques. Cross sections of the formed layers were prepared and analysed using focused ion beam microscopy (FIB) equipped with EDS. The final result of the study is the postulation of a corrosion mechanism for AlSi7Mg0.3 in artificial sea water as a function of sulphide concentration and immersion time.

2. Experimental procedure

2.1. Materials, sample preparation and chemicals

Aluminium alloy ENAC 42100 / ENAC AlSi7Mg0.3 (Si 6.5–7.5 wt%, Fe 0.15 wt%, Cu 0.03 wt%, Mn 0.10 wt%, Mg 0.30–0.45 wt%, Zn 0.07 wt%, Ti 0.18 wt%) produced by TALUM. d.d. (Kidričevo, Slovenia) was used as substrate. This is the alloy used for castings and corresponds to the following standards: International ISO—AlSi7Mg0.3, Germany—3.2371, UNS—A13560, A356.0 and USA—A356.0.

Samples used in experiments were cut in a rectangular shape with dimensions 2.5 cm $\times$ 4 cm $\times$ 0.3 cm. Prior to exposure to immersion

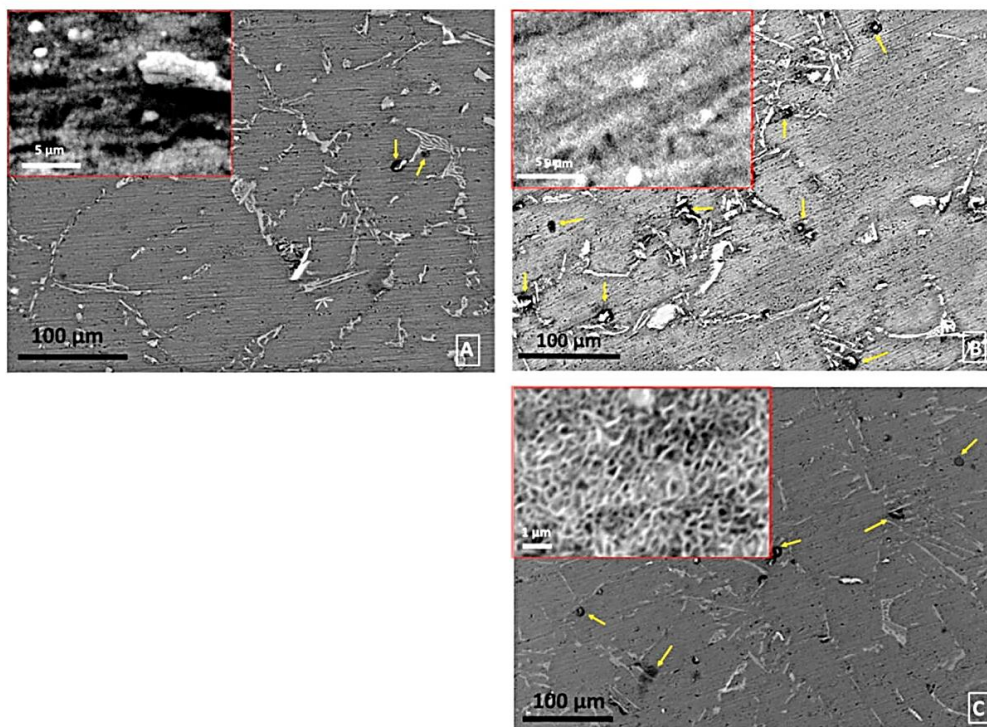


Fig. 2. SEM images of AlSi7Mg0.3 samples immersed in artificial sea water for periods of: a) 14 days, b) 28 days, and c) 42 days. Pits are denoted by yellow arrows. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

solution, samples were ground with SiC papers ranging from 320- to 4000-grit using a grinding/polishing machine LaboPol-20 (Struers, Ballerup, Denmark). Immediately after grinding, samples were ultrasonicated in absolute ethanol for 5 min using an ultrasonic bath Elmasonic P (Elma, Germany) at 37 KHz and 100% power. After cleaning, samples were dried with N_2 and conserved in desiccator until exposed to immersion solution.

The following chemicals were used for experiments: NaCl (for analysis, Merck), absolute ethanol (for analysis, Merck), KCl (99.5–100.5%, p.a., Sigma-Aldrich), H_3BO_3 (99.8%, p.a., Sigma Aldrich), $SrCl_2 \times 6H_2O$ (99+%, ACS reagent, Acros Organics), $MgSO_4 \times 7H_2O$ ($\geq 98\%$, ACS reagent, Sigma Aldrich), $MgCl_2 \times 6H_2O$ (99%, for analysis, Acros Organics), $NaHCO_3$ (99.5–100.5%, BioXtra, Sigma Aldrich), $CaCl_2 \times 6H_2O$ (for analysis, Acros Organics), KBr (99+%, for analysis, Acros Organics), $Na_2S \times 9 H_2O$, NaOH. Milli-Q Direct water with resistivity of 18.2 M Ω ·cm at 25 °C (Millipore, Billerica, MA) was used for rinsing and for solution preparation.

2.2. Immersion solution

The immersion solution was artificial sea water Burkhoder's formulation B (ASW) [49] prepared from 18.2 M Ω ·cm water, composed from: 6.805 g/L $MgSO_4 \times 7H_2O$; 5.01 g/L $MgCl_2 \times 6H_2O$; 0.192 g/L $NaHCO_3$; 0.664 g/L KCl; 26.702 g/L NaCl; 1.469 g/L $CaCl_2 \times 6H_2O$; 0.096 g/L KBr; 0.026 g/L H_3BO_3 ; 0.040 g/L $SrCl_2 \times 6H_2O$ (pH $\approx$ 7.50). pH was adjusted to 7.5 using 0.5 M NaOH solution.

The effect of the addition of Na_2S was studied for concentrations of 20, 50 and 100 ppm. pH of immersion solution was left to adjust naturally by hydrolysis of Na_2S . pH was measured throughout the course of immersion using pH meter 827 pH-lab equipped with Unitrode/Pt1000 (Metrohm AG, Herisau, Switzerland). Samples were placed in a glass vessel with a volume of immersion solution of 650 mL.

2.3. Experimental setup

In order to test influence of Na_2S on corrosion of AlSi7Mg0.3 the samples were exposed to immersion test solution for up to 42 days, in accordance with the standard NACE TM0169/G31 - 12a [50]. Samples were exposed to each solution in duplicate, i.e. each type of condition was repeated by two separate samples in separate vials. Samples in the same concentration were removed one-by-one on the day listed, and not put back to solution. During the course of the test, samples were taken out at different immersion times, i.e. at 1–3, 5, 7, 10, 14, 21, 28 and 42 days. Samples were then rinsed with deionized water and placed into a desiccator for further measurements. Digital images of the samples during the course of immersion were made using the digital camera with a resolution of 13 MP.

Solutions were annotated according to the concentration of Na_2S (S) added and the immersion period, e.g. S-0 ppm-1d and S-100 ppm-42d for samples exposed to ASW for 1 day, and for ASW containing 100 ppm Na_2S for 42 days.

2.4. Electrochemical characterization

Electrochemical experiments were carried out with an Autolab PGSTAT 12 (Metrohm Autolab, Utrecht, Netherlands) potentiostat/galvanostat controlled by Nova 2.1 software. Electrochemical measurements were made for two different samples. Representative measurements are presented in plots and mean values in tables. Measurements were conducted in a standard three electrode flat cell with a volume of 300 mL. The sample was the working electrode, platinum mesh was the counter electrode, and a saturated Ag/AgCl_(sat) electrode was the reference electrode ($E_{SHE} = 0.198$ V). All potentials in the text refer to the Ag/AgCl_(sat) scale. The electrolyte was freshly prepared ASW (pH = 7.5). Electrochemical measurements were

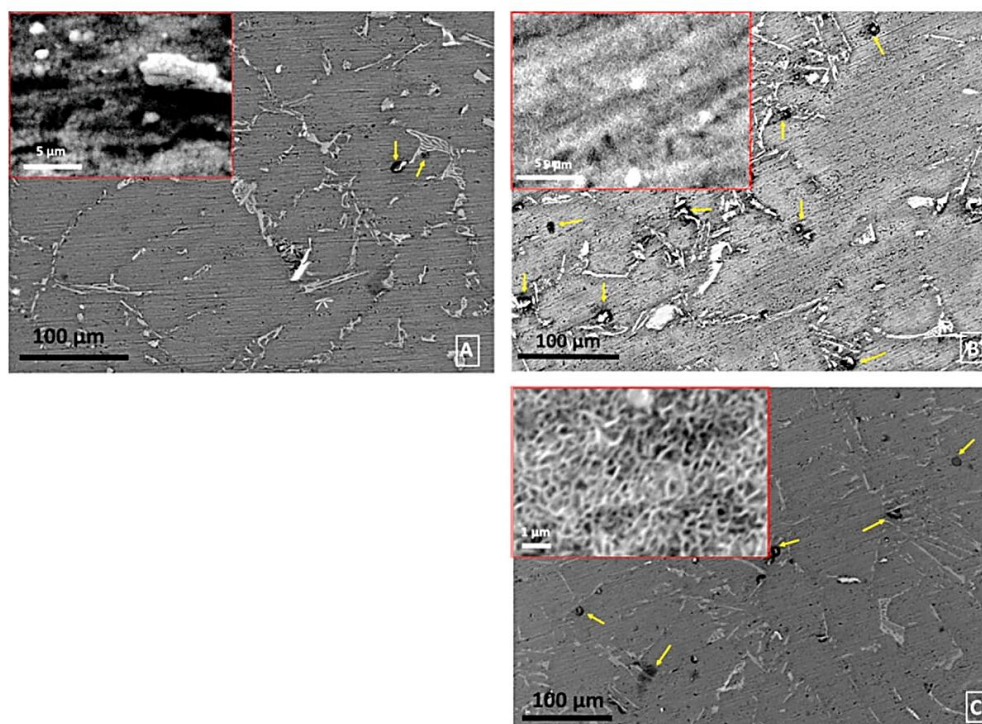


Fig. 3. SEM images of AlSi7Mg0.3 samples immersed in artificial sea water with added 20 ppm Na₂S for periods of: a) 14 days, b) 28 days, and c) 42 days. Pits are denoted by yellow arrows. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

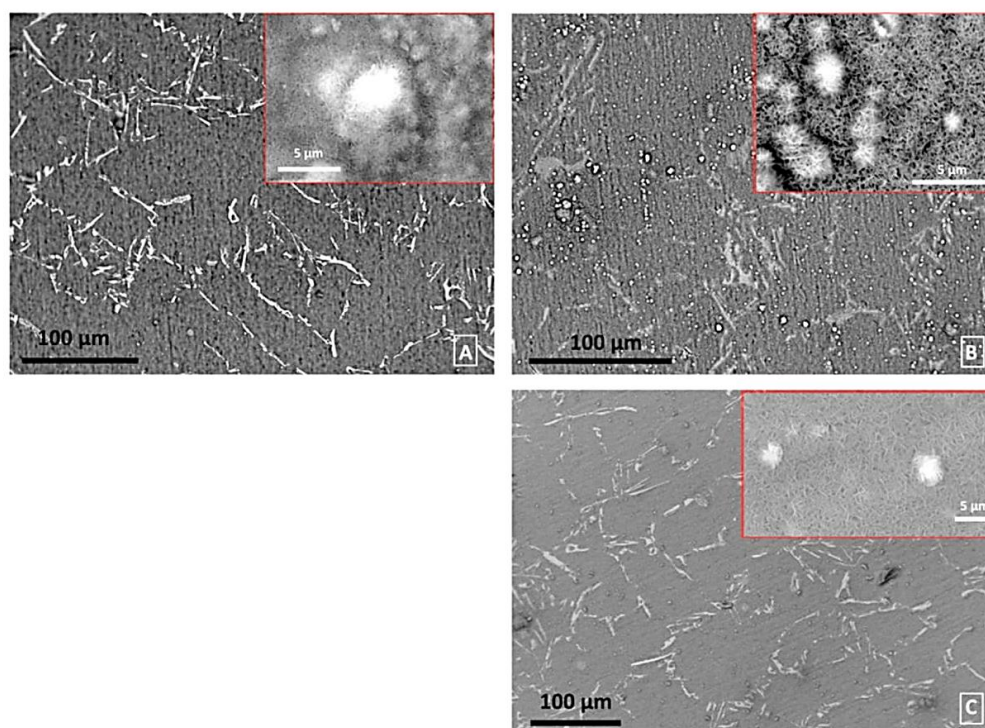


Fig. 4. SEM images of AlSi7Mg0.3 samples immersed for in artificial sea water with added 50 ppm Na₂S for periods of: a) 14 days, b) 28 days, and c) 42 days.

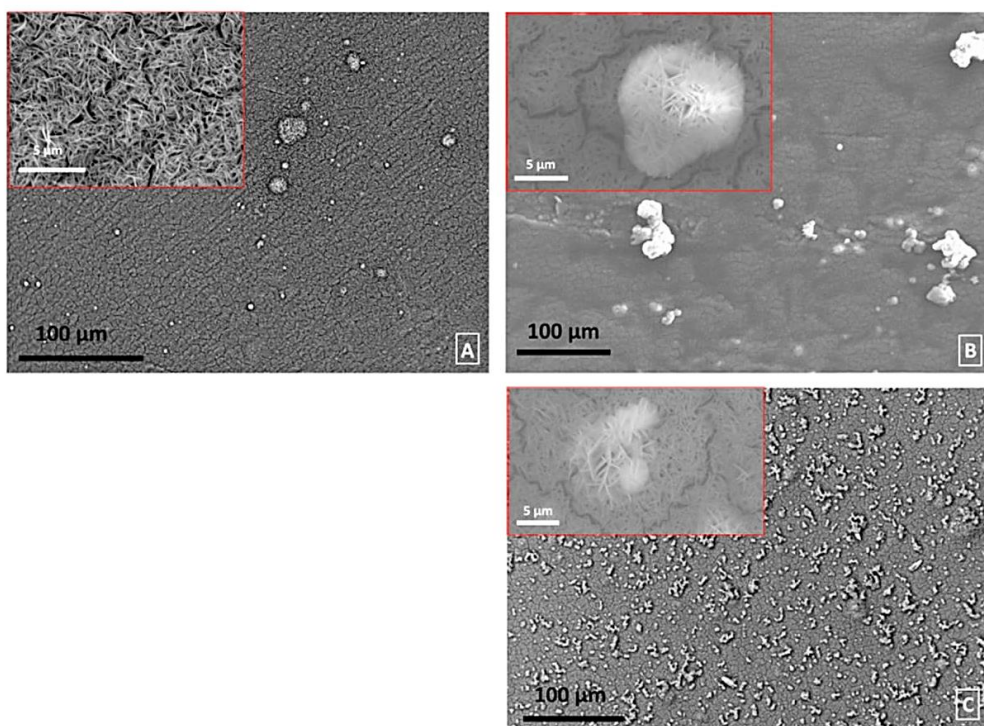


Fig. 5. SEM images of AlSi7Mg0.3 samples immersed in artificial sea water with added 100 ppm Na₂S for periods of: a) 14 days, b) 28 days, and c) 42 days.

conducted in the following sequence from least destructive to more destructive: (i) measurement of the open circuit potential (OCP) as a function of time during 1 h, (ii) recording of electrochemical impedance spectra at the OCP, (iii) recording of linear polarization curves, and (iv) recording of potentiodynamic polarization curves. The system was allowed to rest for 5 min before switching to the next electrochemical technique. The sample was not abraded between these successive measurements.

Linear polarization curves (LPR) were run in the range from -10 to 10 mV vs. OCP using a 0.1 mV/s scan rate. Polarization resistance ($R_{p,LPR}$) was determined as the slope of the fitted potential (E) vs. current density (j) curve using Nova 2.1 software.

Potentiodynamic polarization curves measurements were made in the potential region starting from -250 mV vs. OCP in anodic direction until current reached 1 mA. The scan rate was 1 mV/s.

Corrosion current density and corrosion potentials were determined using Nova 2.1 software based on the Tafel extrapolation method [51]. Polarization resistance was calculated also from parameters obtained with the Tafel extrapolation ($R_{p,Tafel}$) method using Nova 2.1 software based on Eq. (1) in accordance with standard ASTM G59-97 [52].

$$R_{p,Tafel} = \frac{B}{j_{corr}} \quad (1)$$

where B is Stern-Geary constant.

Electrochemical impedance spectroscopy (EIS) spectra were recorded from 100 kHz to 10 mHz frequency using an AC potential amplitude of 10 mV. Spectra were recorded at the OCP. The fitting of EIS data was performed in ZView[®] software (Scribner Associates Inc., Southern Pine, NC, USA) with data-modulus type of data weighting in maximum 1000 iterations. The chi-squared were of the orders of 10^{-3} . With these fitting criteria, the relative error of the equivalent circuit model was up to 10% .

Equivalent electric circuits (EECs) used for fitting of EIS spectra of

samples immersed in ASW with addition of Na₂S during period of 42 days are presented in Fig. 14. The EECs correspond to those usually applied in the literature [53–57] and were used to describe the properties of oxide layers and charge transfer parameters of the corrosion processes at the layer/substrate interface. The electrical properties of a oxide layer are represented by the constant phase element CPE_{oxide} and R_{oxide} in parallel, i.e. by constant phase element and resistor, respectively, describing its porous nature (pore capacitance and resistance). These precede the resistor R_{ct} related to charge transfer resistance in parallel to the capacitor CPE_{dl} due to double layer (dl) charging/discharging at the substrate surface. In some cases, the fitting of the charge transfer response required finite Warburg element (W_{fin}) [58] since charge transfer rate is limited by the diffusion of reacting species through a layer of finite thickness.

Constant phase element (CPE) was used due to deviations from ideal dielectric behaviour related to surface in homogeneities [59,60]. The impedance of CPE is defined as:

$$Z_{CPE} = [Q(j\omega^n)]^{-1} \quad (2)$$

where Q is the frequency-independent parameter of the CPE, j imaginary number ($j^2 = -1$), ω the angular frequency ($\omega = 2\pi f$) and n is the CPE exponent equal to 1 for pure capacitor and to 0 for pure resistor.

The sum of R_s , R_{oxide} , R_{oxide1} and R_{ct} is equal to the polarization resistance (R_p) [61–63]. Larger R_p values indicate higher corrosion resistance and, therefore, a lower corrosion rate. W_{fin} can be calculated from Eq. (3):

$$W_{fin} = R_{fin} \tanh[(j\omega T_{fin})^{1/2}] / (j\omega T_{fin})^{1/2} \quad (3)$$

The fitting yields values of R_{fin} and $T_{fin} = L^2/D$, where L is diffusion thickness and D is effective diffusion coefficient of diffusing species. We used Eqs. (4) and (5) to calculate capacitance (C) and Warburg

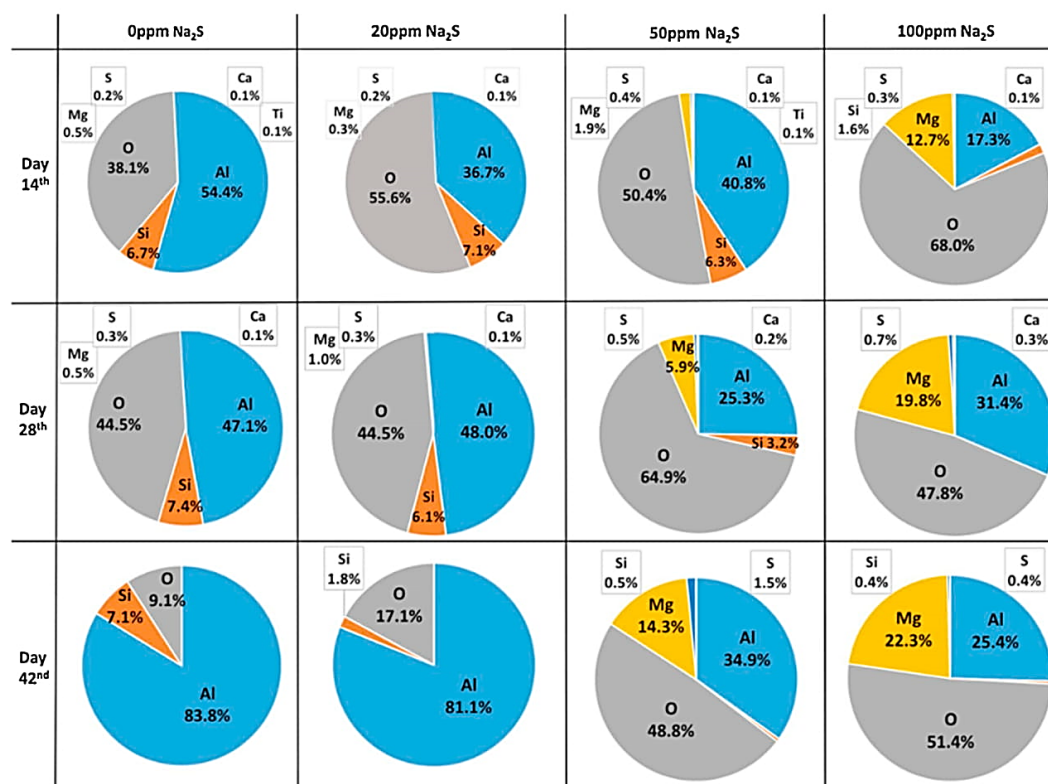


Fig. 6. Chemical composition of the surface of aluminium alloy AlSi7Mg0.3 deduced from EDS analysis. Samples were immersed for periods of 14, 28 and 42 days in artificial sea water with added 0, 20, 50, and 100 ppm Na₂S. Composition is given in atomic percent.

coefficient (σ), respectively, which are given in EECs parameter tables:

$$C = Q^{1/n} R^{(1-n)/n} \quad (4)$$

$$\sigma = R_{fin}/(T_{fin})^{1/2} \quad (5)$$

2.5. Microstructural characterization

Surface characterization was performed using scanning electron microscopy combined with energy dispersive X-ray spectrometry (SEM/EDS) and X-ray diffraction (XRD) techniques. SEM images were taken in compositional electron mode using a JEOL JSM-7600 F microscope, and EDS spectra were taken using a Oxford Instruments INCA system. The analysed area was a few micrometres in diameter and the analysed depth around 1 μ m. Prior to analysis, samples were coated with a thin carbon layer to reduce the charging effect, then analysed at an energy of 15 kV.

Focused ion beam microscopy (FIB) was used to assess the composition within the oxide layers. A FEI HelionNanolab 650, equipped with EDS, was first used to deposit 1 μ m thick Pt protection layer. Then a relative large cross section was made by rough removal of material with Ga ions (30 keV/9.3 nA) followed by a fine polishing (30 keV/79 pA). EDS maps and line scans of the cross-section were recorded with resolution of 512 lines. SEM images were taken at energy 10 kV in the secondary electron mode. Average thickness of oxide layers was evaluated using ImageJ program.

XRD techniques were performed with a X'Pert Pro x-ray diffractometer (PANalytical) in the range of 5–80 $2\theta^\circ$, with a step of 0.034. A totally open detector X'Celerator was used with a time of exposure of 100 s. Al (COD: 96-901-1603) [64], Si (COD: 96-901-3107),

Mg (COD: 96-901-3062), MgO (COD: 96-901-3226) (PDF1/JCP2.CAT:00-045-0946), CaCO₃ (PDF1/JCP2.CAT:00-005-0586), Mg(OH)₂ (PDF1/JCP2.CAT:00-044-1482), MgAl₂O₄ (PDF1/JCP2.CAT:00-021-01152), Al(OH)₃ (PDF1/JCP2.CAT:00-033-0018), AlOOH (PDF1/JCP2.CAT:00-021-1307).

3. Results and discussion

3.1. Images of the sample surface taken during the course of immersion

Optical images of samples during the course of immersion in artificial sea water (ASW) are presented in Fig. S1 up to 28 days of immersion (results for 42 days not shown; no difference compared to 28 days was observed). A layer of corrosion products was formed at the surface of each sample after 5 days of immersion. White dots of corrosion products, presumably precipitated aluminium and/or magnesium hydroxide, were observed on the sample immersed in ASW. The layers formed at the surface of samples were adherent to the substrate and were hydrophilic for S-0 ppm and S-20 ppm, and superhydrophilic for S-50 ppm and S-100 ppm samples, i.e. they absorb water drop. The surface layers formed were investigated in more details by SEM/EDS.

3.2. SEM/EDS characterization

The surface morphology and chemical composition of samples were investigated on a bare AlSi7Mg0.3 sample and on samples immersed for 14, 28 and 42 days in ASW with and without addition of 20, 50 and 100 ppm Na₂S. An SEM image of bare AlSi7Mg0.3 (Fig. 1) shows that this alloy is composed of two main phases that consist of α -aluminium matrix (98 at. % Al, 2 at. % Si), and silicon crystals (98 wt. % Si, 2 wt. %

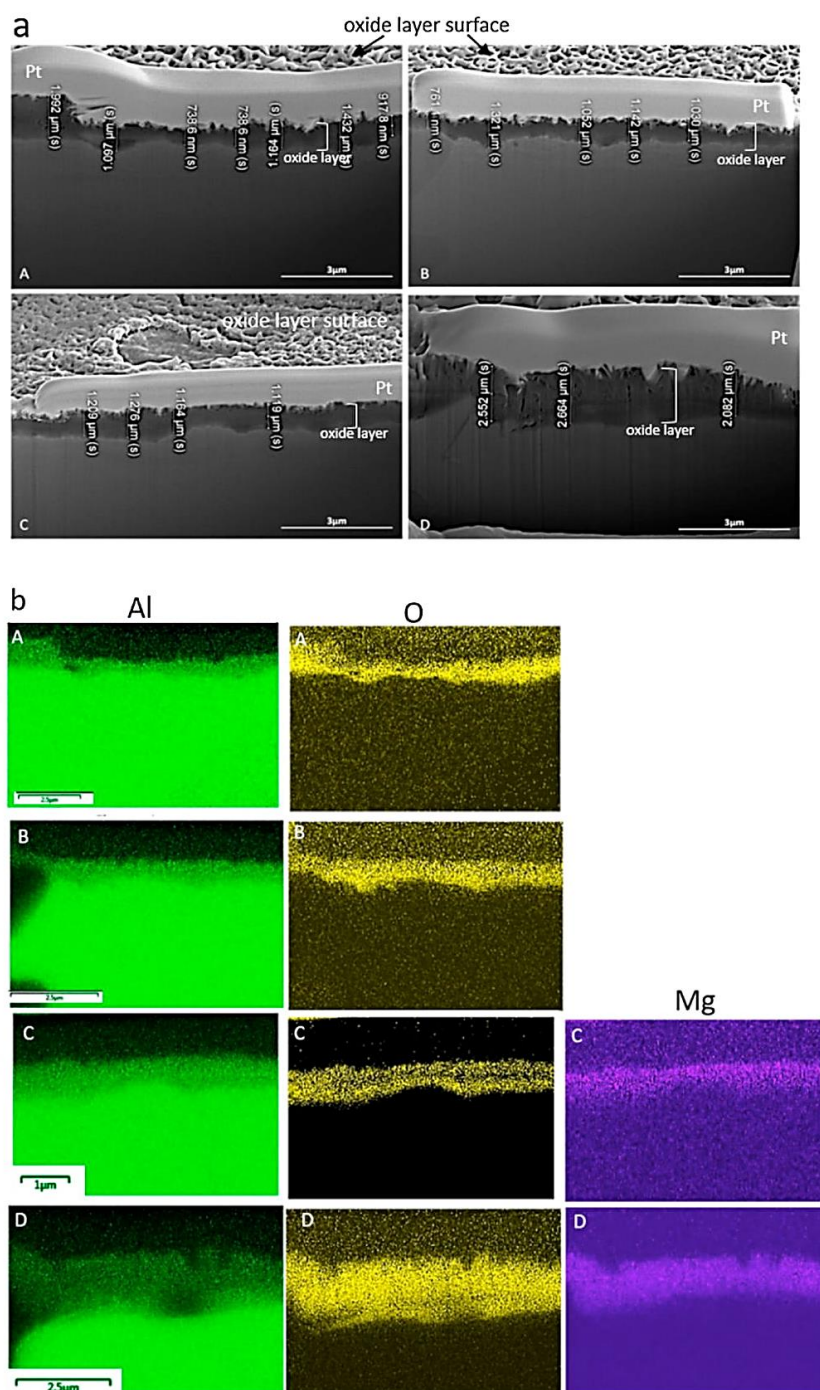


Fig. 7. (a) SEM images and (b) EDS mapping for Al, O and Mg of the cross-sections of the oxide layers formed on AlSi7Mg0.3 samples immersed for 42 days in artificial sea water with added a) 0 ppm Na₂S, b) 20 ppm Na₂S, c) 50 ppm Na₂S and d) 100 ppm Na₂S. Cross-sections were prepared by FIB. Average layer thickness was calculated using Image J programme: a) 813 nm, b) 905 nm, c) 1135 nm and d) 2398 nm (Table 2). Chemical composition of the cross-sections was analysed also by EDS line scans and presented in Fig. S2 in Supplementary material. Elemental composition of oxide layers obtained from EDS line scans is given in Table 2.

Al) [65]. In addition to these main phases, at least 5 different types of IMPs were detected [66], seen as bright spots. The chemical composition of different phases and IMPs was investigated using the point EDS

technique. The average chemical composition of the main phases and IMPs is presented in Table 1 along with the potential difference between them and the α -Al matrix taken from literature data. Due to

Table 2

Elemental composition of the cross-sections of oxide layers of AlSi7Mg0.3 samples (Fig. 7) immersed in artificial sea water with addition of Na₂S for period of 42 days. (Data was obtained with EDS line scan of cross section presented in Fig. S2 in Supplementary material).

Sample	S-0 ppm-42d		S-20 ppm-42d	S-50 ppm-42d		S-100 ppm-42d	
Average oxide thickness/nm	813		905	1135		2398	
Oxide thickness at line scan position/nm	900 ^a	400 ^b	1100	400 ^a	800 ^b	1200 ^a	900 ^b
Al/at. %	60	60	70	60	65	30	40
O/at. %	30	30	25	35	35	45	30
Mg/at. %	/	/	/	5	/	15	/
Si/at. %	/	5	/	/	/	/	25

^a Outer oxide layer.

^b Inner oxide layer formed around Si crystallite.

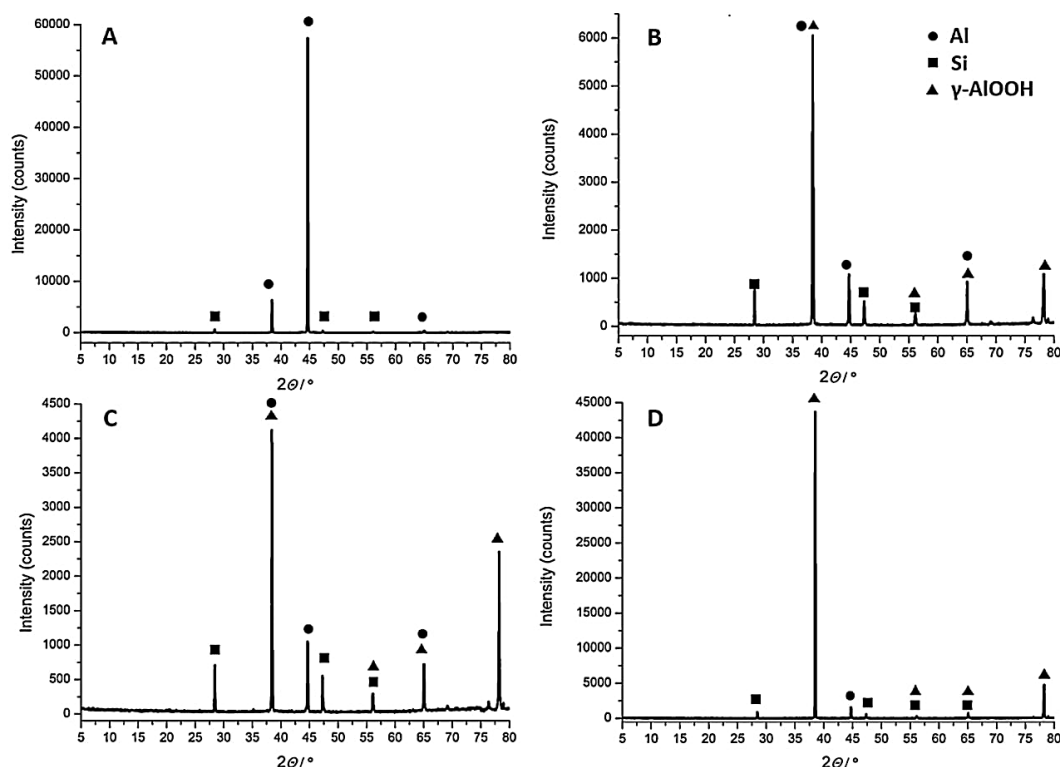


Fig. 8. XRD spectra for (a) bare AlSi7Mg0.3 and AlSi7Mg0.3 samples immersed in artificial sea water for periods of: b) 14 days, c) 28 days, and d) 42 days.

differences in their Volta potentials, different phases and IMPs form local micro corrosion cells and initiate the corrosion process and pitting [3,66–68]. Silicon is cathodic (more noble) with respect to the aluminium-rich matrix, which may lead to the formation of micro-galvanic couples resulting in localised corrosion phenomena. However, the corrosion is minimal due to the low current density resulting from the high degree of polarization of silicon particles [3]. Al–Fe–Si–Mn IMPs improve the mechanical properties and castability of the alloys. Additionally, manganese reduces the cathodic effect of iron, leading to less intense galvanic couples than those with Al–Fe–Si IMPs [69]. Al–Fe–Si–Mg IMPs, which can crystallize in the form of the so-called “Chinese script” [65,70], improve the yield strength, the tensile strength and the hardness of the alloy compared with those that are magnesium free [65,70]. These compounds also behave cathodically with respect to the α -Al phase, although they are expected to be less detrimental than Al–Fe, Al–Fe–Si and Al–Fe–Si–Mn due to the presence of magnesium.

SEM images of samples immersed in ASW with the addition of 0, 20, 50 and 100 ppm of Na₂S for periods of 14, 28 and 42 days are presented

in Figs. 2–5. Samples immersed in ASW (S-0 ppm-14d) were covered with a very thin layer of corrosion products (Fig. 2a) which has a net-like structure (inset in Fig. 2a). Pits were clearly seen as black dots all over the sample surface (marked with arrows in Fig. 2a). The IMPs and grinding marks were still visible beneath the layer of corrosion products. These findings indicate that the layer of corrosion products at the surface of AlSi7Mg0.3 immersed in ASW formed slowly or that the corrosion products were dissolving continuously from the surface, leaving it vulnerable to further corrosion. After 28 days a thicker layer of corrosion products was formed (S-0 ppm-28d) (Fig. 2b). Compared to S-0 ppm-14d, fewer pits were visible which may be due to coverage with the thicker layer; IMPs were still visible. The layer thickness further increased with immersion time (S-0 ppm-42d) (Fig. 2c). There were fewer pits remained; the IMPs were less visible and smaller than the S-0 ppm-28d. The layer formed had a nanosheet structure and was more dense than the S-0 ppm-28d (inset in Fig. 2c).

The surface of the sample immersed for 14 days in the ASW with added 20 ppm Na₂S (S-20 ppm-14d) had fewer pits than did sample S-

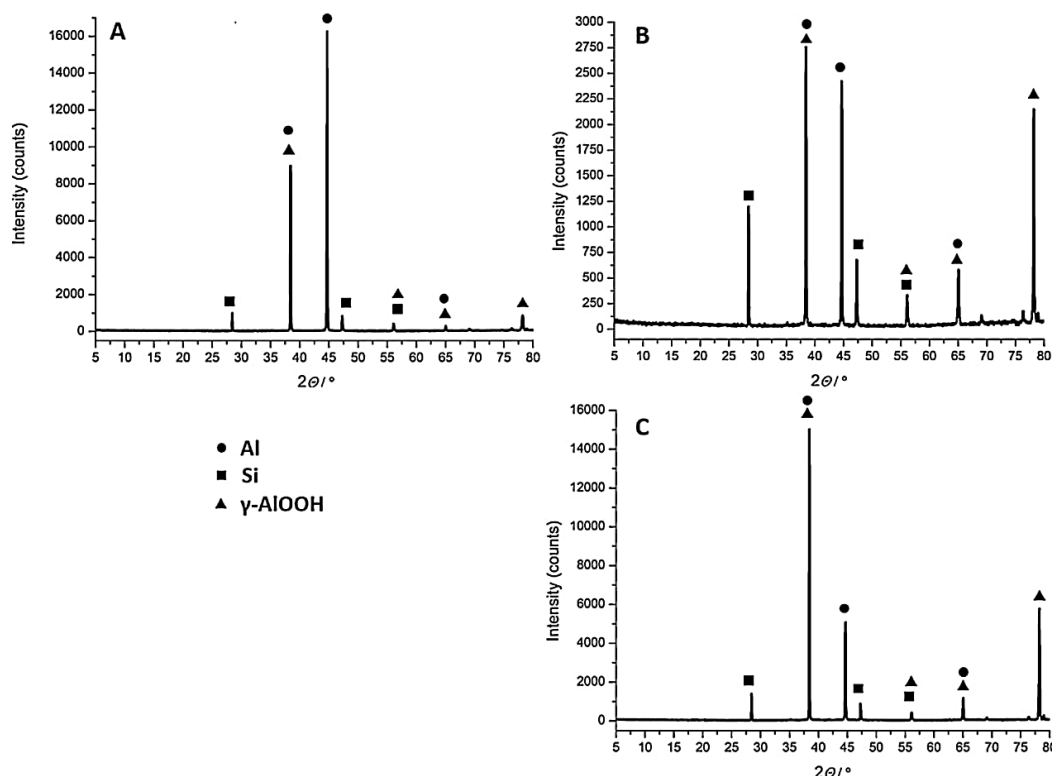


Fig. 9. XRD spectra of AlSi7Mg0.3 samples immersed in artificial sea water with added 20 ppm Na₂S for periods of: a) 14 days, b) 28 days, and c) 42 days.

0 ppm-14d (Fig. 3a). The IMPs and grinding marks were still visible. The layer of corrosion products seemed only slightly thicker than that of the S-0 ppm-14d sample (inset in Fig. 3a). During the course of immersion, after 28 and 42 days (Fig. 3b,c), the layer became more dense and more compact and exhibited a nanosheet morphology, similar to that of S-0 ppm-42, but more highly expressed.

The surface of the sample immersed for 28 days in ASW with added 50 ppm Na₂S (S-50 ppm-14d) was covered with a thicker layer of corrosion products than were the samples S-0 ppm-14d and S-20 ppm-14d (Fig. 4a). There were no visible pits but the IMPs were still clearly visible. A detailed image shows that the surface is now continuously covered with a layer having a sub-micrometre-sized nanosheet morphology (inset in Fig. 4a). At some points agglomerates were formed. After 28 days at the top of this layer there were deposits in the form of a rose-like structure (bright spots on the image), while IMPs were blurred due to their being covered with a thicker layer (Fig. 4b). After 42 days pits were not visible although IMPs were more clearly visible and larger than for S-0 ppm-42d and S-20 ppm-42d. The layer of corrosion products had a nanosheet structure with rose-flower deposits (inset in Fig. 4c).

Already after 14 days it was evident that the surface of the sample immersed in ASW with added 100 ppm Na₂S (S-100 ppm-14d) was covered with a much thicker layer of corrosion product than other samples (Fig. 5a). There were no visible pits or IMPs. The layer formed was compact and homogeneous. At lower magnification this layer had a mud-crack structure, but a higher magnification image shows that it is composed of nanosheets. At several points, deposits of corrosion product in the form of rose-flowers were formed at the surface. After 28 days, the layer of corrosion products was dense and compact (Fig. 5b). This layer had a mud-crack structure and a nanosheet morphology, sporadically covered by larger, rose-flower deposits. There were no

visible pits and IMPs at the surface of this sample. At prolonged immersion, there were significantly more rose-flower deposits present at the top of the layer but they were smaller than those on S-100 ppm-28d (inset in Fig. 5c).

Changes in the chemical composition of the surface of AlSi7Mg0.3 immersed in the ASW with the addition of 0, 20, 50, 100 ppm Na₂S, determined at 14, 28 and 42 days, are presented in Fig. 6. The surface of S-0 ppm-14d was composed mainly of Al, O, Si and minor amounts of Mg and S. It contained the lowest amount of O (38 at. %) and the highest amount of Al (54.4 at. %) compared with S-20 ppm-14d, S-50 ppm-14d and S-100 ppm-14d. A significant amount of Si was present at the surface of both samples, S-0 ppm-14d and S-20 ppm-14d, i.e., 6.7 and 7.1 at. %, respectively, comparable to the amount of Si in the bare alloy. Thus, S-0 ppm-14d and S-20 ppm-14d were covered with the thinnest layer of corrosion products, thin enough to allow Si from the underlying substrate to be detected by EDS. These findings are in good agreement with the SEM images Figs. 2a and 3a. After 28 days (S-0 ppm-28d) a slightly higher content of O (44.1 at. %) and a lower content of Al (47.1 at. %) were noticed than after 14 days indicating the formation of more aluminium oxide/hydroxide. The surface also contained Si (7.4 at. %) and trace amounts of S, Ca and Mg (0.5at. %). After 42 days, a significantly higher content of Al (83.8 at. %) and a lower content of O than after 28 days was obtained, which may be related to several issues: the layer may be thinner due to the advancing process of pitting corrosion leading to exposure of the bare alloy (Fig. 5a). Another reason might be related to the progressive dehydration of the aluminium oxide/hydroxide layer. The content of Si remained similar with increasing immersion time.

The surface of S-20 ppm sample was similar to the S-0 ppm after 14 and 28 days of immersion but the amount of O was higher, indicating the formation of a thicker oxidized layer. This may be substantiated by

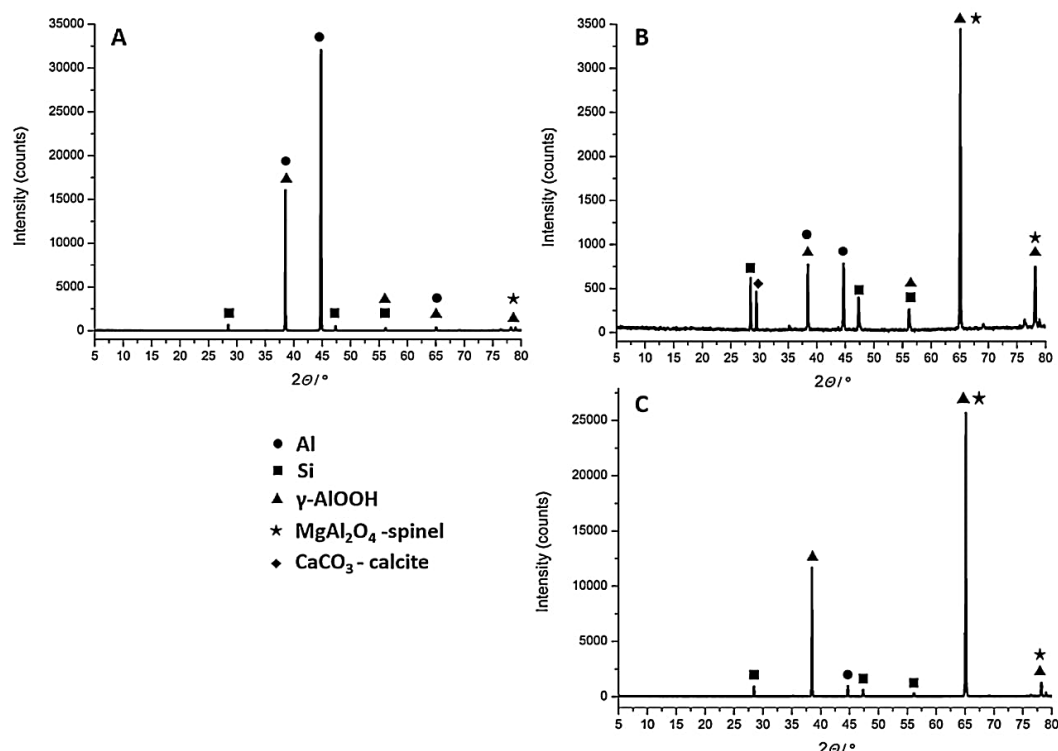


Fig. 10. XRD spectra for AlSi7Mg0.3 samples immersed in artificial sea water with added 50 ppm Na₂S for periods of a) 14 days, b) 28 days and c) 42 days.

a reduced content of Si after 42 days (1.8 at. %) compared to the S-0 ppm-42d.

The surface of S-50 ppm-14d contained a significantly higher amount of Mg (1.9 at. %) and S (0.4 at. %) than S-0 ppm-14d and S-20 ppm-14d. This is related to the addition of larger amounts of Na₂S. The surface of S-50 ppm-14d also contained O (50.4 at. %), Al (40.8 at. %) and Si (6.3 at. %). After 28 days, the content of O increased (64.9 at. %) and those of Al (25.3 at. %) and Si (3.1 at. %) decreased in comparison with the S-0 ppm-28d and S-20 ppm-28d. The surface was thus more oxidized and covered with a thicker layer of corrosion products, in agreement with the SEM images (Fig. 4). The smaller content of Si indicates that the layer was sufficiently thick to mask the Si signal from the underlying substrate. The content of Mg (5.9 at. %) was greater. The trend continued and after 42 days immersion with larger contents of Mg (14.3 at. %) and Al (25.3 at. %) and smaller content of Si (0.5 at. %). This finding indicates that ions of Mg continue to deposit from solution into the layer of corrosion products, so that the layer becomes enriched with magnesium oxide/hydroxide with immersion time. This layer obviously masked the Si present in the underlying substrate.

These results indicate that, in the presence of a larger amount of Na₂S in the ASW, the layer of corrosion products comprised not only aluminium oxides/hydroxide but magnesium oxides/hydroxide as well. Accordingly, the S-100 ppm-14d contained an even larger amount of Mg (12.7 at. %) and a significantly smaller amount of Si (1.6 at. %). The concentration of Al was almost the same as that of Mg (17.3 at. %). With increasing immersion time to 28 and 42 days, respectively, the content of Mg in the surface layer increased and that of Si diminished.

To summarize, examination by EDS of layers formed at the surface of samples on immersion in ASW containing 50 and 100 ppm Na₂S demonstrated the presence of magnesium oxide/hydroxide as well as the formation of aluminium oxide/hydroxide. The content of magnesium increased with increasing concentration of Na₂S and with

immersion time. For all samples investigated, the thickness of the oxidized surface layers became progressively larger with time of immersion, as will be shown in next section.

3.3. Cross-section SEM/EDS analysis and layer thickness

Cross-sections of the layers in ASW formed were prepared and analysed by FIB SEM/EDS techniques (Fig. 7). After 42 days of immersion average thickness of oxide layer for samples S-0 ppm-42d, S-20 ppm-42d, S-50 ppm-42d and S-100 ppm-42d was 813 nm, 905 nm, 1135 nm and 2398 nm. (Fig. 7a, Table 2). Therefore, the oxide layer thickness increases with increasing Na₂S concentration. Oxide layers seem compact and without visible pores, but for sample S-100 ppm-42d was porous with pore channels reaching substrate.

EDS mapping (Fig. 7b) and line scans (Fig. S2 in Supplementary material) showed that oxide layers for S-0 ppm-42d and S-20 ppm-42d consisted of Al₂O₃. The content of Al in the latter sample is larger indicating that the layer is more dehydrated. Oxide layer formed on S-50 ppm-42d consisted mainly of Al₂O₃ with presence of minor amount of magnesium oxide/hydroxide in outer part of oxide layer. Oxide layer for S-100 ppm-42d consisted of Mg and Al oxides/hydroxide probably in form mixture of Al₂O₃ (AlOOH) and MgO, or in form of spinel MgAl₂O₄.

3.4. XRD characterization

XRD spectra of bare AlSi7Mg0.3 and of samples immersed in ASW for periods of 14, 28, and 42 days (S-0 ppm-14d, S-0 ppm-28d, S-0 ppm-42d) are presented in Fig. 8. For bare AlSi7Mg0.3, characteristic peaks for Al are observed at 38.42°, 44.66° and 65.05°, the former two with the highest intensities (Fig. 8a). Peaks for Si are observed 28.40°, 47.28°, 56.07°. The peak of Al could originate from the underlying

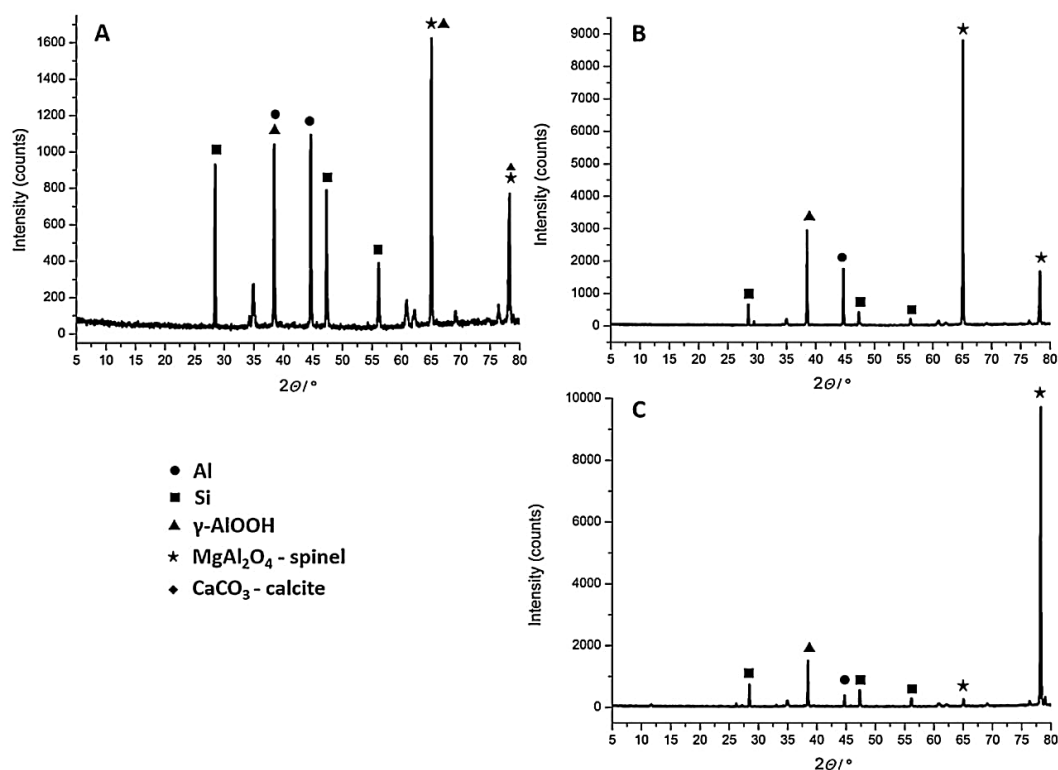


Fig. 11. XRD spectra for samples of AlSi7Mg0.3 immersed in artificial sea water with added 100 ppm Na₂S for periods of: a) 14 days, b) 28 days and c) 42 days.

substrate or be due to the oxidized layer not yet having completely covered the surface. After 14 days immersion in ASW, the peak for Al at 44.66° was significantly lower as it became covered by a surface layer consisting of aluminium oxide/hydroxide (γ -AlOOH and/or Al₂O₃), evidenced by a characteristic peak at 78.20° (Fig. 8b). Since the peak at 38.42° is assigned to both aluminium and aluminium oxide, it had almost the same value prior and after 14 days immersion (reduction of Al content is balanced by the increase in aluminium oxide content). Peaks for Si had almost the same values after 14 days of immersion. After 28 days, the peaks for Al at 38.42° and 44.66° were less intense due to progressive covering of the underlying substrate with aluminium oxide, as evidenced by the increased peak at 78.20° (Fig. 8c). After 42 days, the oxide peak at 38.42° was substantially greater, probably due to better crystallinity and/or increased oxide thickness (Fig. 7a). Peaks related to alloy substrate could not be detected any more.

XRD spectra are presented for samples immersed in ASW with the addition of 20 ppm Na₂S for periods of 14, 28 and 42 days (S-20 ppm-14d, S-20 ppm-28d, S-20 ppm-42d) (Fig. 9). With increased immersion time, the characteristic peaks for Al decreased while those for oxide increased, indicating progressive formation of aluminium oxide at the surface. The peaks related to Si are still detected, suggesting that the surface layer was thinner than the analysis depth of a few micrometres.

When the ASW contained 50 ppm of Na₂S peaks related to the Al signal from the underlying substrate were still present after 14 days (Fig. 10a). The oxidized layer, however, was sufficiently crystalline to give an intense signal related to Al oxide. After 28 days, both peaks decreased due to the formation of a new layer of corrosion products that covered both the aluminium oxide and the underlying aluminium alloy (Fig. 10b). This product is related to the peak at 65.05° and can be assigned to magnesium aluminium spinel, MgAl₂O₄, or possibly to magnesium oxide, MgO (periclase), together with γ -AlOOH (boehmite).

Another peak at 29.63° can be related to CaCO₃ (calcite). After 42 days of immersion, the peak at 65.05° increased significantly, indicating that it had become more crystalline and thicker (Fig. 10c). The peak at 38.42° related to Al oxide also increased. These results correlate well with results of the cross-section analysis (Fig. 7).

XRD spectra for samples immersed in ASW with added 100 ppm Na₂S are presented in Fig. 11. After 14 days peaks for Al oxide at 44.66° and 38.42° were less intense than that for S-50 ppm-14d (Fig. 11a). Peaks at 65.05° and 78.20° expressed counts of 1500 and 750 counts respectively, indicating the formation of MgAl₂O₄. Peak at 78.20° can be assigned to the formation of magnesium oxide/aluminium oxide. After 28 days of immersion, the peak at 65.05° increased relative to that for S-100 ppm-14d, indicating that the layer of MgAl₂O₄/MgO + AlOOH had become more crystalline and thicker. The same is true for aluminium oxide, as evidenced by the peak at 38.42°. The peak at 78.20° had become more intense due to formation of more crystalline MgAl₂O₄/MgO + AlOOH. At the same time the peak at 38.42° decreased, indicating that the layer of aluminium oxide was buried under MgAl₂O₄/MgO + AlOOH.

3.5. Electrochemical potentiodynamic characterization

Potentiodynamic polarization curves for samples immersed in ASW with added 0, 20, 50 and 100 ppm of Na₂S, for periods of 1, 14, 28 and 42 days are presented in Fig. 12. The electrochemical parameters, deduced from potentiodynamic polarization curves, are presented in Fig. 13 and Tables S1–S4 in Supplementary material, along with the values of OCP and R_p . After 1 day of immersion in ASW, AlSi7Mg0.3 still shows relatively high corrosion resistance, as expressed by the shape of the polarization curve and the electrochemical parameters (Fig. 12a and Table S1). The value of $R_{p,LPR}$ was $1.3 \cdot 10^5 \Omega \text{ cm}^2$. With

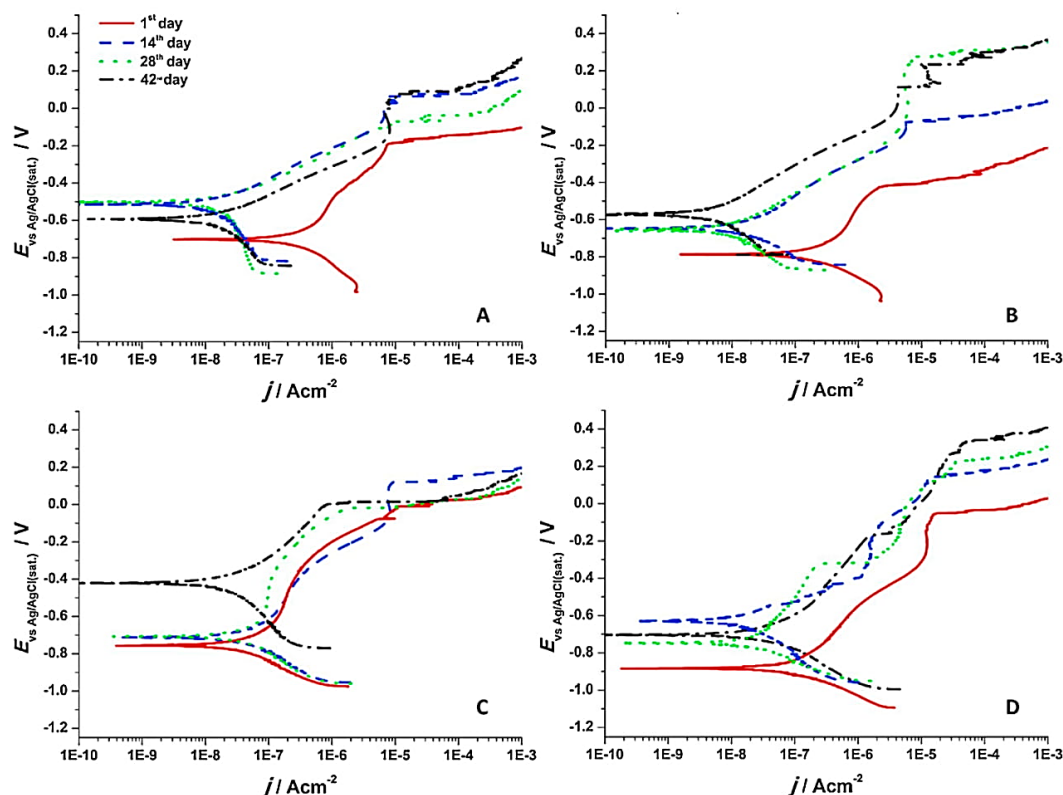


Fig. 12. Potentiodynamic polarization curves recorded for AlSi7Mg0.3 in fresh artificial sea water (pH = 7.5) for samples previously immersed in artificial sea water with added a) 0 ppm, b) 20 ppm, c) 50 ppm, and d) 100 ppm Na_2S for periods of 1 day, 14 days, 28 days, and 42 days. Scan rate = 1 mV/s.

increasing immersion time in ASW up to 42 days, it increased gradually up to $7.1 \cdot 10^6 \Omega \text{ cm}^2$ (Table S1). In the Tafel region of polarization curves, the cathodic curve relates to the reduction of dissolved oxygen and the anodic curve to the dissolution of Al and other alloying elements (Fig. 12a). The value of E_{corr} is -0.74 V and that of j_{corr} , $2.05 \cdot 10^{-7} \text{ A cm}^{-2}$. Following E_{corr} , the current density started to increase, first exponentially but then, at approx. -0.6 V , a passive range was established at which the current density increased much more slowly with increasing potential. At more positive potentials, a local breakdown of the passive layer occurred at the pitting potential, E_{pit} , -0.23 V . The passive window, $\Delta E = |E_{\text{pit}} - E_{\text{corr}}|$, was 0.51 V . With increasing immersion time E_{corr} shifted more positively, up to -0.65 V ; j_{corr} became smaller, $9.84 \cdot 10^{-9} \text{ A cm}^{-2}$, and ΔE increased to 0.82 V (Fig. 12a and Table S1 in Supplementary material).

The presence of 20 ppm Na_2S in ASW over long term immersion affected the polarization curves in ASW (Fig. 12b). After 1 day, values of j_{corr} were comparable to that in ASW, and E_{corr} was shifted 60 mV more negative (Fig. 13b). The presence of Na_2S affected the ΔE which became narrower due to the positive shift of E_{corr} and E_{pit} (Fig. 12b). However, after prolonged immersion, in particular longer than 14 days, corrosion resistance improved, as evidenced by the broadening of ΔE to 0.94 V and a decrease in j_{corr} . After 42 days, j_{corr} was smaller than for the sample previously immersed in pure ASW ($4.46 \cdot 10^{-9} \text{ A cm}^{-2}$ and $9.84 \cdot 10^{-9} \text{ A cm}^{-2}$, respectively) and the $R_{\text{p,LPR}}$ values were larger ($1.1 \cdot 10^7 \Omega \text{ cm}^2$ and $7.1 \cdot 10^6 \Omega \text{ cm}^2$) (Fig. 13). These findings, indicating increased corrosion resistance in the presence of 20 ppm Na_2S , are related to the changed composition and morphology of the surface layer, i.e., to the increased thickness and crystallinity of the Al oxide layer, as demonstrated by the results of SEM, EDS and XRD analyses (Figs. 2–11).

Up to approximately 10 days immersion, the electrochemical parameters reflected greater corrosion resistance in the presence of 50 ppm Na_2S (larger $R_{\text{p,LPR}}$, smaller j_{corr} , more negative E_{corr} and broader ΔE) compared to 20 ppm (Fig. 12b and c). At longer immersion times, however, the trend became reversed and, at the end of the test, the corrosion resistance of the sample immersed in ASW containing 50 ppm Na_2S was lower than that with zero or 20 ppm Na_2S (Figs. 12a, b and 13). This trend continued for the sample previously immersed in ASW containing 100 ppm Na_2S (Figs. 12d and 13), with the difference that the time at which the change in behaviour took place was prolonged. Up to approximately 20 days, the electrochemical parameters reflected greater corrosion resistance than that for other solutions, but at longer times the trend changed. At the end of the test, the sample previously immersed in ASW containing 100 ppm Na_2S expressed the smallest $R_{\text{p,LPR}}$ ($2.2 \cdot 10^5 \Omega \text{ cm}^2$), the largest j_{corr} ($3.92 \cdot 10^{-8} \text{ A cm}^{-2}$) and the most negative E_{corr} (-0.70 V). The value of E_{pit} was more positive (0.33 V) but the related current density was the highest.

To summarize, based on the polarization curves and deduced electrochemical parameters, AlSi7Mg0.3 showed a relatively good corrosion performance in ASW compared to e.g. alloys of the 7xxx series [71–77]. Addition of a low concentration of Na_2S (20 ppm) improved corrosion performance over the whole course of immersion. At the beginning of immersion, Na_2S acted as a cathodic inhibitor [78], shifting E_{corr} in a slightly more negative direction. The addition of higher amount of Na_2S (50 and 100 ppm) was beneficial only up to a certain time of immersion. The changes in electrochemical behaviour reflect the changes in the composition, morphology and dielectric and electrical properties of the surface layers, as will be discussed further based on the analysis of EIS data.

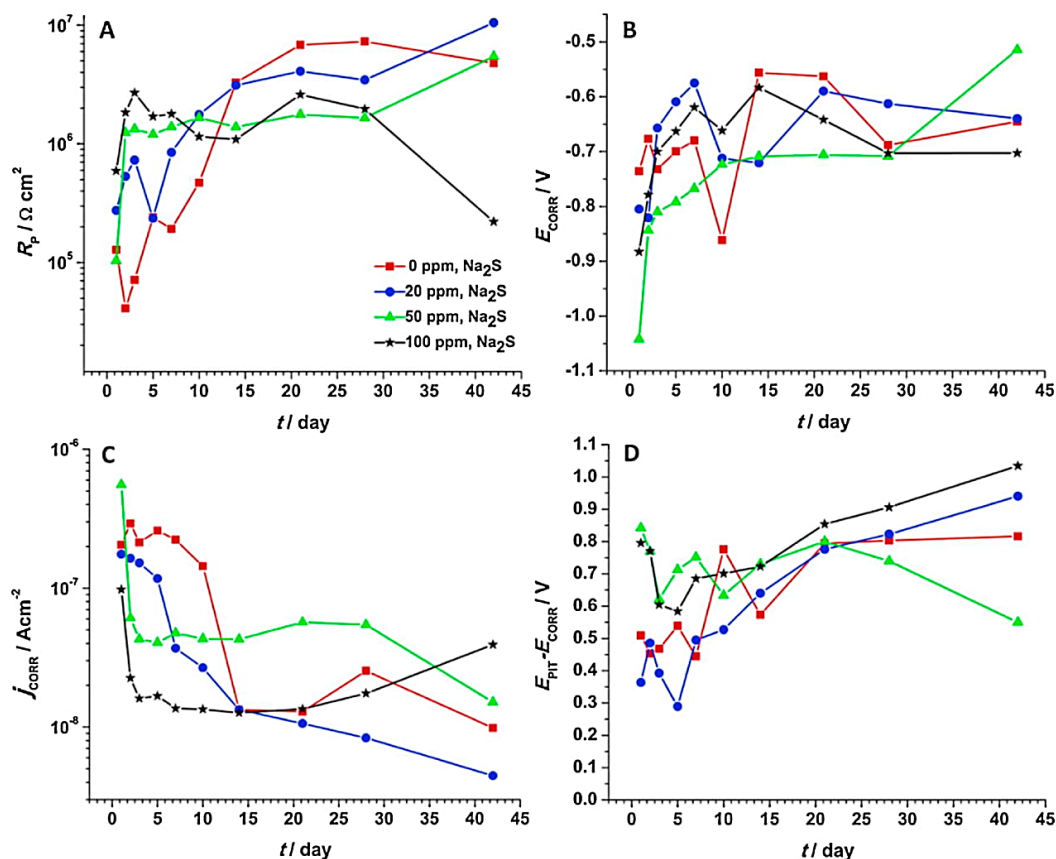


Fig. 13. Electrochemical parameters deduced from potentiodynamic polarization measurements (Fig. 12) recorded for AlSi7Mg0.3 in artificial sea water: a) polarization resistance obtained by the linear polarization technique, b) corrosion potential, c) corrosion current density, and d) extent of the passive range. All values are means of two measurements. Samples were previously immersed in artificial sea water with and without added Na₂S for up to 42 days, as denoted in the Figure.

3.6. Electrochemical impedance analysis

Electrochemical impedance spectra for samples of AlSi7Mg0.3 immersed in ASW with the addition of 0, 20, 50 and 100 ppm of Na₂S for immersion period from 1 to 42 days are presented in form of Bode diagrams of phase angle and modulus of impedance as a function of frequency (φ , ° vs. f , Hz and $|Z|$, $\Omega \text{ cm}^2$ vs. f , Hz), respectively, (Figs. 14 and 15) and as Nyquist plots ($-Z''$ vs. Z') (supplement Fig. S3 in Supplementary material).

Up to 10 days of immersion of AlSi7Mg0.3 in ASW, Bode diagrams of phase angle vs. frequency characteristic of partially stable aluminium alloy were observed (Fig. 14a). The formation of aluminium oxide/hydroxide is accompanied by local dissolution of the alloy [62,79–81]. Two time constants were present, formation of aluminium oxide/hydroxide layer at medium frequency (MF) between 10 and 100 Hz, and the other at low frequency (LF) at 0.01 Hz, related to the charge transfer resistance due to pitting and anodic dissolution of aluminium substrate, respectively. The spontaneously formed oxide layer offers a certain degree of protection. In the course of immersion, closing of pores in the aluminium oxide/hydroxide layer progressively took place and counteracts the dissolution process. Consequently, after 10 days of immersion, the phase angle at LF started to increase—an indication that a compact aluminium oxide film was forming. The maximum at the MF range increased and shifted towards lower frequencies, indicating strengthening of the barrier properties of the inner oxide film. At the 14th day, an additional time constant appeared at high frequency (HF)

between 10–20 kHz, related to the formation of an outer oxide layer. The latter further increased the protection of the underlying substrate. Values of the phase angle in the LF region increased up to -80° , indicating an improved resistance against corrosion. EECs used to fit the impedance data are presented in Fig. 14e (EEC I and II) and quantitative parameters obtained in Table 3. The R_p values are presented in Fig. 16, while the dependence of capacitance, C_{dl} and C_{oxide} , are given in Figs. S4 and S5 in Supplementary material. During the first ten days of immersion, the R_p value was relatively constant; at longer times, it increased significantly, to $2.3 \cdot 10^7 \Omega \text{ cm}^2$, indicating structural changes in the oxide layer related to closure of the pores and formation of an outer oxide layer.

For the sample immersed in ASW with the addition of 20 ppm Na₂S (S-20 ppm), the shape and trend of Bode diagrams were very similar as that for S-0 ppm (Figs. 14b and 15 b). The maximum in the phase angle at MF increased slightly and shifted towards LF during the whole course of immersion, correlating with increased stability of the inner oxide of alumina. The third time constant at HF around 20 kHz, which appeared on the 21st and 28th days of immersion, may be correlated with the formation of an outer oxide layer that acts protectively. Quantitative parameters obtained by fitting using EECs (Fig. 14e) are given in Table 4. The R_p values increased faster during the first 10 days of immersion than for the sample S-0 ppm (Fig. 16). After the 42nd day of immersion, it reached a value of $3 \cdot 10^7 \Omega \text{ cm}^2$. These findings indicate that a more stable and compact layer of corrosion products was formed, providing better protection than that formed in ASW only.

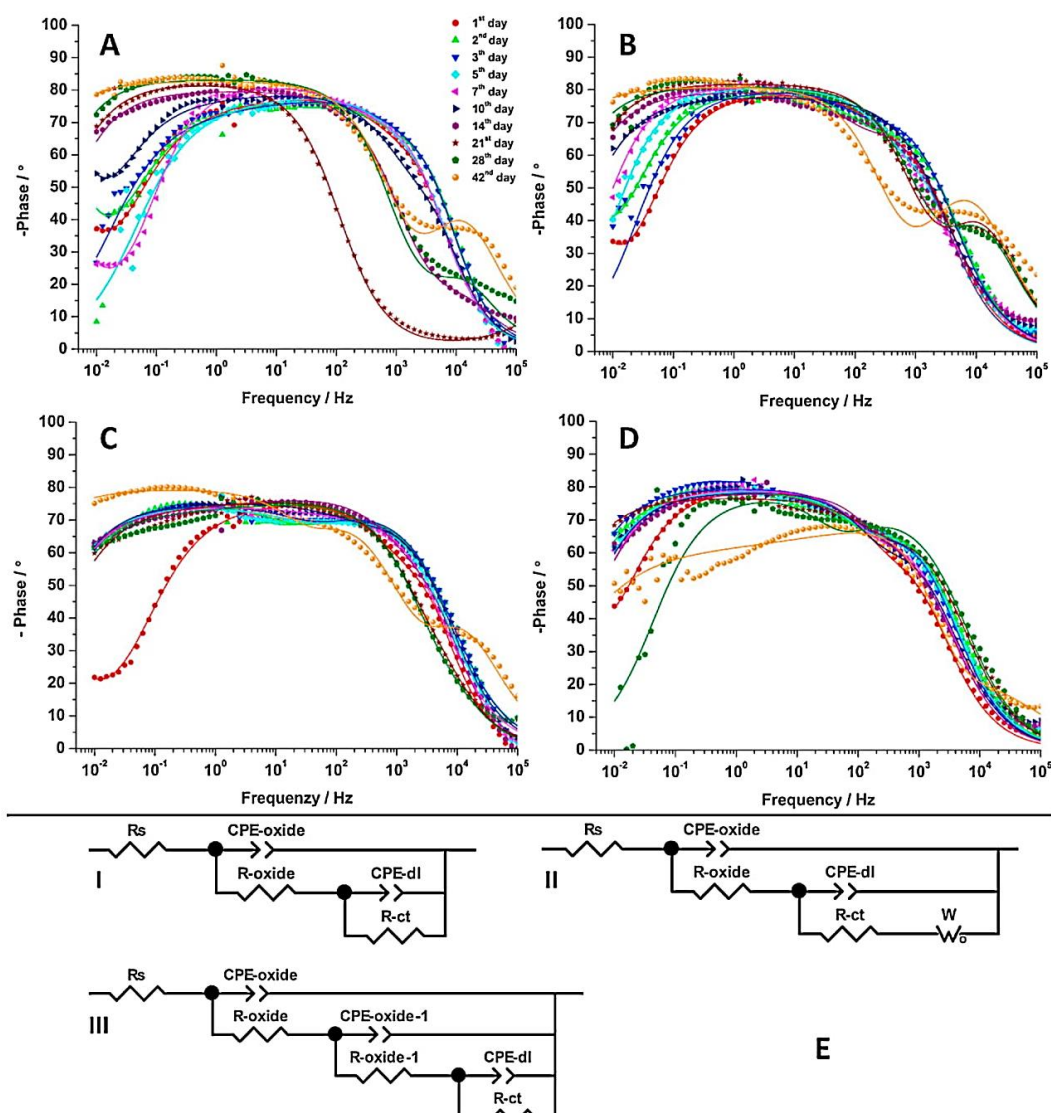


Fig. 14. Bode plots of phase angle as a function of frequency for AlSi7Mg0.3 samples measured in artificial sea water. Prior to measurement, samples were immersed in artificial sea water with added Na_2S of concentrations a) 0 ppm Na_2S , b) 20 ppm Na_2S , c) 50 ppm Na_2S , and d) 100 ppm Na_2S , each for periods of 1–42 days. e) Equivalent electric circuits used to fit electrochemical impedance spectroscopy measurements: R_s – resistance of electrolyte, $\text{CPE}_{\text{oxide}}$ – constant phase element of oxide layer, R_{oxide} – resistance of oxide layer, W – Warburg element, CPE_{dl} – constant phase element of double layer, R_{ct} – charge transfer resistance. Experimental data are represented by symbols and fitted curves by lines.

Bode diagrams for sample immersed in ASW with added 50 ppm Na_2S (S-50 ppm) showed a trend different from those for samples S-0 ppm and S-20 ppm (Figs. 14c and 15 c). After the first day of immersion, the shape of Bode diagrams for S-50 ppm was similar to those for S-0 ppm and S-20 ppm. The phase angle at LF increased significantly after the 2nd day of immersion from -20° up to -60° and remained constant for 28 days. Thus, pores in aluminium oxide were already closed after the 2nd day of immersion, and a stable and compact layer of corrosion products was formed. After the 42nd day of immersion, the phase angle at LF increased again, reaching -75° . Two additional time constants appeared, one at LF around 0.2 Hz, and the other at HF around 20 kHz, indicating formation of a more complex layer structure. These structural changes provided increased corrosion protection of the

underlying AA substrate.

Quantitative parameters obtained by fitting of experimental data (Fig. 14e) are presented in Table 5. The R_p values increased during the first three days of immersion in comparison with sample S-0 ppm (Fig. 16). At longer times, it remained more or less constant up to 28th day. Afterwards, the R_p values started to increase but the maximum value reached ($1.6 \cdot 10^7 \Omega \cdot \text{cm}^2$) was smaller than for the S-0 ppm and S-20 ppm.

Bode diagrams for sample immersed in ASW with the addition of 100 ppm Na_2S (S-100 ppm) are presented in Figs. 14d and 15 d. There were three time constants present already after the first day of immersion (Fig. 14e), related to charge transfer resistance at LF, inner aluminium oxide layer at MF, and outer layer of oxides at HF. The phase

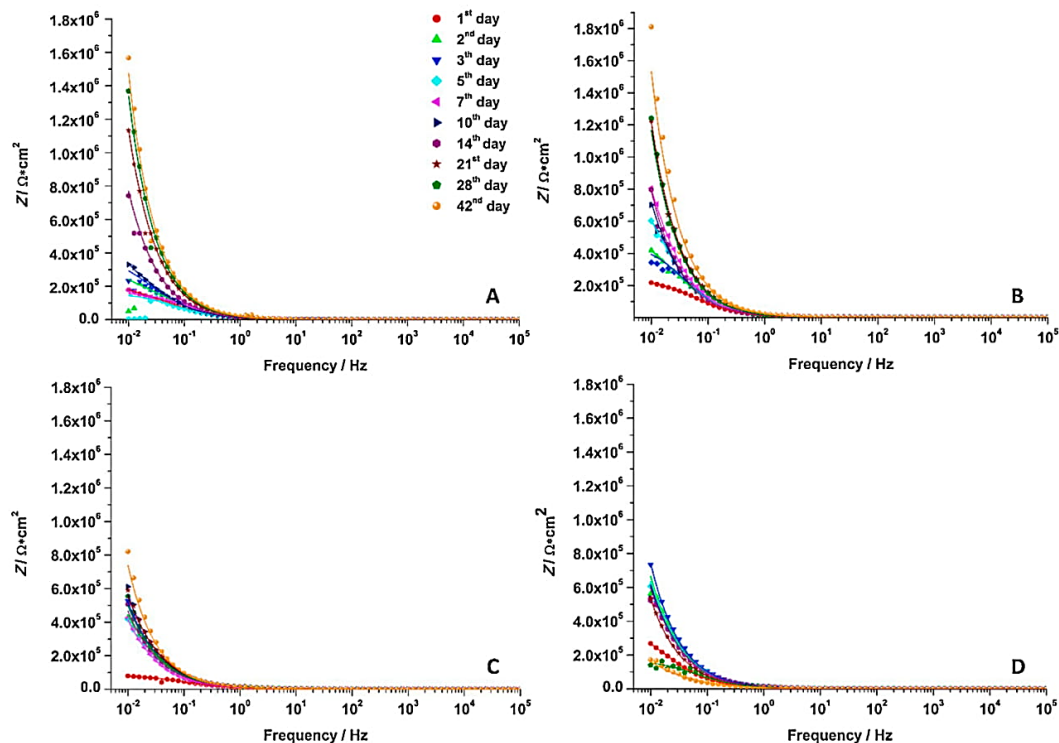


Fig. 15. Bode plots of the modulus of impedance as a function of frequency for samples of AlSi7Mg0.3, measured in artificial sea water. Samples were previously immersed in artificial sea water with added Na₂S concentrations of a) 0 ppm Na₂S, b) 20 ppm Na₂S, c) 50 ppm Na₂S, and d) 100 ppm Na₂S for periods of 1–42 days. Experimental data are represented by symbols and fitted curves by lines.

Table 3

Parameters of equivalent electric circuits deduced from electrochemical impedance spectroscopy measurements for AlSi7Mg0.3 samples in artificial sea water. All samples were previously immersed in artificial sea water with the addition of 0 ppm of Na₂S for periods of 1–42 days.

Immersion time/day	EEC model	Chi square	R_s [$\Omega\text{-cm}^2$]	R_{oxide} [$\Omega\text{-cm}^2$]	C_{oxide} [$\mu\text{F}\text{-cm}^{-2}$]	R_{ct} [$\Omega\text{-cm}^2$]	C_{dl} [$\mu\text{F}\text{-cm}^{-2}$]	σ [$\Omega\text{-cm}^2\text{S}^{-0.5}$]
1	II	1.58×10^{-3}	8	58.5	3.64	2.21×10^5	19.83	5.98
2	II	1.35×10^{-3}	8	74.7	2.72	3.12×10^5	18.13	10.39
3	I	1.77×10^{-3}	7.7	64.4	2.86	4.13×10^5	21.40	/
5	I	1.80×10^{-3}	7.7	53.5	3.78	1.66×10^5	18.04	/
7	II	2.02×10^{-3}	7.6	256.8	5.17	1.64×10^5	4.46	3.59
10	II	1.07×10^{-3}	8.5	33	3.10	5.24×10^5	20.96	66.46
14	I	7.29×10^{-4}	17.8	15.7	1.14	2.83×10^6	17.48	/
21	I	2.82×10^{-4}	5	237	3.97×10^{-4}	4.75×10^6	14.45	/
28	I	1.61×10^{-3}	16.4	26.6	7.92×10^{-1}	7.83×10^6	9.98	/
42	I	1.83×10^{-3}	9.7	49.6	7.28×10^{-1}	2.35×10^7	9.05	/

angle at LF had a value of -40° and was higher than those for other samples, indicating higher resistance to pitting and faster growth of aluminium oxide. After the 2nd day of immersion, it increased to -65° , indicating that pores in the oxide film were already closing and that the process of pitting had stopped. During the period from the 2nd to the 21st day of immersion, the phase angle at LW was stable and had a value between -65° and -70° . On the 28th day of immersion, however, the phase angle at LF decreased significantly to -20° , an indication that coating had become too porous and thick. This allowed whole segments of coating to detach, enabling aggressive Cl^- ions to penetrate to the substrate surface and further promote the process of pitting. On the 42nd day of immersion, the phase angle at LF recovered to a somewhat higher value but still much smaller than for those measured in the presence of 50 and, especially, 20 ppm Na₂S. EEC used to fit the impedance data is given in Fig. 14e and quantitative

parameters in Table 6. The R_p values increased slightly during the first few days, remained approximately constant up to 21th day and then decreased to $6.5 \cdot 10^5 \Omega\text{-cm}^2$ (Fig. 16), i.e. it was smaller than for the S-0 ppm, S-20 ppm and S-50 ppm. This behaviour reflects deterioration of the layer of corrosion products which was not protective to the underlying substrate. Thus, the layer formed quickly during the first 3 days of immersion, providing relatively good corrosion protection against corrosion up to the 21st day of immersion. At longer times it was no longer protective.

Capacitance of oxide layer is related to the structure of oxide layer (porous nature, volume of pores, shape of pores and composition of oxide layer). The C_{oxide} for all samples was of same order $0\text{--}10 \mu\text{F}\text{-cm}^{-2}$. (Fig. S5), being higher in the beginning of immersion and later decreased, this indicating that pore volume was decreasing over time due to growth of oxide layer. Double layer capacitance is directly

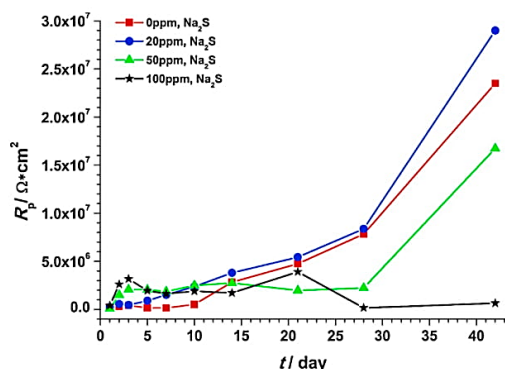


Fig. 16. Changes of polarization resistance (R_p) during the course of immersion of AlSi7Mg0.3 in artificial sea water (ASW). Samples were previously immersed in artificial sea water with added 0 ppm Na_2S , 20 ppm Na_2S , 50 ppm Na_2S , and 100 ppm Na_2S for up to 42 days. R_p values were deduced from impedance fitted parameters given in Tables 3–6.

proportional to exposed substrate area according to equation:

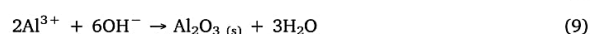
$$C_{dl} = (\epsilon_r \cdot \epsilon_0) / d \cdot A \quad (6)$$

ϵ_r – electric permittivity of electrolyte, ϵ_0 – electric permittivity of vacuum, d – Debye-Hückel length, A – area of substrate/electrolyte interface, C_{dl} – double layer capacitance. As the oxide layer is growing, C_{dl} is expected to decrease, as observed for S-0 ppm and S-20 ppm (Fig. S4 in Supplementary material). The S-50 ppm had higher C_{dl} value after 1st day of immersion, correlated with initial dissolution of naturally protective oxide layer; between 10th and 28th day it increased indicating that substrate surface was exposed to electrolyte due to oxide layer detachment. At the same time, R_p was stable indicating that this oxide layer detachment did not increase rate of corrosion.

3.7. Proposed mechanisms of formation of the layer of corrosion products

Aluminium is protected by its natural oxide film in the pH range 4–9 [2]. This oxide film, that develops in contact with air or oxidizing medium at any temperature is composed of two layers [3,82]. The inner oxide layer next to the metal is a compact, amorphous barrier of a thickness determined solely by the temperature of the environment. At any given temperature, the limiting barrier thickness is the same in oxygen, dry air, or moist air environments. The maximum thickness of this first layer is 4 nm [83,84,85,86]. Covering the barrier layer is a thicker, more permeable outer layer of hydrated oxide. The thickness of this second layer is dependent on its reaction with the environment and on its physicochemical properties. It can reach, after several weeks or even months, a final value of a few hundreds of nanometres. Most of the

interpretation of the aluminium corrosion process has developed in terms of the chemical properties of these layers. Intermetallic particles (Al(FeMn)Si, π -AlFeSiMg – “chinese script”, Al(FeMn)SiMg (Table 1) constitute the weak spots in naturally formed Al oxide at which cathodic reaction takes place [7]. The anodic reaction is aluminium dissolution (Reaction (8)). Released OH^- ions react with Al^{3+} ions and form aluminium oxide (Reaction (9)). At lower temperatures, the predominant form produced by corrosion is bayerite (α -Al(OH)₃), whereas at higher temperatures it is boehmite (γ -AlOOH). Aluminium hydroxide is at first formed in an amorphous form (Al(OH)₃); aluminium trihydroxides (gibbsite and hydrargillite) can also be formed, especially if ions of the alkali metals are present [3,82,87,88].



In the presence of very high concentrations of the aggressive chloride ions, such as in sea water, this oxide film is dissolved at weak spots and the corrosion process starts once again. In a neutral environment, pits may be re-passivated, while the film of aluminium oxide continues to grow and is transformed to its more stable form. If this so-formed oxide is dense and stable, it protects the aluminium alloy from further corrosion and decreases the corrosion rate.

Addition of Na_2S alters the rate of corrosion of aluminium alloy in artificial sea water. Based on published studies on Cu-, Fe-based and Al-brass alloys, [22–41,47], it was expected that the addition of Na_2S would dramatically increase the rate of corrosion of aluminium alloy and induce pitting, but this was not case. Na_2S , when dissolved in ASW, is hydrolysed, leading to increased pH (Reactions (10) and (11)). The dependence of pH on immersion time is presented in Fig. 17. During the course of immersion, pH of ASW varied only within a narrow interval, from 7.99 to 8.07. In contrast, in the presence of Na_2S the pH increased significantly in the first 5 days. The increase followed the increase in Na_2S concentration and reached maximum values of 8.33 at 20 ppm Na_2S , 8.55 at 50 ppm Na_2S and 8.87 at 100 ppm Na_2S . In the course of immersion, the pH of all the immersion solutions equilibrated and, at the end of the test, attained the value of around 8.10.



A schematic presentation of the formation of oxide layers in the absence and presence of Na_2S is given in Fig. 18. In pure ASW the corrosion current density of AA was highest in the first 10 days (Fig. 13). The spontaneously formed thin protective layer was rapidly dissolved, while a new layer of aluminium oxide was unable to form completely. At longer immersion times the layer was stabilized, grew steadily and was gradually transformed into a more stable form. At the end of the test the surface layer consisted of an inner, amorphous, oxide

Table 4

Parameters of equivalent electric circuits deduced from electrochemical impedance spectroscopy measurements for AlSi7Mg0.3 samples in artificial sea water. All samples were previously immersed in artificial sea water with the addition of 20 ppm of Na_2S for periods of 1 to 42 days.

Immersion time/day	EEC model	Chi square	R_s [Ωcm^2]	R_{oxide} [Ωcm^2]	C_{oxide} [μFcm^{-2}]	R_{ct} [Ωcm^2]	C_{dl} [μFcm^{-2}]	σ [$\Omega\text{cm}^2\text{s}^{-0.5}$]
1	II	3.09×10^{-4}	12.4	315.7	5.40	2.48×10^5	2.91	23.52
2	II	6.75×10^{-4}	12	642.2	4.91	5.71×10^5	2.74	47.61
3	I	3.72×10^{-3}	12.3	1689	5.88	4.61×10^5	0.86	
5	I	6.28×10^{-4}	13.8	211.7	4.80	9.11×10^5	3.60	
7	I	1.23×10^{-3}	14.5	49.5	2.65	1.52×10^6	7.25	
10	I	7.21×10^{-4}	12.9	24.3	2.58	2.37×10^6	9.54	
14	I	1.83×10^{-3}	15.8	1008	5.91	3.80×10^6	2.25	
21	I	1.02×10^{-3}	8.7	42.1	0.95	5.44×10^6	9.50	
28	I	1.49×10^{-3}	8.8	38.6	0.97	8.37×10^6	11.07	
42	I	3.10×10^{-3}	16.5	162.8	0.59	2.90×10^7	8.51	

Table 5

Parameters of equivalent electric circuits deduced from electrochemical impedance spectroscopy measurements for AlSi7Mg0.3 samples in artificial sea water. All samples were previously immersed in artificial sea water with the addition of 50 ppm of Na₂S for periods of 42 days.

Immersion time/day	EEC model	Chi square	R_s [Ωcm^2]	R_{oxide} [Ωcm^2]	C_{oxide} [μFcm^{-2}]	R_{ct} [Ωcm^2]	C_{dl} [μFcm^{-2}]	σ [$\Omega\text{cm}^2\text{s}^{-0.5}$]
1	II	7.42×10^{-4}	8.5	40.2	3.40	8.72×10^4	23.42	1.12
2	II	1.12×10^{-3}	7.9	3771.0	8.05	1.51×10^6	5.83	31.74
3	I	1.19×10^{-3}	8	2567.0	6.97	2.08×10^6	6.81	/
5	I	7.52×10^{-4}	8.1	2017.0	7.89	2.06×10^6	11.23	/
7	I	6.27×10^{-4}	8.1	1387.0	8.38	1.88×10^6	8.19	/
10	I	1.22×10^{-3}	8.5	569.8	4.82	2.49×10^6	11.10	/
14	I	1.15×10^{-3}	8	35.8	2.99	2.76×10^6	45.83	/
21	I	1.43×10^{-3}	14.7	32.6	2.27	1.98×10^6	25.90	/
28	I	1.75×10^{-3}	15	12.7	1.86	2.24×10^6	39.63	/
42 ^a	III	1.72×10^{-3}	9.6	42.8	0.88	1.67×10^7	5.85	/

^a $R_{\text{oxide-1}} = 2254.00 \Omega\text{cm}^2$; $C_{\text{oxide-1}} = 4.56 \mu\text{Fcm}^{-2}$.

Table 6

Parameters of equivalent electric circuits deduced from electrochemical impedance spectroscopy measurements for AlSi7Mg0.3 samples in artificial sea water. All samples were previously immersed in artificial sea water with the addition of 100 ppm of Na₂S for period of 42 days.

Immersion time/day	EEC model	Chi square	R_s [Ωcm^2]	R_{oxide} [Ωcm^2]	C_{oxide} [μFcm^{-2}]	R_{ct} [Ωcm^2]	C_{dl} [μFcm^{-2}]	σ [$\Omega\text{cm}^2\text{s}^{-0.5}$]
1	II	3.37×10^{-4}	13.3	180.2	7.51	4.08×10^5	8.77	5.40
2	I	1.27×10^{-3}	12.7	821.1	5.71	2.61×10^6	3.10	/
3	I	1.35×10^{-3}	13.8	500.7	5.23	3.18×10^6	4.28	/
5	I	5.84×10^{-4}	12.8	640.1	5.76	1.95×10^6	3.78	/
7	I	8.96×10^{-4}	14.9	428.7	5.72	1.63×10^6	4.33	/
10	I	1.40×10^{-3}	15.8	393.2	5.13	1.90×10^6	3.69	/
14	I	1.31×10^{-3}	15.8	564.4	6.30	1.72×10^6	1.53	/
21	I	6.63×10^{-4}	9.8	392.0	5.76	3.91×10^6	7.58	/
28	I	4.94×10^{-3}	9.4	1493.0	7.38	1.67×10^5	3.77	/
42	I	2.94×10^{-3}	14.3	29.4	0.97	6.50×10^5	1.68	/

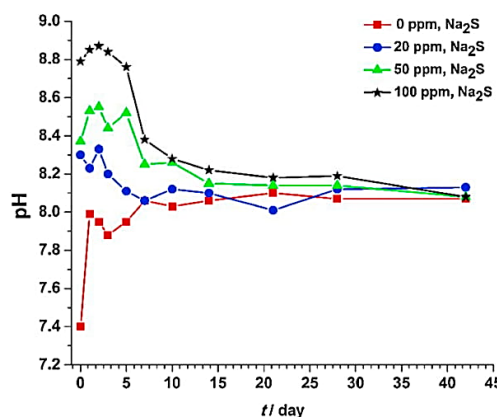


Fig. 17. The change in pH of artificial sea water with added Na₂S at 0, 20, 50 and 100 ppm as a function of immersion time.

layer of Al₂O₃ and an outer, crystalline, aluminium oxide film (Fig. 18).

The addition of 20 ppm of Na₂S caused faster formation of the protective aluminium oxide and increased its stability. The thickness of this layer increased (Fig. 7), being gradually transformed into a more stable form. It provided protection for the underlying AA better than that provided by pure ASW and ASW containing 50 and 100 ppm Na₂S. At the end of the immersion test the surface oxide formed consisted of an inner aluminium amorphous oxide layer, which it could not be observed on cross-section due its small thickness, and an outer crystalline aluminium oxide layer. It is the most compact of the oxide layers of all the samples. Compared to the layer formed in pure ASW, the oxide layer formed in the presence of 20 ppm Na₂S was more crystalline, as

evidenced by EDS and XRD analyses (Figs. 6–11). The process of crystallization was accompanied by dehydration of the layer (Fig. 6).

The addition of 50 ppm of Na₂S in ASW led to a more rapid formation of a protective aluminium oxide film, due to the presence of S²⁻ ions, and increased pH value at the sample surface. At the same time, the increased pH of the solution caused deposition of magnesium hydroxide over the aluminium oxide protective film (Figs. 6–11). Rapid formation of the protective oxide film offered greater protection for the underlying AA during the first 10 days of immersion than that of those formed in the presence of 20 ppm (Figs. 12 and 13). Formation of magnesium hydroxide, (Reaction (12)), caused a drop in the solution pH from 8.55 to 8.10 on the 42nd day of immersion (Fig. 17). The mixed Mg- and Al-oxide layer was thicker but more porous than those formed on S-0 ppm and S-20 ppm. It offered corrosion protection that was better in the first 10 days of immersion, but weaker at longer immersion times due to its porous structure. The surface film thus comprised an inner, amorphous aluminium oxide film, an intermediate aluminium oxide film and an outer layer of magnesium hydroxide/oxide and/or MgAl₂O₄ (Fig. 18).



When 100 ppm Na₂S was added to the ASW, it caused the most rapid growth of surface oxide film. This occurred probably due to the high pH of 8.87, which decreased the stability of natural protective oxide, causing its faster dissolution, although, at the same time, still allowing the formation of aluminium oxide. The high pH and the presence of S²⁻ ions caused a more rapid deposition of Mg²⁺ ions in the form of magnesium hydroxide after 14 and 28 days of immersion. By the 42nd day of immersion this magnesium hydroxide was transformed into magnesium oxide and/or spinel in accordance with Reactions (13)

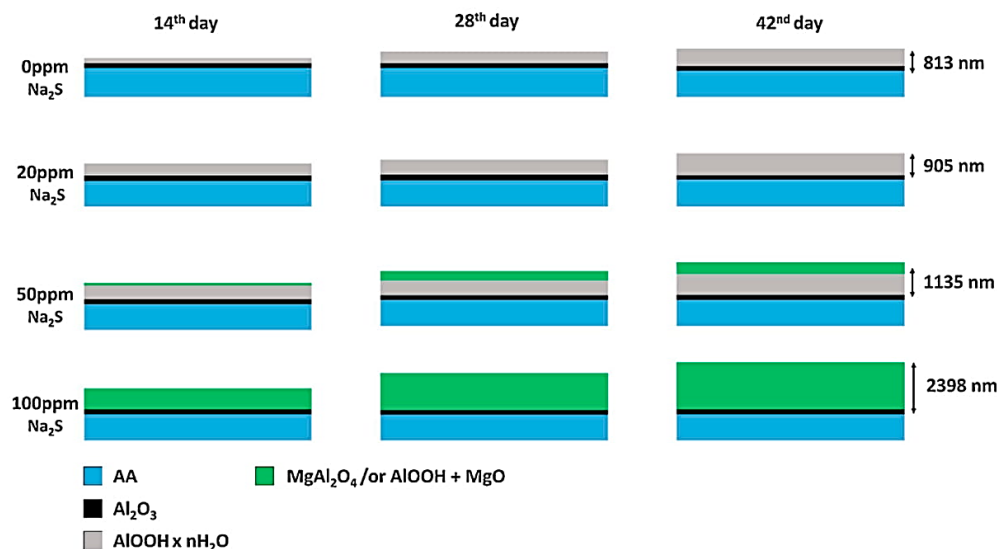


Fig. 18. Schematic presentation of oxide layer formation at the surface of AA EN-ALSi7Mg0.3 during the course of immersion in artificial sea water with added Na_2S .

and (14). In the first 7 days, this oxide film offered the best corrosion protection for the underlying substrate, but the high rate of its growth and the deposition of magnesium hydroxide led gradually to a more porous structure with time; its protective ability started to decrease after 21st day of immersion. At the end of immersion, the surface film formed in the presence of 100 ppm of Na_2S was the thickest (Fig. 7) but also the most porous film, thus offering the lowest degree of corrosion protection of all those formed in other solutions. This film was composed of three layers, an inner layer of amorphous aluminium oxide, an intermediate layer of aluminium oxide/magnesium hydroxide and an outer layer of magnesium hydroxide/magnesium oxide (Fig. 17).

4. Conclusions

The corrosion behaviour of aluminium alloy AlSi7Mg0.3 in artificial sea water with added 0, 20, 50, 100 ppm Na_2S during the course of immersion of 1–42 days was investigated using electrochemical techniques. Microstructural changes at the surface and cross-sections of the samples (S-0 ppm, S-20 ppm, S-50 ppm and S-100 ppm) during the course of immersion were analysed using SEM/EDX and XRD spectroscopies.

- 1 Electrochemical investigations show that the corrosion rate of AlSi7Mg0.3 in all immersion solutions was very low, with values of corrosion current density in the range of 10^{-7} – 10^{-9} A cm^{-2} . Corrosion current densities were lower for samples immersed in ASW with the addition of 50 and 100 ppm of Na_2S during the first ten days of immersion. This was due to the faster kinetics of formation of protective oxide layers. In the period from 14 to 42 days a lower current density was recorded for samples immersed in ASW with the addition of zero and 20 ppm of Na_2S . In the presence of 20 ppm Na_2S the kinetics of oxide formation was slower, but the layers formed were compact, dense and homogenous.
- 2 The combination of surface and cross-section SEM/EDS, XRD and EIS analyses showed that, at the end of the immersion period, the oxide layer for samples S-0 ppm and S-20 ppm was composed of inner and outer layers of aluminium oxide/hydroxide. The layer formed on S-20 ppm was somewhat thicker and more crystalline. Oxide layers formed at surfaces of samples S-50 ppm and S-100 ppm were composed of at least three oxide layers: inner aluminium oxide

layer, an intermediate aluminium oxide/hydroxide layer and an outer layer of spinel and magnesium oxide. Crystallinity and thickness of the oxide layers increased with immersion time. The thickness of oxide films increased with greater concentrations of Na_2S in ASW and was thickest for sample S-100 ppm, followed by S-50 ppm, while it was significantly thinner for sample S-20 ppm and thinnest for sample S-0 ppm.

- 3 The content of magnesium in the oxide layer increased with the concentration of dissolved Na_2S in ASW and with the immersion time. The addition of 50 and 100 ppm Na_2S induces deposition of Mg^{2+} ions from solution and formation of an additional outer oxide layer of spinel and magnesium oxide. This layer provided some additional degree of corrosion protection for the underlying AA, especially in the first 21 days of immersion, but did not guarantee protection over longer immersion times.
- 4 The addition of 20 ppm of Na_2S in ASW has been shown to improve the density, compactness and crystallinity of the aluminium oxide/hydroxide layer that was formed at the surface of AA over that of the oxide formed in pure ASW. This oxide layer improved with ageing, as reflected in the steadily decreasing corrosion current density during the course of immersion. The homogeneous and crystalline layer formed at the end of the immersion period provides increased corrosion protection for the underlying AlSi7Mg0.3 alloy with a corrosion current density of $4.5 \cdot 10^{-9}$ A cm^{-2} and a passive window $\Delta E = 0.94$ V. These parameters express better corrosion resistance compared to that in artificial sea water, i.e. a corrosion current density of $9.8 \cdot 10^{-9}$ A cm^{-2} and passive window $\Delta E = 0.82$ V. Similar behaviour can be expected in sea water containing up to 50 ppm sulphide.

Data availability statement

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations. They will be available on request.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.corsci.2018.08.038>.

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Supplementary Information

Table S1: Electrochemical data deduced from potentiodynamic polarization measurements for samples of AlSi7Mg0.3 in artificial sea water. Samples were previously immersed in pure artificial sea water for periods of 1 to 42 days. (All data are mean values of two measurements).

it d	J_{corr} A cm^{-2}	E_{ocp} V	E_{cor} V	E_{pit} V	ΔE^* V	B_a V/dec	$-\beta_c$ V/dec	$R_{p,LPR}$ $\Omega\ cm^2$	$R_{p,tafel}$ $\Omega\ cm^2$	$ Z _{10mHz}$ $\Omega\ cm^2$
1	2.1×10^{-7}	0.73	0.74	0.23	0.51	0.24	0.19	1.3×10^5	2.7×10^5	1.9×10^5
2	2.9×10^{-6}	0.70	0.68	0.22	0.45	0.27	0.63	4.1×10^4	8.7×10^4	5.9×10^4
3	2.1×10^{-7}	0.69	0.73	0.26	0.47	0.92	0.85	7.1×10^4	2.1×10^5	1.7×10^5
5	2.6×10^{-7}	0.69	0.70	0.16	0.54	0.21	0.37	2.4×10^5	1.8×10^5	1.7×10^5
7	2.2×10^{-7}	0.69	0.68	0.24	0.44	0.10	0.58	1.9×10^5	1.5×10^5	1.4×10^5
10	1.4×10^{-7}	0.71	0.86	0.08	0.78	0.12	0.19	4.7×10^5	2.6×10^5	2.1×10^5
14	1.3×10^{-8}	0.59	0.56	0.02	0.57	0.18	0.48	3.3×10^6	3.2×10^6	9.4×10^5
21	1.3×10^{-8}	0.59	0.56	0.23	0.79	0.19	0.73	6.8×10^6	3.5×10^6	1.2×10^6
28	2.5×10^{-8}	0.74	0.69	0.11	0.80	0.21	0.18	7.3×10^6	4.8×10^6	1.5×10^6
42	9.8×10^{-9}	0.69	0.65	0.16	0.82	0.14	0.26	7.1×10^6	1.0×10^7	1.2×10^6

* $\Delta E = |E_{pit} - E_{corr}|$

Table S2: Electrochemical data deduced from potentiodynamic polarization measurements for AlSi7Mg0.3 samples in artificial sea water. All samples were previously immersed in artificial sea water with the addition of 20 ppm of Na₂S for periods of 1 to 42 days. (All data are means of two measurements).

it d	J_{corr} A cm ⁻²	E_{ocp} V	E_{corr} V	E_{pi} V	ΔE^* V	β_a V/dec	$-\beta_c$ V/dec	$R_{p,LPR}$ Ω cm ²	$R_{p,tafel}$ Ω cm ²	IZI_{10mHz} Ω cm ²
1	1.8 x 10 ⁻⁷	–	–	–	0.36	0.53	0.22	2.8x 10 ⁵	2.6 x 10 ⁵	0.6 x 10 ⁵
2	1.6 x 10 ⁻⁷	–	–	–	0.49	0.41	0.27	5.3 x 10 ⁵	3.9 x 10 ⁵	2.8 x 10 ⁵
3	1.5 x 10 ⁻⁷	–	–	–	0.39	0.11	0.47	7.3 x 10 ⁵	3.3 x 10 ⁵	3.1 x 10 ⁵
5	1.2 x 10 ⁻⁷	–	–	–	0.29	0.25	0.41	2.4 x 10 ⁵	3.9 x 10 ⁵	4.3 x 10 ⁵
7	3.7 x 10 ⁻⁸	–	–	–	0.50	0.18	0.26	8.5 x 10 ⁵	1.4 x 10 ⁶	7.1 x 10 ⁵
10	2.7 x 10 ⁻⁸	–	–	–	0.52	0.29	0.21	1.8 x 10 ⁶	1.2 x 10 ⁶	6.6 x 10 ⁵
14	1.3 x 10 ⁻⁸	–	–	–	0.64	0.22	0.17	3.1 x 10 ⁶	2.3 x 10 ⁶	6.9 x 10 ⁵
21	1.1 x 10 ⁻⁸	–	–	0.19	0.78	0.21	0.31	4.1 x 10 ⁶	4.7 x 10 ⁶	1.3 x 10 ⁶
28	8.4 x 10 ⁻⁹	–	–	0.21	0.82	0.17	0.21	3.5 x 10 ⁶	5.8 x 10 ⁶	1.1 x 10 ⁶
42	4.5 x 10 ⁻⁹	–	–	0.3	0.94	0.18	0.32	1.1 x 10 ⁷	9.5 x 10 ⁶	1.8 x 10 ⁶

$$*\Delta E = |E_{pit} - E_{corr}|$$

Table S3: Electrochemical data deduced from potentiodynamic polarization measurements for AlSi7Mg0.3 samples in artificial sea water. Prior to measurements, samples were immersed in artificial sea water with the addition of 50 ppm of Na₂S for periods of 1 to 42 days. (All data are mean values of two measurements).

<i>it</i> <i>d</i>	J_{corr} A cm ⁻²	E_{ocp} V	E_{corr} V	E_{pit} V	ΔE^* V	β_a V/dec	$-\beta_c$ V/dec	$R_{p,LPR}$ Ω cm ²	$R_{p,tafel}$ Ω cm ²	$ ZI _{10mHz}$ Ω cm ²
1	5.6 x 10 ⁻⁷	—	—	-0.20	0.84	0.92	0.22	1.0 x 10 ⁵	8.8 x 10 ⁴	6.6 x 10 ⁴
2	6.1 x 10 ⁻⁸	—	—	-0.07	0.77	0.63	0.18	1.2 x 10 ⁶	5.8 x 10 ⁵	3.6 x 10 ⁵
3	4.3 x 10 ⁻⁸	—	—	-0.19	0.62	0.46	0.17	1.3 x 10 ⁶	3.6 x 10 ⁶	4.7 x 10 ⁵
5	4.1 x 10 ⁻⁸	—	—	-0.08	0.71	0.38	0.19	1.2 x 10 ⁶	7.3 x 10 ⁵	3.9 x 10 ⁵
7	4.8 x 10 ⁻⁸	—	—	-0.02	0.75	0.43	0.21	1.4 x 10 ⁶	7.3 x 10 ⁵	4.1 x 10 ⁵
10	4.3 x 10 ⁻⁸	—	—	-0.09	0.63	0.12	0.35	1.7 x 10 ⁶	1.1 x 10 ⁶	5.3 x 10 ⁵
14	4.3 x 10 ⁻⁸	—	—	0.02	0.73	0.62	0.31	1.4 x 10 ⁶	1.1 x 10 ⁶	4.8 x 10 ⁵
21	5.7 x 10 ⁻⁸	—	—	-0.02	0.80	0.21	0.67	1.8 x 10 ⁶	1.0 x 10 ⁶	5.3 x 10 ⁵
28	5.4 x 10 ⁻⁸	—	—	0.04	0.74	0.56	0.30	1.7 x 10 ⁶	1.1 x 10 ⁶	5.5 x 10 ⁵
42	1.5 x 10 ⁻⁸	—	—	0.04	0.55	0.30	0.50	5.5 x 10 ⁶	2.6 x 10 ⁶	6.9 x 10 ⁵

$$*\Delta E = |E_{pit} - E_{corr}|$$

Table S4: Electrochemical data deduced from potentiodynamic polarization measurements for AlSi7Mg0.3 in artificial sea water. Samples were previously immersed in artificial sea water with the addition of 100 ppm Na₂S for periods of 1-42 days. (All data are means of two measurements).

<i>it</i> <i>d</i>	J_{corr} A cm ⁻²	E_{ocp} V	E_{corr} V	E_{pit} V	ΔE^* V	β_a V/dec	$-\beta_c$ V/dec	$R_{p,LPR}$ Ω cm ²	$R_{p,tafel}$ Ω cm ²	$ ZI _{10mHz}$ Ω cm ²
1	9.8 x 10 ⁻⁸	—	—	0.09	0.80	0.41	0.17	5.9 x 10 ⁵	3.8 x 10 ⁵	2.4 x 10 ⁵
2	2.3 x 10 ⁻⁸	—	—	0.01	0.77	0.50	0.18	1.8 x 10 ⁶	1.5 x 10 ⁶	5.6 x 10 ⁵
3	1.6 x 10 ⁻⁸	—	—	0.10	0.60	0.44	0.19	2.7 x 10 ⁶	2.3 x 10 ⁶	7.1 x 10 ⁵
5	1.7 x 10 ⁻⁸	—	—	0.08	0.58	0.29	0.14	1.7 x 10 ⁶	1.7 x 10 ⁶	5.4 x 10 ⁵
7	1.4 x 10 ⁻⁸	—	—	0.07	0.69	0.17	0.09	1.8 x 10 ⁶	5.5 x 10 ⁶	5.3 x 10 ⁵
10	1.3 x 10 ⁻⁸	—	—	0.04	0.70	0.29	0.21	1.2 x 10 ⁶	1.5 x 10 ⁶	4.4 x 10 ⁵
14	1.3 x 10 ⁻⁸	—	—	0.14	0.72	0.18	0.20	1.1 x 10 ⁶	2.3 x 10 ⁶	4.9 x 10 ⁵
21	1.3 x 10 ⁻⁸	—	—	0.21	0.85	0.39	0.30	2.5 x 10 ⁶	2.6 x 10 ⁶	5.6 x 10 ⁵
28	1.7 x 10 ⁻⁸	—	—	0.21	0.91	0.43	0.19	2.0 x 10 ⁶	2.0 x 10 ⁶	2.9 x 10 ⁵
42	3.9 x 10 ⁻⁸	—	—	0.33	1.03	0.41	0.25	2.2 x 10 ⁵	9.2 x 10 ⁵	1.2 x 10 ⁵

$$*\Delta E = |E_{pit} - E_{corr}|$$

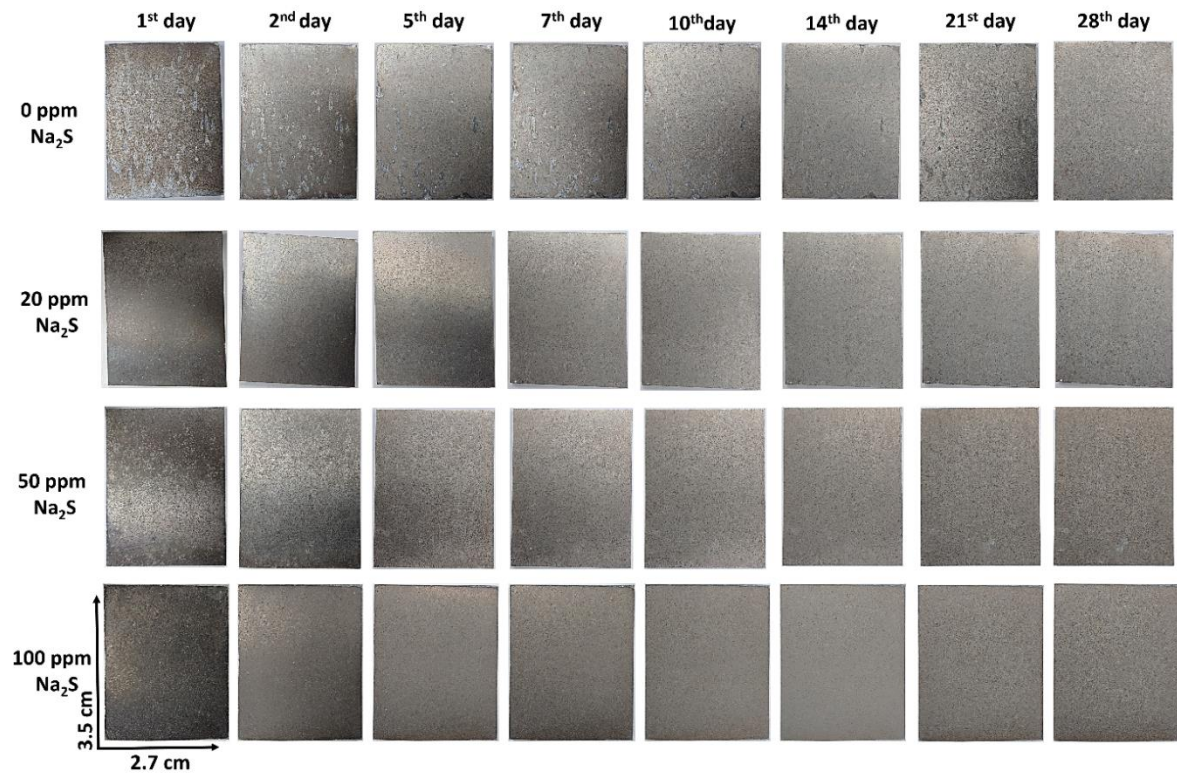


Figure S2.1: Digital images of aluminium alloy AlSi7Mg0.3 immersed in artificial sea water (ASW) with the addition of 0, 20, 50, 100 ppm Na_2S for periods from 1 to 28 days.

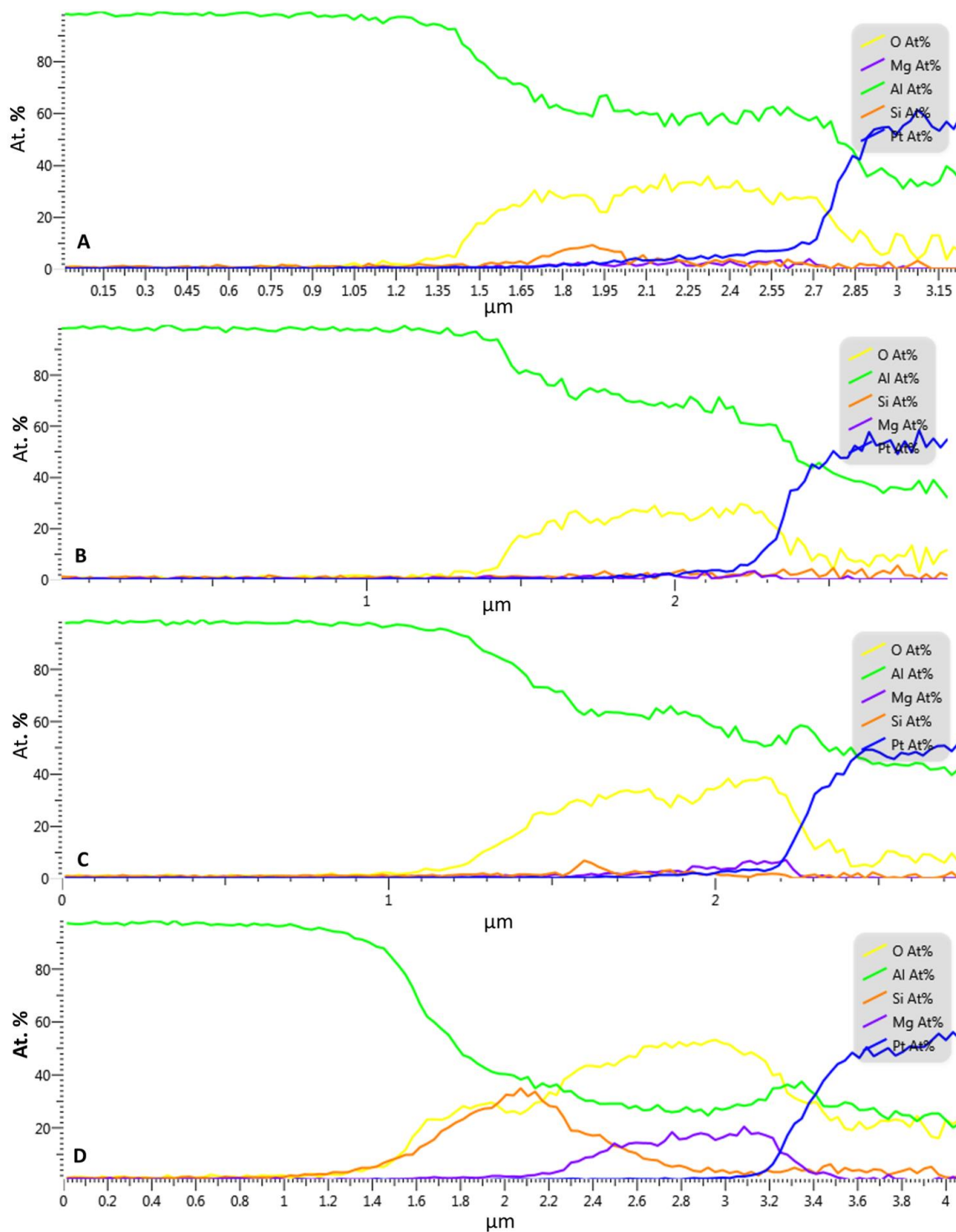


Figure S2: EDS line scan of cross sections for AlSi7Mg0.3 samples immersed for 42 days in artificial sea water with the addition of Na₂S: a) 0 ppm Na₂S, b) 20 ppm Na₂S, c) 50ppm Na₂S, and d) 100 ppm Na₂S. Cross sections were prepared by FIB. SEM images are presented in Fig. 7a, EDS mapping in Fig. 7b, and elemental composition deduced from line scans in Table 2.

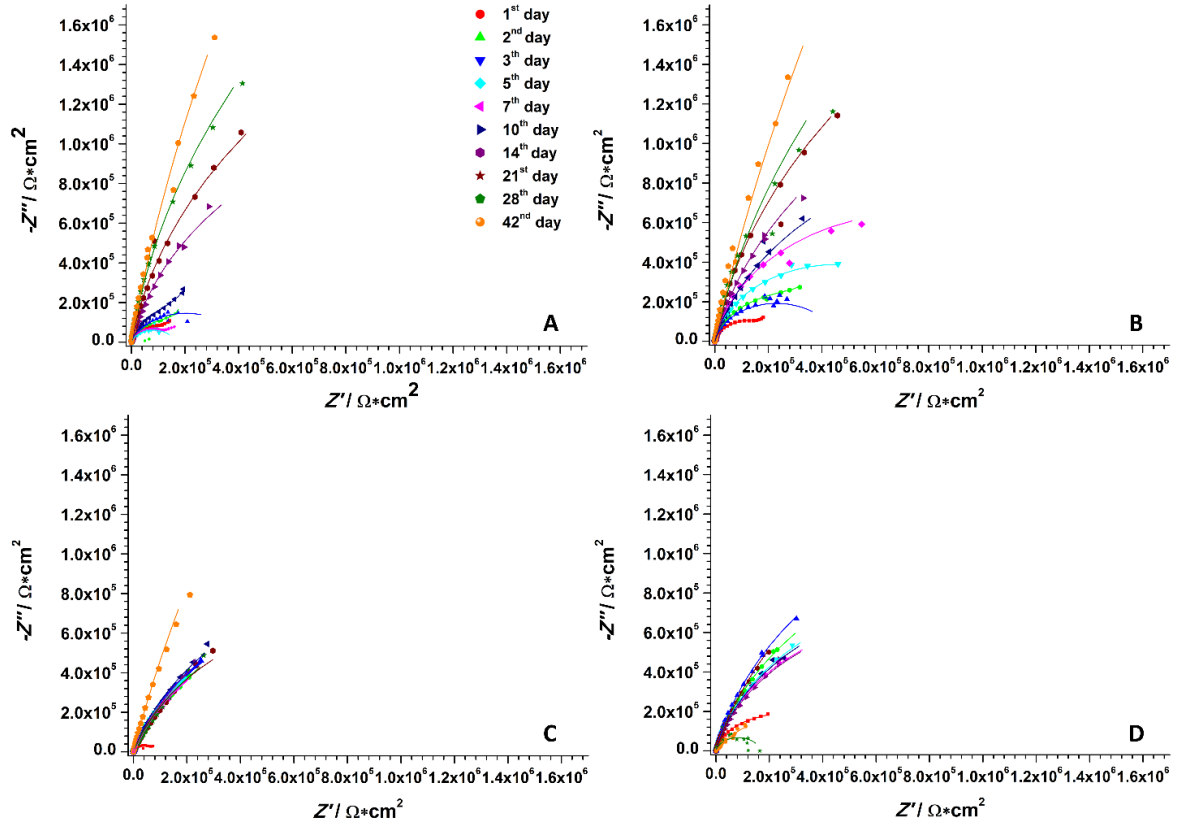


Figure S3: Nyquist plots for samples of AlSi7Mg0.3 measured in artificial sea water. Samples were previously immersed in artificial sea water with added Na_2S : a) 0 ppm Na_2S , b) 20 ppm Na_2S , c) 50 ppm Na_2S , and d) 100 ppm Na_2S for periods of 1 to 42 days.

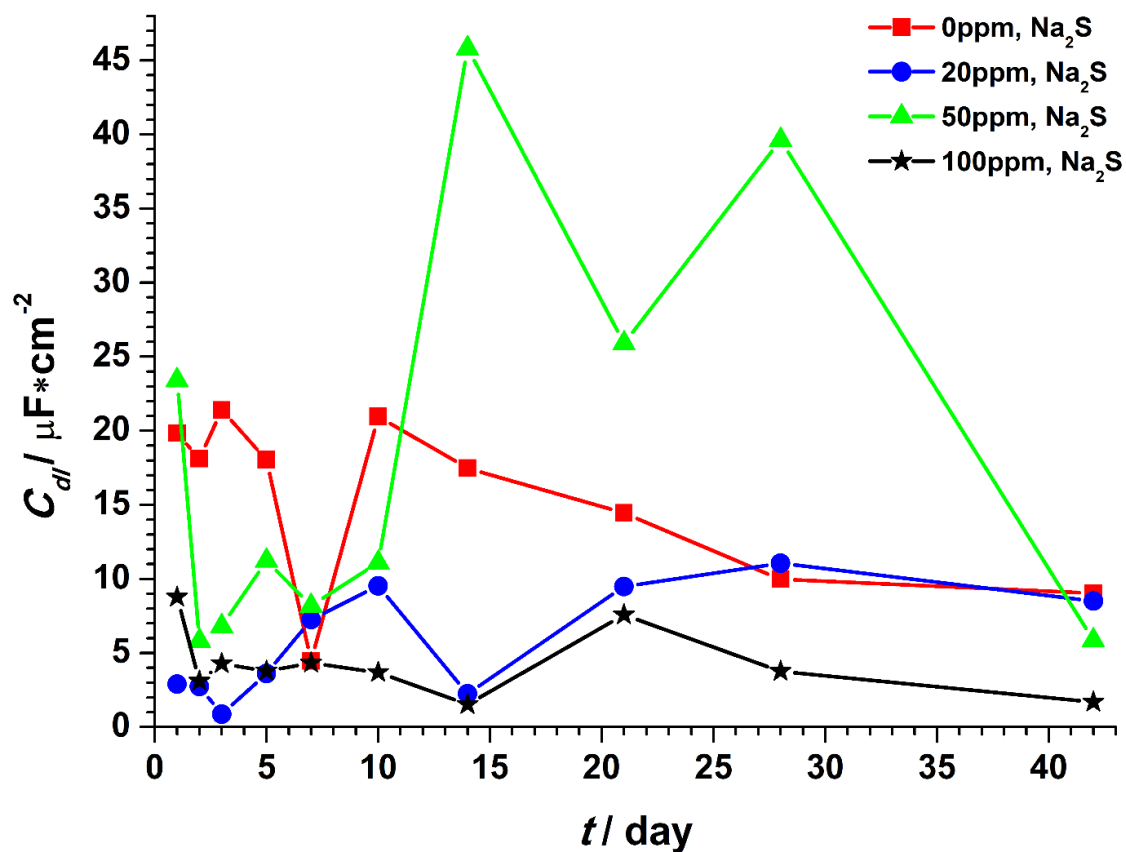


Figure S4: Changes of double layer capacitance during the course of AlSi7Mg0.3 immersion in artificial sea water (ASW) with the addition of 0, 20, 50, 100 ppm of Na_2S .

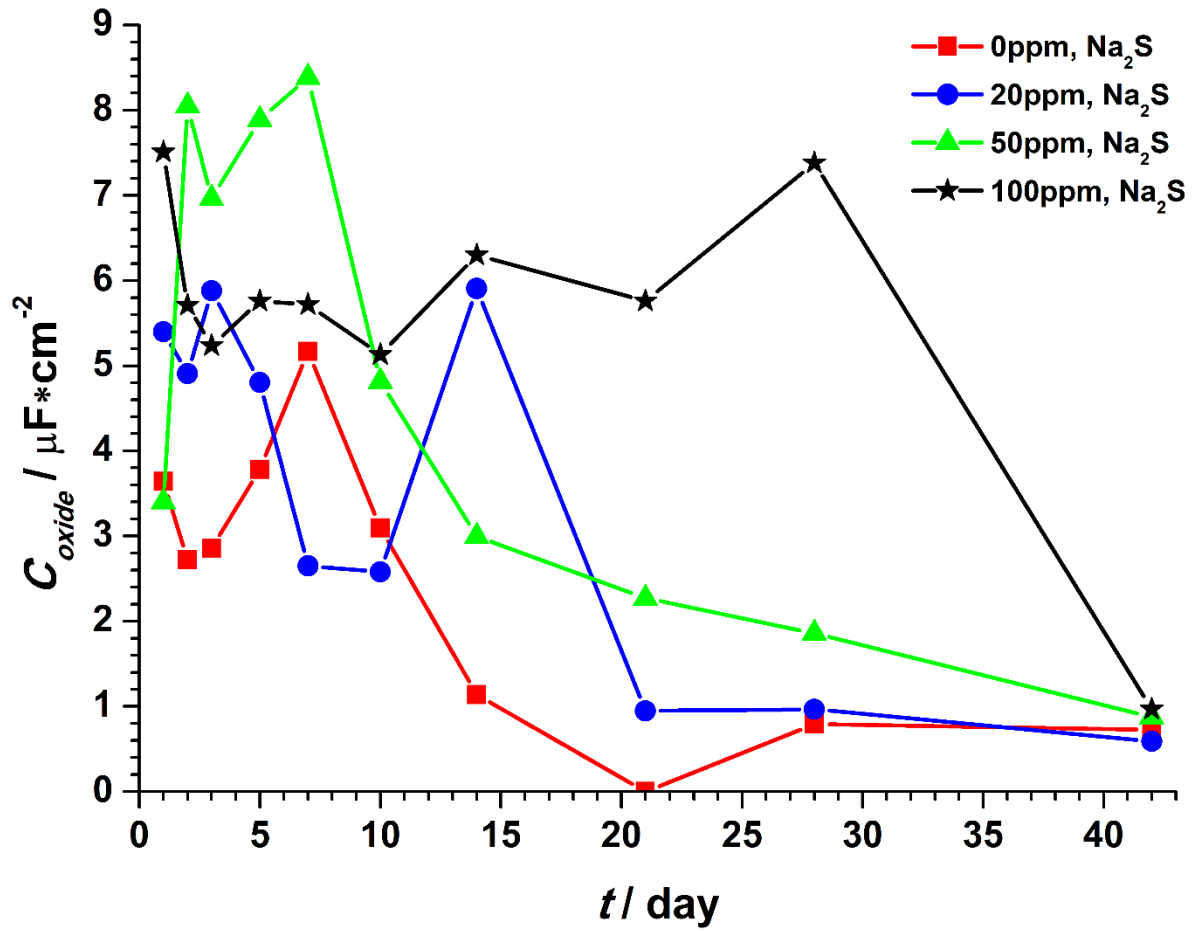


Figure S5: Changes of oxide layer capacitance during the course of AlSi7Mg0.3 immersion in artificial sea water (ASW) with the addition of 0, 20, 50, 100 ppm of Na_2S .

Chapter 3

Electrochemical Behavior and Self-Sealing Ability of Zirconium Conversion Coating Applied on Aluminum Alloy 3005 in 0.5 M NaCl Solution

This chapter presents the study of electrochemical behaviour and self-sealing ability of zirconium conversion coating applied on AA 3005 in 0.5 M NaCl solution. Electrochemical behaviour was studied with open circuit potential vs time curves, linear polarization resistance, potentiodynamic polarization curves and electrochemical impedance spectroscopy techniques. Microstructural and surface characterization was performed with FIB-SEM-EDX, TEM, XPS and ToF-SIMS techniques. In this study, self-sealing/active corrosion protection behaviour of zirconium conversion coatings applied to aluminium alloys was reported for the first time. During immersion in 0.5 M NaCl, the corrosion resistance of zirconium conversion coating was improved due to self-sealing of zirconium conversion coatings. The mechanism of self-sealing of conversion coating during the course of immersion was proposed.

This chapter addresses thesis Objective 2) from Chapter 1, Section 1.6.

Regarding my contribution: I made a literature overview of the topic, planned and performed the experiments and jointly prepared the manuscript with co-authors.



Electrochemical Behavior and Self-Sealing Ability of Zirconium Conversion Coating Applied on Aluminum Alloy 3005 in 0.5 M NaCl Solution

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Zirconium conversion coating (ZrCC) was prepared on aluminum-manganese alloy AA3005 by immersion in 200 ppm of H_2ZrF_6 bath for 10 min at room temperature. Potentiodynamic polarization curves and electrochemical impedance spectra were measured up to 10 and 40 days, respectively, in 0.5 M NaCl solution. Microstructural characterization of samples was carried out using scanning electron microscopy equipped with energy dispersive X-ray spectrometry, X-ray photoelectron spectroscopy, time-of-flight secondary ion mass spectrometry, focus ion beam microscopy and transmission electron microscopy. The coating had a tri-layer structure with a thickness of 200 nm in the proximity of intermetallic particles and 30 nm far from intermetallic particles at the coating matrix. Electrochemical measurements showed that the corrosion resistance of ZrCC on AA3005 was improving during immersion in NaCl solution, i.e., impedance value at low frequency increased with immersion time reaching the average value $8.5 \cdot 10^6 \Omega \cdot \text{cm}^2$ at 3 mHz after 10 days immersion. Microstructural and compositional characterization showed that this behavior is related to the change in composition and structure of conversion coating including a transformation of $\text{ZrF}_4/\text{ZrO}_x\text{F}_y$ to $\text{ZrO}_2 \cdot 2\text{H}_2\text{O}_{(\text{s})}$ and formation of $\text{Al}(\text{OH})_3$ in the top layer of ZrCC, respectively, accompanied by the change in thickness of individual layers within the coating.

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Supplementary material for this article is available [online](#)

Chemical conversion coatings are formed by immersion, spraying, rinse or no-rinse process in which metal reacts with ions/substance from conversion bath forming an insoluble oxide-based coating at the surface of a metal.^{1–5} They are usually inorganic in nature. The main purpose of these coatings is to improve the adhesion of organic paints and lacquer to the substrate; to facilitate adhesion, organic polymers and additives are often added.^{1,6–12} Additionally, conversion coatings should improve the corrosion resistance of the substrate and the whole painted system.

For the last 100 years, state of the art conversion coatings were chromium conversion coatings (CCCs)^{13,14} for aluminum/light metals and phosphate conversion coatings for ferrous metals.^{15,16} As CCCs are nowadays being replaced due to carcinogenicity and toxicity of chromates, and phosphate conversion coatings are reconsidered due to environmental and economic issues, there is a great need to find a comparable, economical and green conversion processes. The most promising and already commercialized processes are the zirconium conversion coatings (ZrCCs), so-called Zirconization, and the trivalent chromium process (TCP).^{1,2,17} Zirconization has developed very quickly since the first patents/pioneering scientific work in the early 1990s,^{6,18–21} followed by the 1st generation ZrCCs in 2002^{22,23} and 2nd generation in 2010.^{24,25} The ZrCC process operates at room temperature, there is minimal waste disposal, rinsing water can be recirculated and the control of bath parameters is simple.^{26,27} The main advantage of the ZrCC process is that it can be applied to almost all metals, so is a “multi-metal process.” In defense and aerospace industries, the TCP process is a preferable choice over the ZrCC due to its better corrosion resistance. TCP coating is basically ZrCC with embedded Cr^{3+} ions as an active corrosion protection agent.^{2,17,28,29} Due to indirect hazards related to resources, extraction, disposal of Cr^{3+} ions and new evidence that even Cr^{3+} ions can also cause genotoxicity and cancer in humans, it could be forbidden in the future.^{14,30,31} So there is a great need in the industry to develop a completely Cr-free process with corrosion performance at the level of CCCs.

The formation of ZrCC is an electrochemical driven process by a difference of Volta potential between intermetallic particles (IMPs) and Al matrix.^{11,32,33} It starts by thinning of a native protective oxide layers and activation of the surface. At the same time, the oxygen reduction reaction and hydrogen evolution reactions take place at exposed IMPs causing a local alkalization that establishes the conditions for precipitation of zirconium oxide/hydroxide. After the coating covers the IMPs, it starts to grow laterally covering the whole surface. Due to the nature of this process, conversion coating is much thicker at/in the proximity of IMPs.³²

There have been many studies of ZrCC on aluminum alloys,^{6,8,11,19,32–48} magnesium alloys,^{49,50} zinc,^{51–54} steel.^{10,55–60} Addition of a small amount of Cu speeds up the conversion process and produces thicker coating,^{39,54,61} while addition of a small amount of Si can also produce thicker conversion coatings.⁴⁴ Surface pre-conditioning has an important role in the microstructure and properties of ZrCCs.^{40,41,43} Additionally, surface pre-treatment influences acid-base properties and the amount of OH^- groups in the final ZrCC.^{47,51,52} Coating thickness increases with the agitation of the bath by factor 2–4 depending on the substrate.⁴² ZrCCs are usually 30–80 nm and were reported to exhibit a bi- or even tri-layer structure.⁴⁶ ZrCCs improve adhesion of top organic coats, reduce the rate of cathodic delamination and improve corrosion resistance on different substrates.^{7,59,62–65} Addition of corrosion inhibitors such as Ce, V, Mo into ZrCC can provide a certain degree of active corrosion protection to these coatings.^{35,37,38}

Aluminum-manganese alloy AA3005 has good workability, medium strength, good electrical and thermal conductivity and excellent corrosion resistance. It is used as a heat exchanger in automotive and other industries, in architectural industries, for brazing and cladding, etc. There have been several studies on the nature and stability of Al_2O_3 formed on 3xxx alloys,^{66–68} but only a few studies about conversion pre-treatment of this alloy. Smit et al. studied no-rinse pre-treatment of AA3003 in conversion bath containing 0.1 M solution of H_2TiF_6 .^{9,69} When coated with titanium conversion coating the corrosion resistance in NaCl was initially not so good but it improved with immersion time. TEM images showed that the coating was 30 nm thick.⁶⁹ Thermal treatment had a beneficial effect on the corrosion properties of H_2TiF_6 -pre-treated

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AA3003.⁷⁰ Banczek et al. studied Ce conversion coatings on AA3003 and compared it with a commercial TCP conversion coating (SurTec 650 Chromital).⁷¹

Therefore, there is a lack of studies about zirconium conversion coatings applied to AA3xxx alloys. Moreover, the extraordinary behavior of titanium conversion coating on AA3003 which improved with time, as noticed by Smit et al.⁶⁹ deserves further mechanistic understanding. In our previous study, the commercial TCP coating SurTec®650 containing Cr(III) and Zr deposited on AA3003 was studied.⁷² This commercial coating exhibited good corrosion resistance in simulated acid rain and sodium chloride solution but only after longer immersion in solution, i.e., 24 h. This interesting behavior is studied in more detail in this study devoted to Zr-based coatings only deposited over AA3005. The electrochemical behavior of ZrCCs prepared by immersion of AA3005 in the conversion bath of hexafluorozirconic acid (H_2ZrF_6) was investigated.

Microstructural characterization of the coated substrate was carried out using scanning electrochemical microscopy equipped with energy X-ray dispersive spectrometer (SEM/EDS), cross section focus ion beam microscopy (FIB), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS). Electrochemical characterization of samples was carried out in a 0.5 M NaCl solution by measuring open circuit potential (OCP) vs time curves, potentiodynamic polarization curves and electrochemical impedance spectra. Special attention was devoted to the long-term corrosion resistance in NaCl, up to 40 days. An interesting behavior of improvement of corrosion characteristics of coated samples with time was confirmed. Based on the results obtained we were able to address this phenomenon and postulate the mechanism of self-sealing or active protection of Zr-conversion coatings on Al-Mn alloy AA3005.

Experimental

Materials, sample preparation and chemicals.—Aluminum alloy AA3005 / UNS-A93005 (Mn 1–1.5 wt%, Mg 0.2–0.6 wt%, Fe 0–0.7 wt%, Si 0–0.6 wt%, Cu 0–0.3, Zn 0–0.25 wt%, Cr 0–0.1 wt%, Ti 0–0.1 wt%, residuals 0.15 wt%) in form of foil (thickness 70 microns) produced by Impol 2000 d.d. (Slovenska Bistrica, Slovenia) was used as a substrate. The composition given was provided by the supplier. Samples used in experiments were cut in a rectangular shape with dimensions of 3 cm × 3 cm.

The following chemicals were used for experiments: NaCl (for analysis, Fischer Scientific, Leicestershire), H_2ZrF_6 (50 wt% in water, Sigma-Aldrich, Saint Louis, USA), NH_4HCO_3 (reagent grade, Sigma-Aldrich, Steinheim, Germany) and Metaclean® (alkaline cleaner, Amity international, Barnsly, United Kingdom). Milli-Q Direct water with the resistivity of 18.2 MΩ·cm at 25 °C (Merck, Darmstadt, Germany) was used for rinsing and for solution preparation.

pH was measured using pH meter 827 pH-lab equipped with Unitrode/Pt1000 (Metrohm AG, Herisau, Switzerland). Teflon beakers (V = 1 L) were used for conversion baths, while glass beakers (V = 600 ml) were used for alkaline cleaner and rinsing baths. Sample holders were made of teflon and conversion coating solutions were stored in polyethylene bottles.

Preparation of conversion coatings.—Conversion bath contained $1 \cdot 10^{-3}$ mol L⁻¹ (200 ppm) of H_2ZrF_6 and pH was set to 4.8 using 15 wt.% NH_4HCO_3 . The conversion was carried out at room temperature.

Samples were chemically cleaned by immersion in 5 wt.% Metaclean solution (T = 57 °C, stirring rate 150 rpm) for 3 min. Immediately afterward, samples were washed off with Milli-Q Direct water and then rinsed by dipping in Milli-Q Direct water bath for 45 s. Immediately afterward, the sample was dipped in a conversion coating bath (T = 25 °C, stirring rate 450 rpm) for

10 min. Immediately afterwards the sample was rinsed with Milli-Q Direct water and washed off by dipping it in Milli-Q Direct water bath for 1 min. The sample was then dried with N₂ stream and left to dry in air for 24 h.

As-received (bare) samples refer to AA3005 used in as-received conditions without any chemical cleaning.

Electrochemical characterization.—Electrochemical experiments were carried out with a Multi Autolab/M204 (Metrohm Autolab, Utrecht, Netherlands) potentiostat/galvanostat controlled by Nova 2.1 software. Electrochemical measurements were repeated for each condition for at least three different samples. Representative measurements are presented in plots and average values together with standard deviation in tables. Measurements were conducted in a standard three-electrode flat cell with a volume of 250 mL. The sample was the working electrode, a carbon rod was the counter electrode, and a saturated Ag/AgCl_(sat) electrode was the reference electrode ($E_{\text{SHE}} = 0.198$ V). All potentials in the text refer to the Ag/AgCl_(sat) scale. The electrolyte was freshly prepared 0.5 M NaCl.

Prior to electrochemical measurement samples were allowed to rest at open circuit potential (OCP) for 5 min, 1 h, 2 h, 1 day, 2 days, 3 days, 4 days, 5 days and 10 days.

Electrochemical measurements were conducted in the following sequence from least destructive to more destructive: (i) measurement of the (OCP) as a function of time during for 5 min, (ii) recording of linear polarization curves, and (iii) recording of potentiodynamic polarization curves. The system was allowed to rest for 10 s before switching to the next electrochemical technique.

Linear polarization curves (LPR) were run in the range from –10 to 10 mV vs OCP using a 0.1 mV s⁻¹ scan rate. Polarization resistance ($R_{p, \text{LPR}}$) was determined as the slope of the fitted potential (E) vs current density (j) curve using Nova 2.1 software.

Potentiodynamic polarization curves measurements were made in the potential region starting from –250 mV vs OCP in the anodic direction until current reached 0.1 mA. The scan rate was 1 mV s⁻¹.

Corrosion current density and corrosion potentials were determined using Nova 2.1 software based on the Tafel extrapolation method.⁷³ Polarization resistance was calculated also from parameters obtained by Tafel extrapolation ($R_{p, \text{Tafel}}$) method using Nova 2.1 software based on Eq. 1 in accordance with standard ASTM G59–97.⁷⁴

$$R_{p, \text{Tafel}} = \frac{B}{j_{\text{corr}}} \quad [1]$$

where B is the Stern-Geary constant.

Electrochemical impedance spectroscopy (EIS) spectra were recorded from 100 kHz to 3 mHz frequency using an AC potential amplitude of 10 mV. Spectra were recorded at the OCP, periodically every day up to 40 days of immersion or until the samples were pitted.

Microstructural characterization.—Surface characterization was performed using scanning electron microscopy combined with energy dispersive X-ray spectrometry (SEM/EDS), focused ion beam microscopy (FIB) equipped with EDS, transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS).

SEM images were taken in secondary electron (SE) and back-scattered electron (BSE) modes using a FEI Helios Nanolab 650 microscope. EDS spectra were taken using an Oxford Instruments AZtec system with X-max SDD (50 mm²) detector. The analysed area was 100 nm² with an analysis depth of 100 nm (near surface condition) at 3 kV beam energy, to few micrometers in diameter and the analysed depth around 1 μm for higher beam energies. EDS mapping was recorded with 3 kV beam energy and resolution of 1024 lines. Prior to analysis, samples were coated with a thin carbon layer to reduce the charging effect.

FIB was used to analyse the cross-section of conversion coatings. A FEI Helios Nanolab 650, equipped with EDS, was first used to

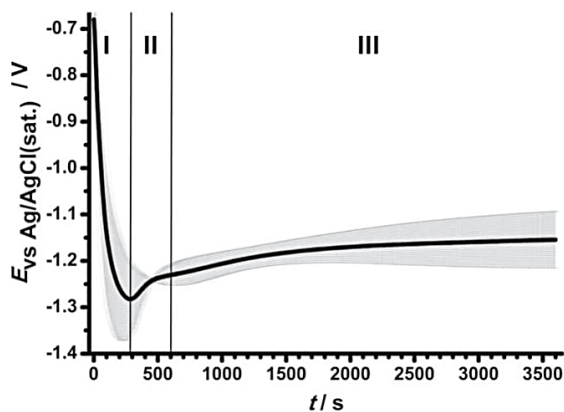


Figure 1. Open circuit potential measurement during the formation of zirconium conversion coating on AA3005 in $1 \cdot 10^{-3}$ M H_2ZrF_6 conversion bath. Average value of 3 repetitions on different samples is presented by solid curve and standard deviation as grey area. Numerals I, II and III denote the regions of surface activation, initial coating formation and growth, respectively.

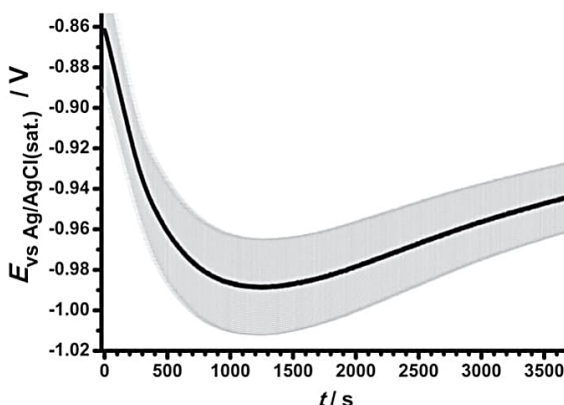


Figure 2. Open circuit potential during the first 2 h after immersion of zirconium conversion coated AA3005 samples in 0.5 M NaCl. Average value of 4 repetitions on different samples is presented by solid curve and standard deviation as grey area.

deposit a $1 \mu\text{m}$ thick Pt protection layer. Then, a relatively large cross-section was made by a rough removal of material with Ga ions (30 keV/48 nA) followed by a rough polishing (30 keV/22 nA) and a fine polishing (30 keV/9 nA). EDS maps of the cross-section were recorded with a resolution of 1024 lines. The average thickness of oxide layers was evaluated using ImageJ programme.

TEM was used to analyse the cross section of the conversion coatings and assess its thickness, composition and structure. Detailed structural investigations of the sample were performed using a conventional 200 kV transmission electron microscope (JEM-2010F, Jeol Ltd., Tokyo, Japan). Chemical analysis was performed using a Si(Li) EDS detector.

For TEM cross-section analysis, the sample was mounted and fitted into 3 mm brass cylinders using epoxy glue between two silicon blocks on each side to improve strength. The TEM specimen was ground to a thickness of $100 \mu\text{m}$ and dimpled down to $15 \mu\text{m}$ at the disc center (Dimple grinder, Gatan Inc., Warrendale PA, USA). The TEM specimen was finally ion-milled (PIPS, Precision Ion Polishing System, Gatan Inc., USA) using 3 kV Ar^+ ions at an incidence angle of 8° until perforation.

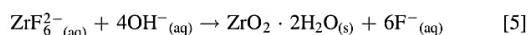
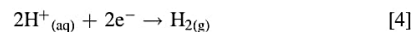
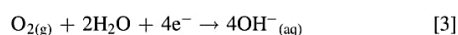
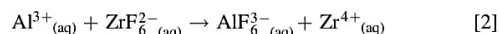
XPS was carried out using a PHI-TFA XPS spectrometer (Physical Electronic Inc.). The vacuum during the XPS analysis was in the range of 10^{-9} mbar. The analysed area was 0.4 mm in diameter and the depth about $3\text{--}5 \text{ nm}$. X-rays were provided from a monochromatic Al $\text{K}\alpha$ source at a photon energy of 1486.6 eV . XPS spectra were analysed by Multipack software, version 8.0 (Physical Electronics Inc.). Spectra were calibrated relative to the position of C 1 s peak at 284.8 eV .

ToF-SIMS ion depth profiles were made using a ToF-SIMS V spectrometer (ION TOF GmbH—Munster, Germany). The analysis chamber was operated at a pressure below $\sim 10^{-9}$ mbar. Ion depth profiles for positive ions were recorded by interlacing a pulsed 30 keV Bi^+ primary ion source delivering 1 pA of target current over a $100 \times 100 \mu\text{m}^2$ area with sputtering using a 2 keV O_2 source beam delivering 544 nA of target current over a $400 \times 400 \mu\text{m}^2$ area. Depth profiles for negative ions were recorded by interlacing a pulsed 30 keV Bi^+ primary ion source delivering 1.2 pA of target current over a $100 \times 100 \mu\text{m}^2$ area with sputtering using a 2 keV Cs^+ source beam delivering 523 nA of target current over a $400 \times 400 \mu\text{m}^2$ area.

Results and Discussion

OCP measurements during the formation of conversion coating.—OCP during coating formation was measured in order to follow the kinetics of conversion coating formation and to determine when the formation of the coating was completed. OCP curves measured during immersion in the H_2ZrF_6 conversion bath are presented in Fig. 1. The formation of the coating from the conversion bath can be described with the following steps.

Activation of the surface caused by the initial attack of aggressive ZrF_6^{2-} ions leads to the dissolution of naturally formed aluminum oxide layer Al_2O_3 (Eq. 2) that corresponds to decay of OCP (Fig. 1, region I). At the same time, oxygen reduction and hydrogen evolution reactions take place at cathodic sites and lead to local alkalization up to $\text{pH} = 8.5$ near cathodic sites (Eqs. 3 and 4).⁴⁵ This establishes the conditions for the initiation of coating formation (Eq. 5). At the OCP minimum the processes of natural oxide dissolution and conversion coating formation are in equilibrium. Region II, denoted by the progressive shift in OCP to more positive values, marks an increased growth of conversion coating over film dissolution. In this region, the formation and growth of conversion coating in the form of zirconium oxide/zirconium oxyfluoride takes place caused by the increased value of pH.



At the end of region II, the OCP again makes an inflection point indicating that a steady state deposition process is reached. This point denotes the beginning of region III. At longer conversion times the conversion coating still continues to grow but due to thickness increase the cracking of the coating occurs and it loses its protective ability.^{54,75–77} Based on the OCP measurements during ZrCC formation we conclude that the coating formation was completed after 10 min. This conversion time was then taken for the preparation of ZrCCs for all further experiments.

Open circuit potential during immersion of conversion coatings in 0.5 M NaCl.—Within the first 1000 s to 1200 s after immersion of conversion coated AA3005 sample in 0.5 M NaCl, the OCP decreases rapidly (Fig. 2). This indicates the initial dissolution of the conversion coating in chloride containing solution and

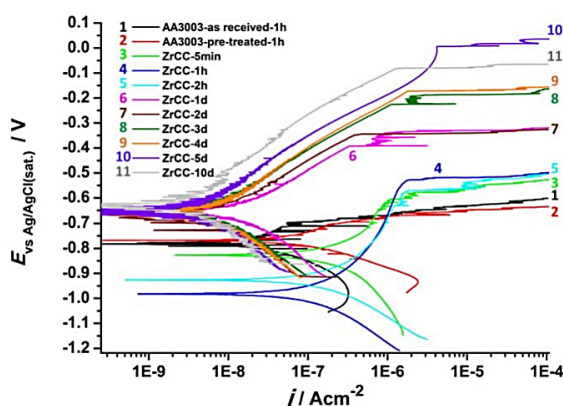


Figure 3. Potentiodynamic polarization curves recorded in 0.5 M NaCl for as-received (bare), chemically pre-treated and zirconium conversion coated AA3005. As-received and chemically pre-treated samples were stabilized for 1 h at the OCP prior measurement; conversion coated samples were stabilized for different periods of time (from 5 min up to 10 days). Electrochemical data deduced from polarization curves are given in Table I.

penetration of electrolyte through the conversion coating to the substrate and intermetallic particles (IMPs). After that period, the OCP started to recover and during the next 6000 s shifted towards more positive values, indicating a progressive recovery or sealing of conversion coatings.⁷⁸ This is a first order approximation of potential active corrosion protection, which is further examined in the following experiments.

Electrochemical potentiodynamic characterization.—Potentiodynamic polarization curves were recorded for as-received (bare), chemically pre-treated and conversion coated AA3005 samples to evaluate the performance of conversion coatings

(Fig. 3, Table I). Bare and chemically cleaned samples were allowed to stabilize for 1 h at the OCP prior to electrochemical measurements, whereas for the conversion coated samples the immersion (stabilization) times at the OCP were up to 10 days.

Polarization curves for bare and chemically pre-treated samples are typical for aluminum alloys in chloride solution with cathodic process related to oxygen reduction and anodic process related to the dissolution of aluminum oxide and localized corrosion at the IMPs.⁷⁹ Prior to breakdown at the pitting potential (E_{pit}), the AA3005 alloy exhibits a passivity region ($\Delta E = |E_{\text{pit}} - E_{\text{corr}}|$) of approximately 100–150 mV indicating that it is quite resistant in chloride environment, especially compared to for example copper- or zinc-containing Al alloys.⁸⁰ Chemically pre-treated AA3005 exhibited 2-times larger corrosion current density and reduced ΔE in comparison with bare AA3005 sample (Fig. 3, Table I). Chemical pre-treatment cleaned and activated the surface of AA3005 for the conversion process by removing organic contaminants and natural aluminum oxide from alloy surface thus resulting in larger current densities.

After 1 h of immersion in 0.5 M NaCl solution, both bare AA3005 and chemically pre-treated AA3005 exhibited smaller j_{corr} and narrower ΔE window in comparison with conversion coated samples measured after 5 min, 1 h and 2 h immersion in 0.5 M NaCl. These results indicate that the conversion coating process did not provide—significant protection to AA3005. In order to monitor and evaluate corrosion behavior further, conversion coated AA3005 samples were immersed for longer times prior to electrochemical measurements, i.e. up to 10 days. Please note that data on all repetitions and electrochemical parameters deduced are presented in Supplemental material (Figs. SI–S3, Table SI are available online at stacks.iop.org/JES/167/021509/mmedia).

With the prolongation of immersion time above 1 h, the j_{corr} of ZrCC samples progressively decreased, E_{corr} shifted more positive and ΔE increased. After 24 h of immersion, the j_{corr} was smaller by 1 order of magnitude, while OCP was shifted towards more positive values reaching -0.71 V. This was a significant improvement in the performance of ZrCC compared to the short immersion

Table I. Electrochemical data deduced from potentiodynamic polarization measurements for as-received, chemically pre-treated and zirconium conversion coated AA3005 exposed to 0.5 M NaCl for different periods of time prior to electrochemical measurement. In table, average values and standard deviation (SD) are given obtained on different samples.

Sample	j_{corr} A cm^{-2}	OCP V	E_{corr} V	E_{pit} V	ΔE^{a} V	β_a mV/dec	β_c mV/dec	$R_{\text{p-LPB}}$ $\Omega \text{ cm}^2$	$R_{\text{p-Tafel}}$ $\Omega \text{ cm}^2$
As-received-1h	3.9E-08	-0.83	-0.82	-0.67	0.15	220	116	8.6E + 05	9.3E + 05
+SD	1.1E-08	0.02	0.03	0.03	0.04	23	19	1.5E + 05	3.2E + 05
Pre-treated-1h	7.5E-08	-0.74	-0.78	-0.68	0.10	176	102	4.6E + 05	3.8E + 05
SD	1.2E-08	0.01	0.01	0.02	0.02	44	4	2.0E + 05	4.4E + 04
ZrCC-5 min	2.4E-07	-0.87	-0.83	-0.61	0.22	367	320	1.8E + 05	3.0E + 05
SD	4.5E-08	0.02	0.03	0.02	0.02	72	43	1.3E + 04	3.0E + 04
ZrCC-1h	2.3E-07	-0.93	-0.94	-0.63	0.31	416	177	2.6E + 05	2.4E + 05
SD	4.4E-08	0.01	0.03	0.02	0.02	56	30	3.3E + 04	3.7E + 04
ZrCC-2h	1.6E-07	-0.89	-0.90	-0.59	0.34	285	194	3.6E + 05	3.1E + 05
SD	1.1E-08	0.02	0.02	0.01	0.04	28	9	6.7E + 04	3.5E + 04
ZrCC-1d	1.4E-08	-0.71	-0.70	-0.40	0.29	150	188	2.8E + 06	3.2E + 06
SD	8.1E-09	0.02	0.02	0.12	0.11	50	64	1.2E + 06	1.2E + 06
ZrCC-2d	8.0E-09	-0.69	-0.69	-0.36	0.33	176	188	3.0E + 06	5.4E + 06
SD	3.5E-09	0.03	0.03	0.11	0.11	26	44	1.5E + 06	1.4E + 06
ZrCC-3d	6.9E-09	-0.69	-0.68	-0.25	0.43	209	189	5.8E + 06	6.7E + 06
SD	2.6E-09	0.03	0.03	0.09	0.09	46	29	5.6E + 06	1.5E + 06
ZrCC-4d	5.5E-09	-0.67	-0.67	-0.32	0.35	203	197	4.1E + 06	9.1E + 06
SD	2.1E-09	0.03	0.04	0.10	0.12	23	27	2.8E + 06	3.5E + 06
ZrCC-5d	5.1E-09	-0.66	-0.67	-0.17	0.49	220	184	4.0E + 06	9.6E + 06
SD	2.0E-09	0.03	0.04	0.20	0.20	55	41	3.4E + 06	3.2E + 06
ZrCC-10d	3.2E-09	-0.65	-0.67	-0.22	0.45	235	173	5.3E + 06	1.6E + 07
SD	1.8E-09	0.03	0.04	0.13	0.09	29	54	5.0E + 06	5.1E + 06

a) $\Delta E = |E_{\text{pit}} - E_{\text{corr}}|$.

of 1 h. The trend of decreasing corrosion current densities continued up to 10 days of immersion in 0.5 M NaCl solution reaching OCP of -0.65 V, j_{corr} of $3 \cdot 10^{-9}$ A·cm $^{-2}$, and ΔE of 0.45 V. This electrochemical behavior indicates that ZrCC on AA3005 acts as an anodic inhibitor and that some kind of self-sealing/active corrosion protection takes place during prolonged immersion in 0.5 M NaCl.

Electrochemical impedance spectroscopy.—To evaluate the performance of conversion coatings the electrochemical impedance spectra (EIS) were measured at OCP for as-received, chemically pre-treated and ZrCC coated AA3005 samples until pitting occurred. Curves of OCP and impedance modulus at 3 mHz ($|Z|_{3\text{mHz}}$) measured during the course of immersion are presented in Fig. 4. Bode and Nyquist diagrams for all repetitions are presented in Supplement material (Figs. S4–S6). Impedance at low frequencies represents total polarization resistance of the coating and it is proportional to the corrosion resistance of a coating.^{81–83} For ZrCC samples the impedance modulus was $3 \cdot 10^5$ Ω ·cm 2 after 1 h of immersion in 0.5 M NaCl; however, it increased over one order of magnitude during the first 6 to 7 days of immersion reaching the average value of $7.5 \cdot 10^6$ Ω ·cm 2 . After 10 days of immersion, $|Z|_{3\text{mHz}}$ impedance modulus formed a plateau at the average value $8.5 \cdot 10^6$ Ω ·cm 2 (Fig. 4b). The same trend was noticed with Bode phase angles diagrams (Figs. S4–S6) where phase angle at low frequencies (ϕ , ϕ) continuously increased up to 20 days of immersion, or even longer, depending on the sample. The highest increase was noted during the first 10 days of immersion indicating self-sealing /active corrosion protection within ZrCC. Drops in $|Z|_{3\text{mHz}}$ and ϕ occurred after 20 days of immersion (Fig. 4b) but afterwards $|Z|_{3\text{mHz}}$ recovered to a higher average value of $6.5 \cdot 10^6$ Ω ·cm 2 ; this indicates increased probability that pitting

will occur after 20 days of immersion in 0.5 M NaCl solution. Finally, after 30 days of immersion, a decrease in $|Z|_{3\text{mHz}}$ and ϕ indicates that samples underwent pitting corrosion.

According to Buchheit et al., if conversion coating applied on AA3003 exhibits R_p (defined as apparent integrated pitting resistance) of $2.3 \cdot 10^7$ Ω ·cm 2 (range $1.1 \cdot 10^7$ to $4.8 \cdot 10^7$ Ω ·cm 2) after 168 h immersion in 0.5 M NaCl, it has a probability of $>80\%$ to pass 168 h neutral salt spray test (NSST) test.^{84,85} It was pointed out that EIS is more sensitive than salt spray chamber exposure for detecting the corrosion of a coating when the inspection interval was > 24 h.⁸⁵ The ZrCCs on AA3005 showed exceptional performance with impedance modulus of $8.5 \cdot 10^6$ Ω ·cm 2 after 168 h of immersion. This value is smaller than that proposed by Buchheit et al.⁸⁵ but it has to be taken into account that the low frequency limit was higher than in the present work (10 mHz and 3 mHz, respectively). When taking that into account, the fitted average values of EIS parameters obtained in this work are R_p (96 h) = $1.2 \cdot 10^7$ Ω ·cm 2 and R_p (168 h) = $1.61 \cdot 10^7$ Ω ·cm 2 after 96 h and 168 h of immersion in 0.5 M NaCl. Based on these values we therefore assume that the coatings will pass 168 h NSST mark.^{84,85} More data are given in supplement material (Table SVII.)

The time dependence of EIS spectra and progressive improvement of corrosion resistance is in agreement with results of PD measurements indicating that ZrCC coating on AA3005 has excellent corrosion performance, even better than TCP conversion coatings.^{71,72} During the course of immersion in NaCl, the time dependence of OCP indicate that ZrCCs act as anodic inhibitors: OCP shifted from approximately -0.9 V after 1 h of immersion, to -0.7 V after 24 h of immersion, reaching values -0.6 V to -0.65 V after 10 days of immersion (Fig. 4a). Trends in OCP and impedance modulus were in correlation since the drop in $|Z|_{3\text{mHz}}$ was followed by a drop in OCP, as characteristic for pitting and exposure of AA3005 substrate to the electrolyte.

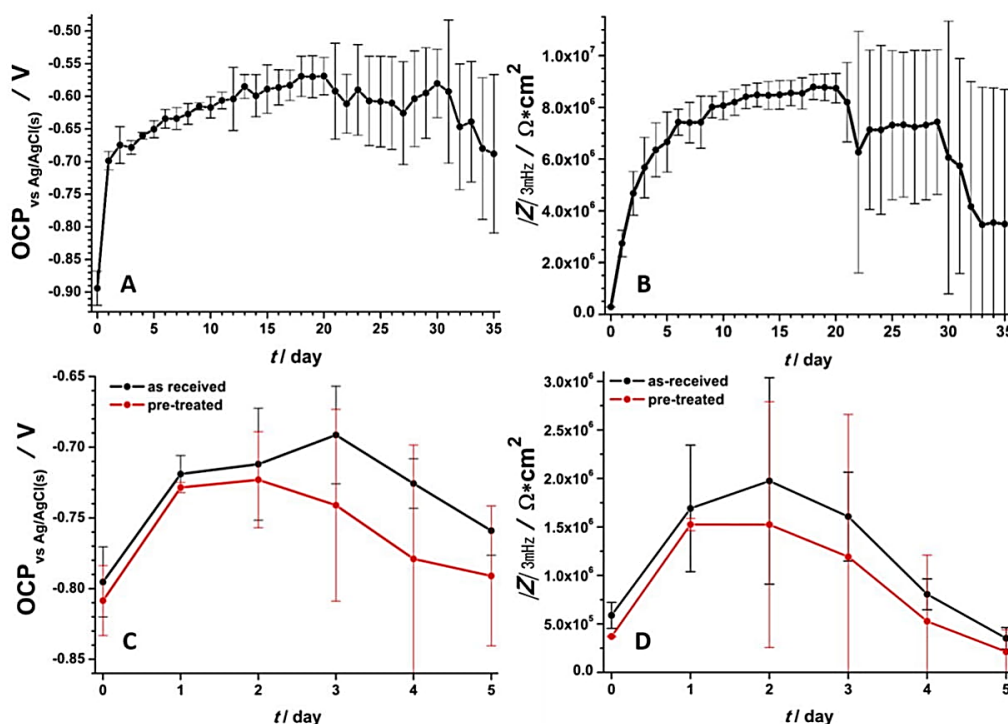


Figure 4. Impedance module at 3 mHz and open circuit potential as a function of immersion time for: (a, b) zirconium conversion coated AA3005; (c, d) as-received AA3005 (black symbols) and chemically pre-treated AA3005 (red symbols). Average values of 3 repetitions on different samples are presented by solid curves and standard deviation as error bars. Lines were drawn to guide the eye.

Compared to ZrCCs coated samples, the EIS behavior was quite different for bare and chemically pre-treated samples. For the latter, the $|Z|_{3\text{mHz}}$ showed an initial increase with immersion time but the values are approximately 3–4 times smaller compared to ZrCCs coated samples (Fig. 4d) and reached the maximum of $2.0 \cdot 10^6 \Omega \cdot \text{cm}^2$. However, this value is still comparatively high and indicates that even bare AA3005 has substantial corrosion resistance. At longer immersion times, $|Z|_{3\text{mHz}}$ decreased, reflecting the initiation of the localized corrosion process. The time dependencies of OCP and Bode plots show a similar trend (Fig. 4c, S5). The same trend was noted with Bode phase angle plots (Fig. S5). Chemically pre-treated AA3005 showed very similar behavior as bare AA3005 but it was less corrosion resistant which is in good agreement with PD curves (Fig. 3, Table I).

SEM/EDS characterization of the coating surface.—SEM images of surface morphology and microstructure of chemically pre-treated AA3005, as-prepared ZrCC coated AA3005, and after immersion in NaCl are given in Fig. 5 recorded at lower and higher magnification. As-prepared ZrCC (Fig. 5b) was obviously very thin as no significant change was observed at the majority of the surface using SE at lower magnification mode compared to a chemically pre-treated sample (Fig. 5a, 5b). At higher magnification the coating is visible, especially around IMPs (inset in Fig. 5b). After 2 days of immersion in 0.5 M NaCl, the most significant feature was the appearance of a bloated area around IMPs (denoted as a “hat”) (Fig. 5c). After 5 days of immersion, this area was not bloated anymore. There were no visible corrosion or pits in conversion coatings after 5 days of immersion in 0.5 M NaCl.

As-received AA3005 was composed of: Al (96.7 at. %), O (1.8 at. %), Mn (0.6 at. %), Fe (0.3 at. %), Mg (0.5 at. %) and Si (0.1 at. %) (Table II). The microstructural characteristics of AA3005 were typical as reported for this alloy.^{86,87} The main intermetallic particles were $\text{Al}_6(\text{Mn}, \text{Fe})$ composed of Mn and Fe in an atomic ratio approximately 1, 1.3 and 1.6, respectively, for each spot, (Fig. 6a,

spot 3, Table II and Fig. 6b, spots 4, 5, Table III). $\alpha\text{-Al}(\text{Fe}, \text{Mn})\text{Si}$ IMPs containing Mn, Fe and Si were also detected (Fig. 6a, spot 4, Table II and Fig. 6b, spots 3, 6, Table III). The atomic ratios Mn/Fe and Mn/Si were similar, i.e. between approximately 1 and 2 (Table III). A large number of dispersoids (little white dots) sized below $1 \mu\text{m}$ containing mainly of Mn were present (Fig. 6a spot 2, Table II). There were no visible changes in the microstructure and elemental composition of AA3005 after alkaline cleaning using Metaclean (Fig. 6b, Table III). This confirms that Metaclean pre-treatment removed just grease and organic contamination from the surface.

SEM-BSE images of the as-prepared ZrCC and after immersion in 0.5 M NaCl for 2 and 5 days are presented in Figs. 7b–7d (SE images are presented in Fig. 5b–5d). For the sake of comparison, Fig. 6b for chemically pre-treated AA3005 is repeated as Fig. 7a. These samples were analysed by point EDS using an electron beam voltage of 3 kV or 11 kV corresponding to the analysed depth of approximately 100 nm and $1 \mu\text{m}$, respectively (Tables IV–VII and SII–SIV). Results of EDS point analysis are presented in the form of atomic ratios (Table IV) or atomic % (Tables V–VII and SII–SIV). Further, EDS mapping was recorded for all the samples at 3 kV electron beam voltage (Fig. 8).

After conversion for 10 min in the conversion bath, the formation of ZrCC was completed over the whole surface (Fig. 7b and Tables IV, VII, SIII). The coating was cracked and much thicker at the (Mn, Fe) IMPs and in their proximity. These areas are denoted as hats. The atomic ratios of O/Zr, F/Zr and Al/Zr in the matrix of the as-prepared ZrCC were 2.39, 0.61 and 4.86 respectively (Fig. 7b, spot 2, Table VII), while the atomic ratios of O/Zr and F/Zr in coating at the hat above (Mn, Fe) IMPs were 1.68 and 0.31, respectively (Fig. 7b, spot 4, Table VII). The latter values indicate that the hat consists of $\text{ZrO}_{1.68}\text{F}_{0.31}$ and does not contain Al. There were darker areas in the coating with a smaller concentration of Zr, F and O, and a higher concentration of Al indicating that coating was thinner at these areas (Fig. 7b, spot 5, Table IV). EDS mapping

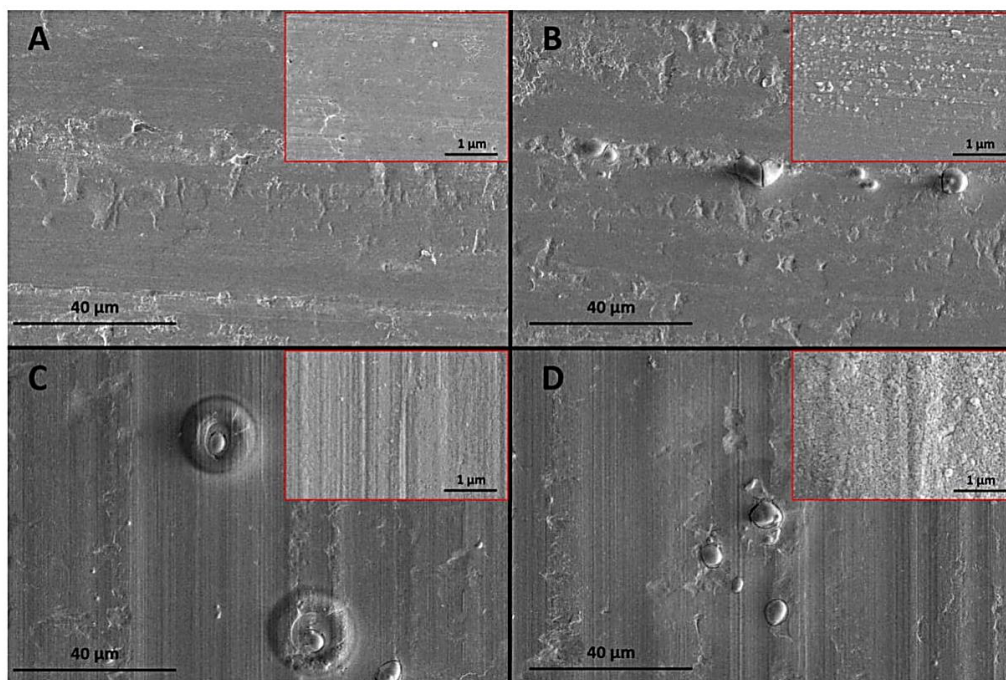


Figure 5. SEM secondary electron images of AA3005: (a) pre-treated with Metaclean; (b) zirconium conversion coating as prepared; (c) zirconium conversion coating after 2 days of immersion in 0.5 M NaCl and (d) zirconium conversion coating after 5 days of immersion in 0.5 M NaCl. Insets show images at higher magnification.

Table II. EDS analysis of as-received (bare) AA3005 (Fig. 6a); electron beam voltage of analysed spots 1–3 was 3 kV (denoted 1-4) or 11 kV (denoted 1*-4*) differing in the depth on the analysed region (approximately 100 nm and 1 μm , respectively).

Spot	at.% Al	at.% O	at.% Mn	at.% Fe	at.% Mg	at.% Si
1	89.2	10.4	—	—	0.4	—
2	87.5	12.1	—	—	0.4	—
3	79.2	20.8	—	—	—	—
4	81.5	18.5	—	—	—	—
1*	96.7	1.8	0.6	0.3	0.5	0.1
2*	98	1.5	—	—	0.5	—
3*	79.3	2.8	8.8	9.0	—	—
4*	83.6	4.1	5.0	3.2	—	4.1

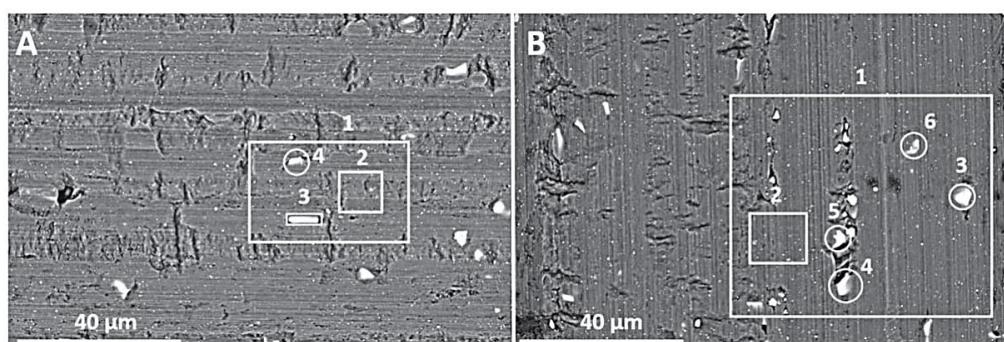


Figure 6. SEM-BSE images of (a) as-received and (b) chemically pre-treated AA3005. Squares 1, 2 and 3 denote spots where EDS analysis was carried out (Table II).

clearly shows that ZrCC was preferentially formed at and around IMPs (Fig. 8).

After 2 days of immersion in a 0.5 M NaCl solution, the most visible change at the coating was a dark circle around (Mn, Fe) IMPs (Fig. 7c and Tables V, VII, SIII). Apparently the cracks around (Mn, Fe) IMPs were weak spots in the coating where electrolyte penetrated and the corrosion process initiated. This would usually lead to the dissolution of IMPs, degradation of conversion coating and pit growth but in this case a densification and closing of cracks/pit around (Mn, Fe) IMPs occurred. This is clearly visible from EDS analysis/mapping which shows a very high concentration of O (65.8 at.%) and Al (30.7 at.%) at dark circle area around (Mn, Fe) IMPs indicating the formation of mostly oxide-containing area (Fig. 7c, spot 5, Table V). The atomic ratio of O/Zr at the hat increased to 2.69, while Al and F were not detected (Fig. 7c, spot 4, Table VII); therefore, the composition changed from $\text{ZrO}_{1.68}\text{F}_{0.31}$ to $\text{ZrO}_2 \cdot 0.7 \text{H}_2\text{O}$. This

indicates that the process of densification and closing of pores occurs in the whole coating and not just around (Mn, Fe) IMPs. The most significant change in ZrCC occurred during immersion in NaCl was a 5-fold reduced concentration of fluorine, i.e. from 6.9 at.% down to 1.3 at.% (Tables IV, V, spot 2). Atomic ratios of Al/Zr, O/Zr and F/Zr changed to 5.63, 2.86, and 0.125 (Fig. 7c, spot 2, Table VII). A decrease in fluorine concentration in the ZrO_2 hats and around them is clearly visible from EDS mapping (Fig. 8).

After 5 days of immersion in 0.5 M NaCl solution most visible change was a change of the dark circle around the Zr-oxide hat from dark to light white color with further spreading to a surrounding area (Fig. 7d and Tables VI, VII, SIV). It was difficult to select the right area for the comparison due to different samples. The area selected to be similar as in Fig. 7c seems to contain a significantly reduced O concentration (down to 31.0 at.%) and increased concentrations of Zr and Al (up to 10.2 at.% and 57.7 at.%, respectively) (Fig. 7d, spot

Table III. EDS analysis of chemically pre-treated AA3005 (Fig. 6b); electron beam voltage of analysed spots 1–3 was 3 kV (denoted 1-6) or 11 kV (denoted 1*-6*) differing in the depth on the analysed region (approximately 100 nm and 1 μm , respectively).

Spot	at.% Al	at.% O	at.% Mn	at.% Fe	at.% Mg	at.% Si
1	88.8	10.6	—	—	0.6	—
2	88.8	10.6	—	—	0.6	—
3	82.3	17.7	—	—	—	—
4	83.1	16.9	—	—	—	—
5	82.4	17.6	—	—	—	—
6	87.7	12.3	—	—	—	—
1*	96.6	1.9	0.6	0.3	0.5	0.1
2*	97	1.8	0.5	0.1	0.5	—
3*	78.4	2.1	7.2	7.8	0.2	4.3
4*	87.3	3.7	5.0	3.9	—	—
5*	88.2	3.7	4.7	3.0	0.4	—
6*	87.9	2.0	5.1	2.5	—	2.6

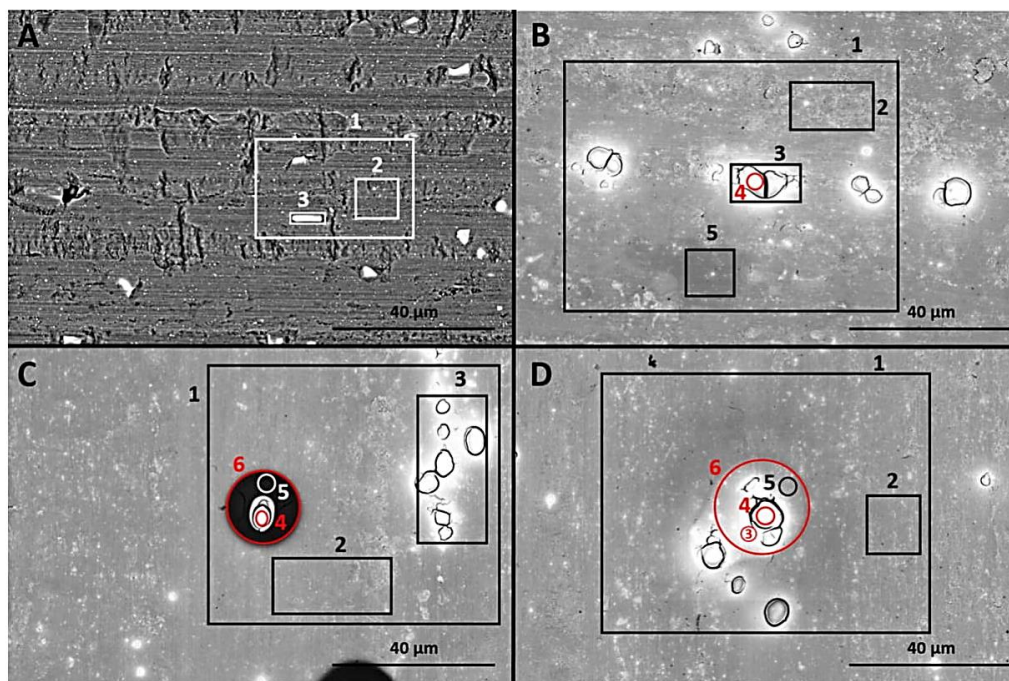


Figure 7. SEM-BSE images of AA3005: (a) pre-treated with Metaclean; (b) zirconium conversion coating as prepared; (c) zirconium conversion coating after 2 days of immersion in 0.5 M NaCl and (d) zirconium conversion coating after 5 days of immersion in 0.5 M NaCl. EDS mapping of areas denoted by square 1 is presented in Fig. 8. Squares 1, 2, 3, 4, 5, 6, present spots in Tables IV–VI and SII–SIV. Figure 7a is the same as 6b and is given for comparison's sake.

Table IV. EDS analysis of as-prepared zirconium conversion coatings on AA3005 (Fig. 7b); electron beam voltage of analysed spots 1–5 was 3 kV corresponding to the depth on the analysed region of approximately 100 nm. The results of the analysis carried out at 11 kV are presented in Table SII.

Spot	at.% Al	at.% Zr	at.% O	at.% F
1	55.4	12.7	25.5	6.4
2	54.9	11.3	27.0	6.9
3	22.3	23.9	45.1	8.7
4	—	33.5	56.2	10.3
5	74.9	7.6	13.9	3.6

5, Table VI) compared to that after 2 days immersion. The fluorine concentration was only 1.3 at.%. Atomic ratios Al/Zr, O/Zr and F/Zr were 5.14, 3.15 and 0.142 (Fig. 7d, spot 2, Table VII) indicating further densification of ZrCC. In the zirconium oxide hat the atomic ratio O/Zr was 3.16 (Fig. 7d, spot 4, Table VII).

Table V. EDS analysis of zirconium conversion coatings on AA3005 immersed in 0.5 M NaCl solution for 2 days (Fig. 7c); electron beam voltage of analysed spots 1–6 was 3 kV corresponding to the depth on the analysed region of approximately 100 nm. The results of the analysis carried out at 11 kV are presented in Table SIII.

Spot	at.% Al	at.% Zr	at.% O	at.% F
1	53.1	10.9	34.6	1.4
2	58.6	10.4	29.7	1.3
3	33.0	17.8	47.8	1.5
4	—	27.1	72.9	—
5	30.7	0.7	65.8	2.8
6	30.3	5.0	62.1	2.6

Summarizing, during the course of immersion in NaCl, the Al/Zr and O/Zr ratios at the coating matrix increased and that of F/Zr decreased indicating densification with Al- and Zr-oxides and depletion with fluoride or oxyfluoride. At the hat above (Mn, Fe) IMPs, Al was not detected and F was detected only prior to immersion. A change of O/Zr ratio reflects a progressive transformation from $\text{ZrO}_{1.68}\text{F}_{0.31}$ to $\text{ZrO}_2 \cdot 0.7 \text{H}_2\text{O}$ and finally $\text{ZrO}_2 \cdot 1.2 \text{H}_2\text{O}$.

SEM/EDS characterization at the coating cross-section.—SEM images of cross section and related EDS mapping of as-prepared ZrCC and ZrCC after 5 days immersion in 0.5 M NaCl were taken in the region near (Mn, Fe) IMPs of the AA3005 sample (Fig. 9). In this area the coating was thicker and its structure is fully developed. The thickness of the coating before and after immersion in NaCl solution was 200 nm. Based on SEM images and EDS mapping it appears that coating had a tri-layer structure. In the as-prepared ZrCC, Zr and O were concentrated in the upper layer of the coating, while F, Mn, Mg were equally distributed across whole coating (Fig. 9a). Distribution of elements in ZrCC changed after 5 days of immersion in 0.5 M NaCl: an upper layer of the coating consisted mainly of Zr, Mg and Mn; the middle layer consisted of O, F and Al, while the bottom layer contained mainly Al, O, F, Mn and Mg (Fig. 9b).

Atomic ratios of elements within ZrCC better describe the structure of coatings (Table VIII). (Please note that the atomic concentrations at spots 1–4 were reconstructed from EDS maps where the analysis spot is larger than the analyzed spot. Therefore, relative error is always similar and allows for relative comparison of concentrations). Atomic ratios O/Zr, Al/Zr, Mg/Zr increased from the upper to the inner part of the ZrCC coating indicating the enrichment of the inner part with Al, O, F and Mn. Ratios F/Zr and Mn/Zr were lower, or F and Mn were not detected at all, in the middle layer of ZrCC. In the bottom layer of the ZrCC, atomic ratios F/Zr and Mn/Zr were higher in comparison with the top layer of coating.

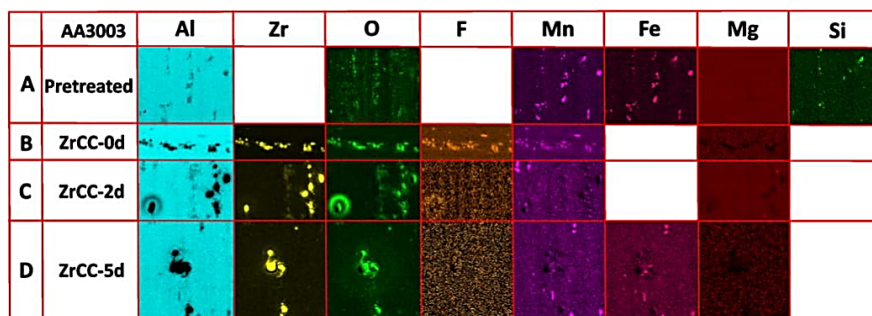


Figure 8. EDS mapping of AA3005 at the area marked in Fig. 7: (a) pre-treated with Metaclean; (b) zirconium conversion coating as-prepared (ZrCC-0d); (c) zirconium conversion coating after 2 days of immersion in 0.5 M NaCl (ZrCC-2d) and (d) zirconium conversion coating after 5 days of immersion in 0.5 M NaCl (ZrCC-5d).

Table VI. EDS analysis of zirconium conversion coatings on AA3005 immersed in 0.5 M NaCl solution for 5 days (Fig. 7d); electron beam voltage of analysed spots 1–6 was 3 kV corresponding to the depth on the analysed region of approximately 100 nm. The results of the analysis carried out at 11 kV are presented in Table SIV.

Spot	at.% Al	at.% Zr	at.% O	at.% F
1	53.9	11.0	33.7	1.4
2	54.5	10.6	33.4	1.5
3	9.4	23.5	67.2	—
4	—	24.0	76.0	—
5	57.7	10.2	31.0	1.1
6	35.2	18.7	45.0	1.1

The same trend was found after 5 days of immersion in 0.5 M NaCl (Table VIII). A substantial increase in O/Zr ratio up to 17.75 was noticed at the coating/substrate interface, and increased Mn/Zr and Fe/Zr ratios are the most significant changes. These indicate that Mn, Fe and O were incorporated in the bottom layer. The ratio of F/Zr was larger as well compared to the coating top. These findings are in agreement with SEM/EDX analysis of coating (Figs. 5–8) and confirm the densification and self-sealing of ZrCC during immersion in a 0.5 M NaCl solution.

SEM images and EDS mapping of the cross-sections of as prepared ZrCC and a Zr-oxide hat above an (Mn, Fe) intermetallic particle are presented in Fig. 10. As shown by EDS mapping, the hat was composed mainly of Zr, O, F and Al with atomic ratios for O/Zr, F/Zr Al/Zr of 1.31, 0.23 and 0.34, respectively (Figs. 10c, 10e and Table IX, spot 1). IMPs had an Mn/Fe atomic ratio of 0.65 (Fig. 10b, spot 2, S5). Fig. 10d presents the cross-section taken in the proximity of an IMP (detailed in Fig. 10b and imaged at higher magnification in Fig. 9a). The coating was uniform in the proximity of (Mn, Fe) IMPs. It had a tri-layer structure with a thickness of 200 nm.

Table VII. Atomic ratios in the matrix area of zirconium conversion coatings and at the hat for as-prepared ZrCC and ZrCC immersed in 0.5 M NaCl solution for 2 and 5 days. Atomic ratios were calculated from spots 2 and spots 4 (Figs. 7b–7d and Tables IV–VI) for matrix area and hat respectively.

Sample	Al/Zr	O/Zr	F/Zr
ZrCC-0d, spot 2	4.86	2.39	0.61
ZrCC-2d, spot 2	5.63	2.86	0.125
ZrCC-5d, spot 2	5.14	3.15	0.142
ZrCC- hat-0d, spot 4	—	1.68	0.31
ZrCC- hat-2d, spot 4	—	2.69	—
ZrCC- hat-5d, spot 4	—	3.16	—

SEM images and EDS mapping of the cross-sections of ZrCC and Zr-oxide hat above (Mn, Fe) IMP after 5 days of immersion in 0.5 M NaCl are presented in Fig. 11. As shown by EDS mapping, the hat was composed mainly of Zr, O and Al with atomic ratios for O/Zr, Al/Zr of 1.41 and 0.25, respectively (Figs. 11c, 11e and Table X, spot 1). The main change in the composition of Zr-oxide hat was the complete disappearance of F. IMPs had an Mn/Fe atomic ratio of 0.75 (Fig. 11c, spot 2) and 1.42 (Fig. 11c, spot 3). In the area between two IMPs there was a dense layer of Al, O and Zr with atomic ratios Al/Zr, O/Zr of 5.33 and 5.63, respectively (Fig. 11c, spot 4). It seems that the corrosion process was initiated around (Mn, Fe) IMPs but the channels around them then filled with a dense layer of aluminum oxide and passivated after 5 days of immersion in a 0.5 M NaCl solution. A small amount of Mn, Fe, F and Zr was present in aluminum oxide as well. These elements may be therefore incorporated in the growing layer of aluminum oxide formed around and above (Mn, Fe) IMPs (Fig. 11e). Figure 11d presents the cross-section taken in the proximity of IMP (detailed in Fig. 11b and imaged at higher magnification in Fig. 9b). The coating was uniform and undamaged in the proximity of (Mn, Fe) IMPs even after 5 days of immersion in 0.5 M NaCl. It had a tri-layer structure with a thickness of 200 nm.

TEM characterization of the coating cross section.—Transmission electron images of cross-sectioned ZrCC taken at the coating matrix are presented in Fig. 12. As-prepared ZrCC exhibited a tri-layer structure with a total thickness of 29 nm. The top layer had a thickness of 21.5 nm, middle layer 5 nm and the inner layer 2.5 nm. The coating was homogenous and without cracks. It is noteworthy that there is a difference in thickness obtained using SEM (Figs. 9–11) and TEM (Fig. 12) analyses, the latter being much smaller. This difference can be ascribed to the uneven thickness of the coating over the AA3005 surface, i.e., the coating is much thicker at and around the IMPs (Figs. 7, 9, 10, 11) than at the matrix (Fig. 12). The ratio between thickness near (Mn, Fe) IMPs and coating matrix far from IMPs ($d_{\text{ZrCC-IMP}}/d_{\text{ZrCC}}$) was 6.9 as determined based on SEM and TEM analyses, respectively.

Based on the thickness of individual layers within the coating determined by TEM analysis (Fig. 12), the contribution of individual layers before and after immersion in NaCl was calculated (Table XI). Based on such normalized layer thickness it can be stated that the contribution of the top layer decreased from 74.2% to 49.2%; the middle layer increased from 17.2 to 21.0%, and that of bottom layer increased from 8.6% to 29.8%. These findings are in good correlation with SEM/EDS data that confirmed an increased concentration of O, Mn and Fe in bottom layers of ZrCC after 5 days of immersion in NaCl (Fig. 9). ZrCC was still homogenous; no cracks or pores were observed and the coating seemed denser and more compact in comparison with as-prepared ZrCC (Figs. 12b, 12d).

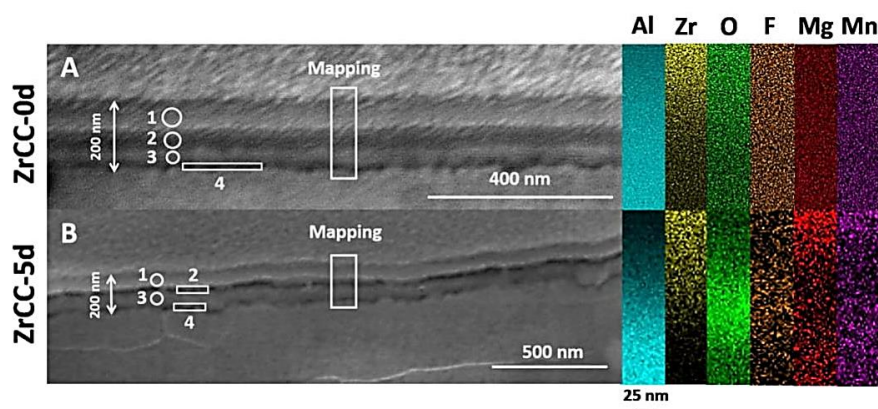


Figure 9. SEM images and EDS mapping of a cross-section of zirconium conversion coatings on AA3005: (a) zirconium conversion coating as-prepared; (b) zirconium conversion coating after 5 days of immersion in 0.5 M NaCl. The area where the mapping was recorded is denoted by vertical rectangles, circles and horizontal rectangles denote the spots where EDS analysis was carried out (Table VIII).

Table VIII. EDS analysis given in atomic ratios of elements at the cross-section of as-prepared zirconium conversion coating on AA3005 (Fig. 9a) and after 5 days immersion in 0.5 M NaCl (Fig. 9b).

Spot	Al/Zr	O/Zr	F/Zr	Mn/Zr	Mg/Zr	Fe/Zr
as-prepared						
1	7.37	1.53	0.233	0.023	0.035	—
2	15.60	1.49	0.189	—	0.076	—
3	34.92	2.15	—	—	0.192	—
4	39.17	2.43	0.435	0.087	0.217	—
Mapping average	14.30	1.87	0.226	0.038	0.076	—
After 5 days immersion						
1	6.91	1.88	0.174	0.070	0.070	0.023
2	6.74	1.84	0.202	—	0.061	—
3	15.16	3.04	0.255	0.020	0.020	0.020
4	226.5	17.75	0.5	1.25	1	1
Mapping average	18.12	3	0.220	0.123	0.098	0.073

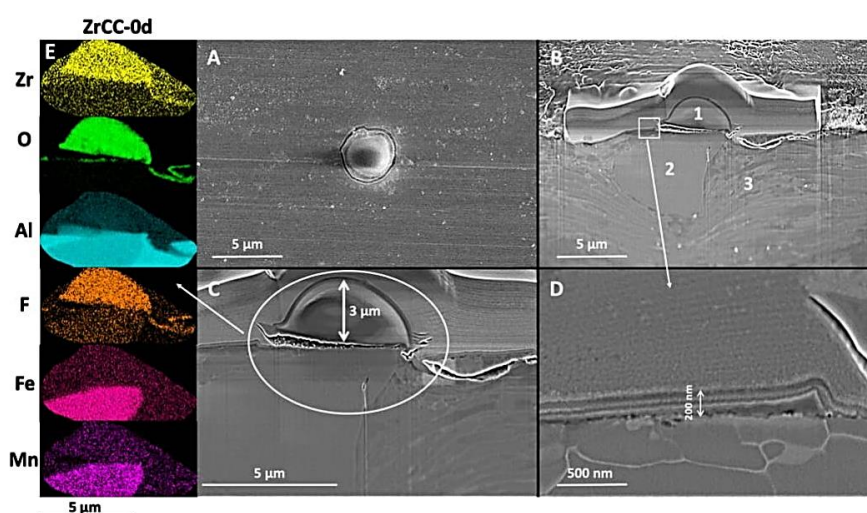


Figure 10. SEM images with EDS mapping of cross section of as prepared ZrCC. (a) top view, (b,c) side view, (d) the cross-section of coating in the proximity of (Mn, Fe) IMPs, as indicated by an arrow in (b), and (e) EDS mapping of the cross-section. The results of EDS analysis are given in Table IX and S5.

Table IX. EDS analysis of the cross-section of as prepared ZrCC at MnFe intermetallic particle (Fig. 10c). The results of the analysis carried out at 11 kV are presented in Table SV.

Spot	at.% Al	at.% Zr	at.% O	at.% F	at.% Mn	at.% Fe	at.% Mg
1	11.7	34.7	45.6	8.1	—	—	—
2	95.6	—	4.5	—	—	—	—
3	95.8	—	3.4	—	—	—	0.8

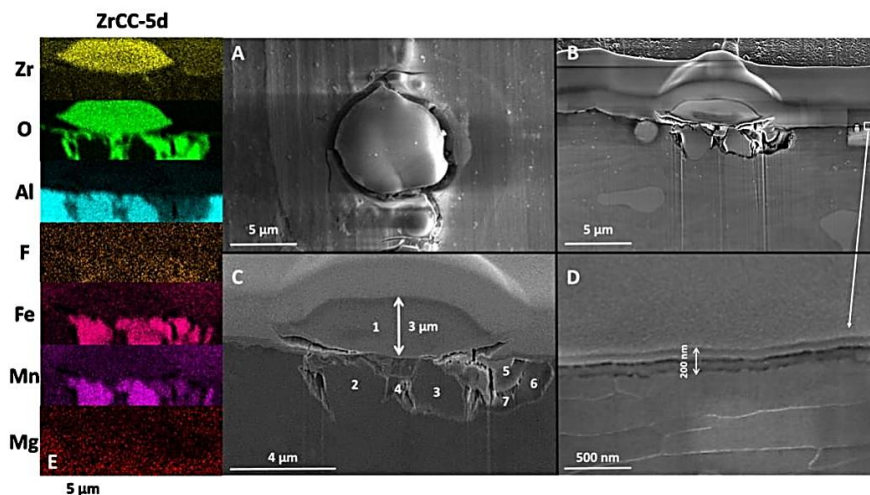


Figure 11. SEM images with EDS mapping of the cross-section of ZrCC after 5 days of immersion in a 0.5 M NaCl solution. (a) top view, (b,c) side view, (d) the cross-section of coating in the proximity of (Mn, Fe) IMPs, as indicated by an arrow in (b), and (e) EDS mapping of the cross-section. Results of EDS analysis are given in Table X, SVI.

XPS characterization of the coating surface.—XPS analysis was carried out on as-received and chemically pre-treated AA3005, as prepared ZrCC and ZrCC immersed in 0.5 M NaCl solution for 2 and 5 days. XPS technique has a probing depth up to 10 nm thus giving information from the upper-most layer of the ZrCC. The composition of samples deduced from XPS survey spectra are presented in Table XII. The surface of an as-received sample contained Al, O, Mg, and N, while chemically pre-treated sample contained Al, O, Mg, P, Si and Na. Na and P originate from Metaclean alkaline cleaner that contains NaSiO₃ and probably some P based corrosion inhibitor/surfactant. Chemical cleaning does not cause an enrichment in Mn (detected concentration < 0.2 at.%).

Aluminum and oxygen are related to the formation of aluminum oxide/hydroxide. After the conversion coating process with hexafluorozirconic acid, aluminum almost diminished due to coverage with ZrCC, as evidenced by the appearance of Zr and F originating from the conversion coating. After 2 days of immersion in NaCl, however, F completely disappeared from the top layer of ZrCC and, at the same time, Al appeared in the top layer. The concentration of Al increased with immersion time, while that of Zr decreased. Si

appeared after 2 days of immersion in a 0.5 M NaCl solution and originates from AA3005.

High resolution XPS spectra recorded for major elements detected in survey XPS spectra are presented in Fig. 13. High resolution Al 2p spectra are presented in Fig. 13a. The Al 2p peak is usually presented as a single peak rather than two split component peaks 2p_{3/2} and 2p_{1/2}. Two 2p peaks are noted in the Al 2p spectrum for as-received and chemically pre-treated Al centered at binding energy (*E_b*) 72.4 and 74.8 and corresponding to Al metal and Al(OH)₃, respectively.^{88,89} Considering the intensity ratio between the two peaks, it can be stated that the surface is covered by a thin, few nanometers thick, the layer of Al(OH)₃ which allows the detection of Al metal. After the conversion coating process, however, peaks for Al diminished due to coverage of AA3005 with ZrCC. After 2 and 5 days of immersion, a small peak at 74.5 eV re-appeared suggesting the formation of Al(OH)₃ in the top layer of coating.

High resolution O 1s spectra are presented in Fig. 13b. For as-received and chemically pre-treated samples, the peak was centered at 531.9 eV suggesting the prevalence of hydroxide over oxide.

Table X. EDS analysis of the cross-section of ZrCC at MnFe intermetallic particle after 5 days of immersion in 0.5 M NaCl solution (Fig. 11c). The results of the analysis carried out at 11 kV are presented in Table SVI.

Spot	at.% Al	at.% Zr	at.% O	at.% F	at.% Mn	at.% Fe	At.% Cu
1	9.4	37.3	52.5	0.8	—	—	—
2	74.6	—	4.1	—	9.1	12.2	—
3	76.4	—	3.4	—	12.2	8.6	—
4	44.2	8.3	46.7	0.8	—	—	—
5	27.1	0.9	53.8	0.4	—	17.8	—
6	50.9	—	40.1	0.9	1.4	3.1	3.5
7	41.8	0.5	48.9	4.0	—	4.7	—

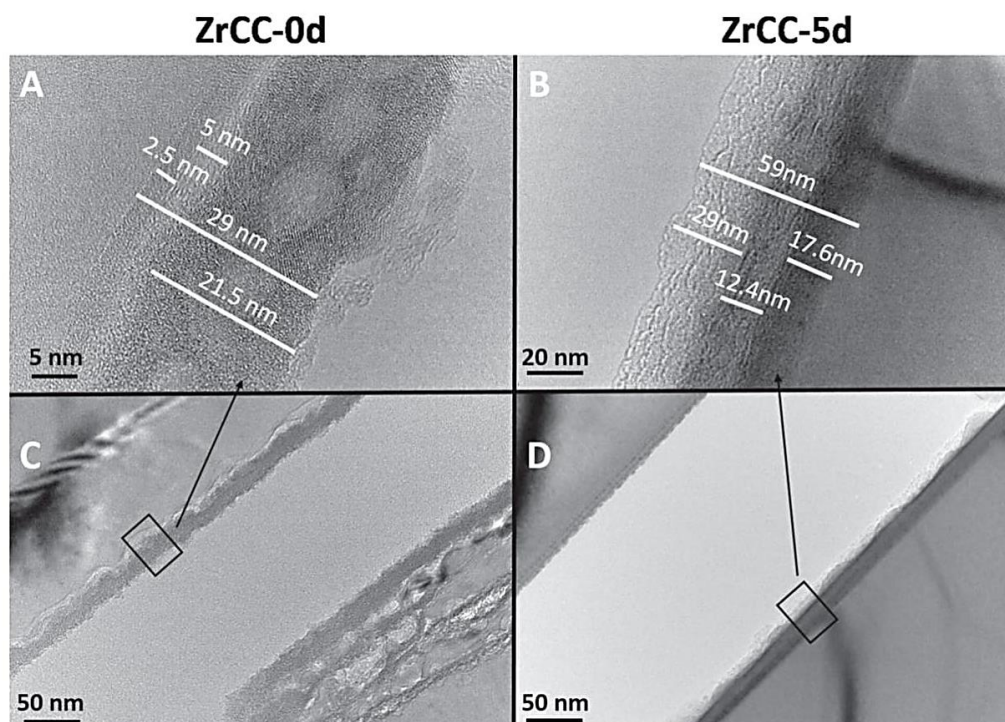


Figure 12. Transmission electron microscopy images of (a, c) as-prepared zirconium conversion coating and (b, d) after 5 days immersion in 0.5 M NaCl solution.

Table XI. Percentage of individual layer thickness to total coating thickness for as prepared zirconium conversion coating and zirconium conversion coating immersed in 0.5 M NaCl solution for 5 days (calculated from layer thickness in Fig. 12).

	ZrCC-0d	ZrCC-5d
Top layer, %	74.2	49.2
Middle layer, %	17.2	21.0
Bottom layer, %	8.6	29.8

Considering the presence of hydrated Zr oxide (see below), this peak could be deconvoluted into peaks for bound H_2O , $\text{Al}(\text{OH})_3$ and $\text{ZrO}_2 \cdot 2\text{H}_2\text{O}$ at binding energies at 533 eV, 532 (531.9) eV and 531.5 eV, respectively.^{89,90} After the conversion process, the O 1s peak shifted to 531.2 eV and is now related to predominantly hydrated Zr oxide and/or oxyfluoride ($\text{ZrO}_2 \cdot 2\text{H}_2\text{O}$ / ZrF_xO_y). After 2 and 5 days of immersion ZrCC in a 0.5 M NaCl solution, the center of the O 1s peak was shifted back to slightly higher E_b of 531.6 eV corresponding to the presence of $\text{ZrO}_2 \cdot 2\text{H}_2\text{O}$ and $\text{Al}(\text{OH})_3$.

The F 1s peak was located at E_b of 684.8 eV and was noted only for the as-prepared ZrCC indicating the presence of $\text{ZrF}_4/\text{ZrF}_x\text{O}_y$ in the top layer of as-prepared coating (Fig. 13d). After 2 and 5 days of immersion, the F 1s peak disappeared, indicating dissolution of fluorine and transformation of $\text{ZrF}_4/\text{ZrF}_x\text{O}_y$ into $\text{ZrO}_2 \cdot 2\text{H}_2\text{O}$.

High resolution spectra Zr 3d spectra recorded after the conversion coating process are presented in Fig. 13c. The Zr 3d_{5/2} and 3d_{3/2} peaks for the as-prepared coating are centered at 185.5 eV and 183.2 eV, respectively. Considering a relatively high fluorine and oxygen contents (Fig. S7), this spectrum reflects the presence of a mixture of $\text{ZrF}_4/\text{ZrF}_x\text{O}_y$ and $\text{ZrO}_2 \cdot 2\text{H}_2\text{O}$.⁹¹ After 2 and 5 days of immersion in 0.5 M NaCl solution, however, the peaks shifted to lower E_b of 184.9 eV and 182.5 eV, respectively, indicating the progressive transformation of Zr-fluoride/oxyfluoride to $\text{ZrO}_2 \cdot 2\text{H}_2\text{O}$. These findings are in correlation with the disappearance of the fluorine peak in the F 1s spectrum.

ToF-SIMS characterization of coating microstructure.—In order to analyse the coating structure and composition, ToF-SIMS negative ion profiles were recorded for as prepared ZrCC and for ZrCC immersed in 0.5 M NaCl solutions (Fig. 14). The sputtering

Table XII. Concentration of elements obtained by XPS analysis of as-received, chemically pre-treated and zirconium conversion coated AA3005 samples.

Sample	at.% Al	at.% Zr	at.% O	at.% F	at.% Mg	at.% Si	at.% P	at.% Na	at.% N	at.% Cl
as received	19.6	—	69.1	—	9.9	—	—	—	1.4	—
pre-treated	18.9	—	66.6	—	5.9	0.5	3.7	4.3	—	—
ZrCC-0d	1.0	23.4	67.2	8.4	—	—	—	—	—	—
ZrCC-2d	4.9	17.4	74.7	—	—	3.0	—	—	—	—
ZrCC-5d	8.1	14.6	69.2	—	—	—	—	—	—	8.1

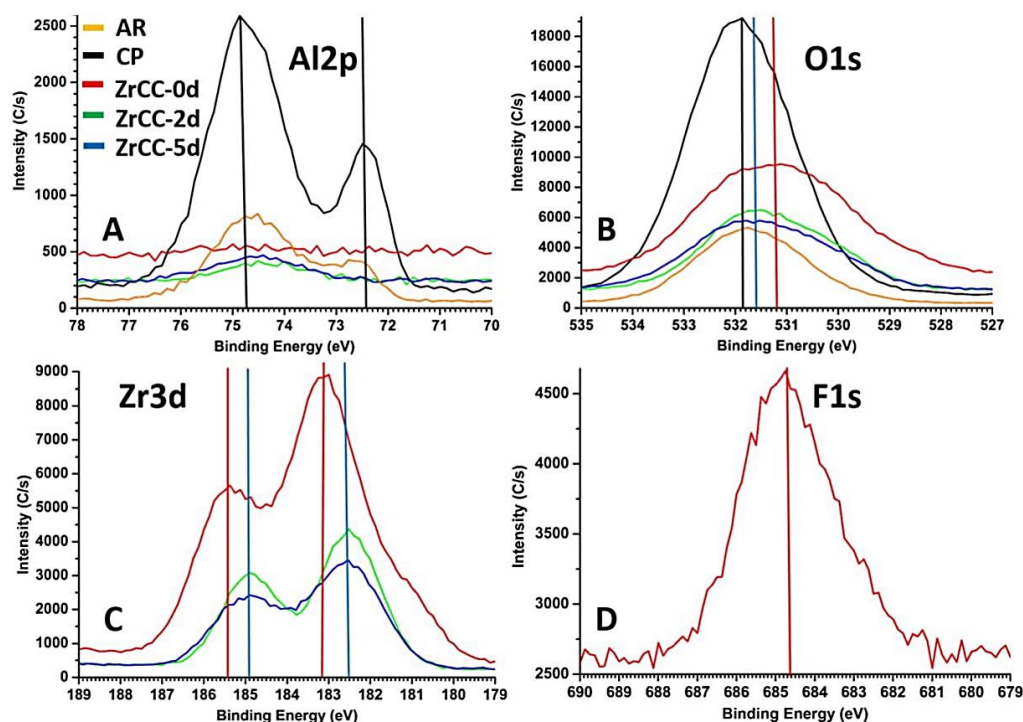


Figure 13. High resolution XPS spectra (a) Al 2p, (b) O 1 s, (c) Zr 3d in (d) F 1 s for as-received (AR) and chemically pre-treated (CP) AA3005 and zirconium conversion coatings on AA3005 as-prepared ZrCC and immersed in 0.5 M NaCl solution for 2 and 5 days. Spectra were not normalized on the intensity scale.

rate was 0.30 nm s^{-1} ($\pm 0.02 \text{ nm s}^{-1}$). As-prepared ZrCC was approximately 30 to 40 nm thick. It consisted of an outer layer that had the highest concentration of ZrO^- and a lower concentration of AlOF^- (Fig. 14, region 1); therefore, its structure can be correlated with $\text{ZrO}_2 \cdot 2\text{H}_2\text{O}/\text{ZrO}_x\text{F}_y$ species. A significant amount of CuO^- ions was detected in the outer layer. The highest amount of AlOF^- ions was detected in the middle layer, accompanied with peaks for AlO^- , MgO^- and Al_2O_4^- ions (Fig. 14, region 2). ZrO^- ions were present in the middle layer but in a smaller amount than in the outer layer. The same ions were found in the middle layer and at the interface (Fig. 13, region 3) so it was hard to distinguish the border between these two regions.

After 5 days of immersion in 0.5 M NaCl, the profile of ZrO^- ions remained approximately the same with a maximum in the outer layer (Fig. 14, region 1). The most important change was a decrease in intensity (concentration) of F^- and AlOF^- ions. At the same time, the concentration of Cl^- ions increased significantly following the same profile shape as that of F^- and AlOF^- ions. This indicates that Cl^- ions were exchanged with F^- ions and incorporated within the ZrCC structure. The concentration of AlO^- was larger throughout the ZrCC showing two maxima in the outer and, especially, the middle part, respectively. This increased concentration extended over the interface with the substrate for approximately 10–15 nm. This finding indicates the segregation of Al_2O_3 in middle layer/interface of ZrCC which may be responsible for the increased corrosion resistance of ZrCC coating, as proved experimentally (Figs. 3 and 4).

In the course of immersion in NaCl, the intensity profile related to CuO^- ions decreased due to dissolution or ZrCC heterogeneities; that of MgO^- ions increased and was shifted deeper to the substrate as well. The amount of Al_2O_4^- ions in the middle layer/interface increased 2-fold. We correlate these ions with a spinel structure in middle/interface layers but this is only our speculations because it

can be also correlated with aluminium oxide as well and other oxides.

Mechanism of active corrosion protection/self-sealing.— Electrochemical results obtained for zirconium conversion coatings on AA3005 suggest that these coatings enable self-sealing and active corrosion protection when immersed in a 0.5 M NaCl solution. These following results substantiate this statement: (i) rapid decay and recovery of OCP during the first 2 h immersion, (ii) a 50-fold increase in impedance modulus at 3 mHz and the ability to sustain it at values in the megaohm- cm^2 range ($7.5 \cdot 10^6$ to $9.5 \cdot 10^6 \Omega\text{-cm}^2$) and to resist pitting up to at least 21 days, and (iii) increased passive window (from 0.22 to 0.45 V) and decreased corrosion current density of two orders of magnitude (from $2.32 \cdot 10^{-7} \text{ A}\cdot\text{cm}^{-2}$ down to $3 \cdot 10^{-9} \text{ A}\cdot\text{cm}^{-2}$) after 10 days of immersion.

The electrochemical study was complemented with microstructural and compositional studies. The microstructural investigation by XPS showed the disappearance of fluorine in the top layer of ZrCC after 2 days in 0.5 M NaCl and the transformation of $\text{ZrF}_4/\text{ZrF}_x\text{O}_y$ into $\text{Zr}(\text{OH})_2 \cdot 1.2\text{H}_2\text{O}$ and $\text{Al}(\text{OH})_3$. SEM/EDS investigation confirmed that the concentration of F decreased and that of Al and O increased during immersion. FIB/EDS investigation showed that coating was 200 nm thick in the proximity of IMPs, homogenous with tri-layer structure, while (Mn, Fe) IMPs were covered with a dense hat of zirconium oxide. During immersion in NaCl, channels around (Mn, Fe) IMPs became progressively filled with a dense layer of aluminum oxide containing a small content of Zr and F. This process results in the passivation of the IMPs. At the same time, (Mn, Fe) IMPs were dissolving, leading to the incorporation of Mn and Fe in ZrCC. We believe that their incorporation has a role in the stabilization of aluminum oxide around IMPs and contributes to the passivation. Especially important seems to be Mn which was integrated in the bottom layer of ZrCC accompanied with the

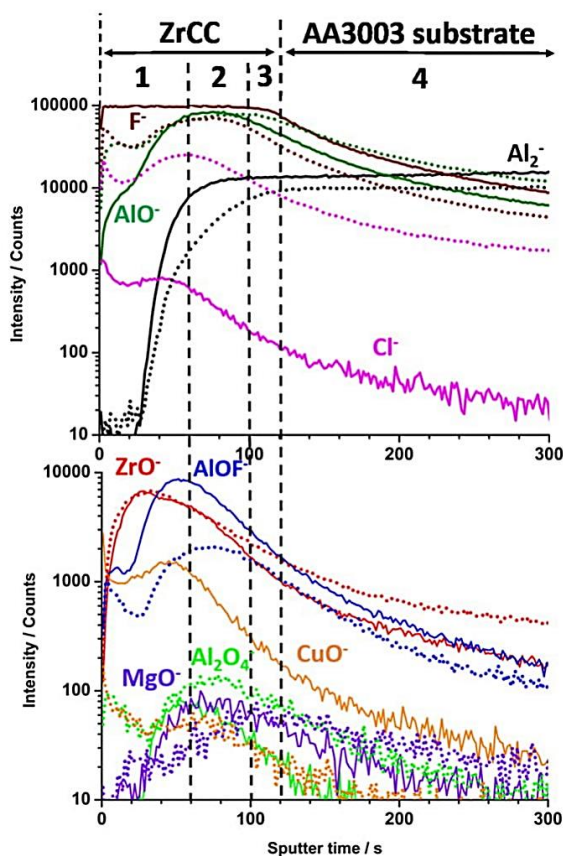


Figure 14. ToF-SIMS negative ions depth profiles of zirconium conversion coating applied on AA3005. (full lines)—as prepared ZrCC; (dotted lines)—ZrCC after 5 days of immersion in 0.5 M NaCl solution. 1-outer layer, 2-middle layer, 3-inner layer/or interface, 4-substrate.

highest increase in O. TEM investigation showed that the tri-layer structure consisting of top, middle and bottom layer changed from 74.2%, 17.2%, 8.6% of layer in the as-prepared ZrCC to 49.2%, 21.0% and 29.8% after 5 days immersion in 0.5 M NaCl solution.

Based on these facts we propose the following mechanism of self-sealing/active corrosion protection in ZrCC applied on AA3005 (Fig. 15).

First, H_2O diffuses inside ZrCC through cracks and pores down to IMPs and Mn dispersoids where hydrogen evolution and oxygen reduction reactions take place. This leads to an increased concentration of OH^- and release of hydrogen gas (Eqs. 6 and 7). Released $\text{H}_{2(\text{g})}$, especially around (Mn, Fe) IMPs, causes a bloating around IMPs after 2 days of immersion in NaCl (Fig. 7c). At the same time, OH^- ions cause a dissolution of aluminum oxide and its precipitation in the form of dense $\text{Al}(\text{OH})_3$ around (Mn, Fe) IMPs thus closing cracks and channels (Eq. 8). Excess in OH^- ions together with $\text{H}_{2(\text{g})}$ is transported towards outside part of ZrCC expelling F^- ions from the coating interior and thus transforming $\text{ZrF}_4/\text{ZrO}_x\text{F}_y$ to $\text{ZrO}_2 \cdot 2\text{H}_2\text{O}_{(\text{s})}$ (Eq. 9). Excess of F^- ions is transported to a solution where it is balanced with Na^+ ions. It can be also postulated based on obtained results that, along with the H_2 evolution reaction, manganese is dissolved from IMPs and dispersoids (Eq. 11). Dissolved Mn^{2+} incorporates in the bottom layer of ZrCC forming spinel $\text{MnAl}_2\text{O}_{4(\text{s})}$ (Eq. 12). It is known that spinels have great chemical and thermal stability.^{92,93}

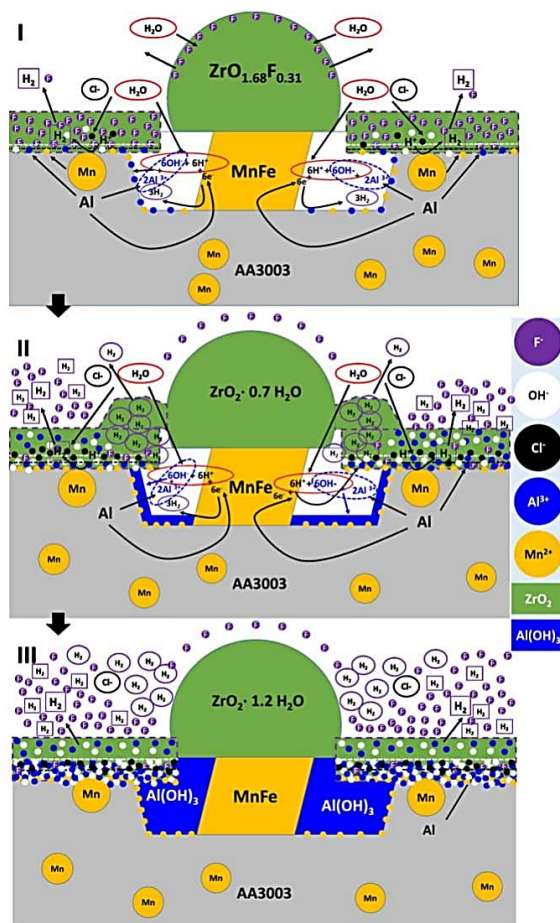
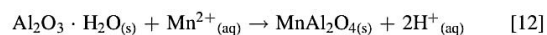
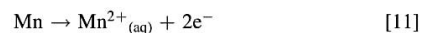
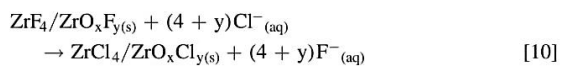
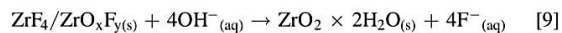
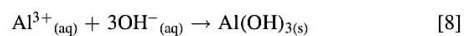
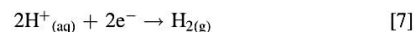
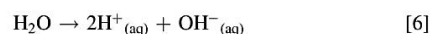


Figure 15. Self-sealing mechanism of zirconium conversion coating applied on AA3005 during its immersion in 0.5 M NaCl solution.



Conclusions

1. The formation of zirconium conversion coating on AA3005 was completed after 10 min of immersion in 200 ppm hexafluoro-zirconic acid bath at pH = 4.8 at room temperature.
2. Zirconium conversion coating applied to AA3005 showed excellent corrosion performance. Bode modulus at 3 mHz increased 50-fold during immersion in 0.5 M NaCl solution

and sustained at $7.5 \cdot 10^6 \Omega \cdot \text{cm}^2$ to $9.5 \cdot 10^6 \Omega \cdot \text{cm}^2$ for at least 21 days with no pitting observed. The shift of the open circuit potential in nobler direction indicates anodic inhibition behavior of these coatings.

3. The as-prepared coating was uniform with thickness that varied from 30 nm at the coating matrix up to 200 nm at/around IMPs. A tri-layer structure was noted, with the upper layer being enriched in Zr and O and bottom layer enriched in Al, F, Mn and Mg.
4. After immersion of 5 days in 0.5 M NaCl solution, the overall thickness of the coating did not change, but the proportion of individual layer changed, as well but the microstructure and composition. The thickness of the top layer decreased and that of the middle, and especially, the bottom layer increased. A transformation from $\text{ZrF}_4/\text{ZrO}_x\text{F}_y$ to $\text{ZrO}_2 \cdot 1.2\text{H}_2\text{O}_{(s)}$ occurred suggesting densification and sealing of ZrCC. Mn segregated in the bottom layer of ZrCC.
5. Upon immersion in NaCl, a hat consisting mainly of ZrO_2 with a small amount of Al formed above and around (Mn, Fe) IMPs. However, at prolonged immersion channels around IMPs became filled with a dense layer of aluminum oxide leading to passivation. At the same time, the concentration of fluorine decreased, while that of O increased, especially in the middle and bottom layer of ZrCC.
6. Based on the above facts it can be stated that ZrCC on AA3005 alloy exhibits a self-sealing/active corrosion protection behavior during immersion in a 0.5 M NaCl solution. Its corrosion performance seems to be equal or better compared to that usually observed for chromium conversion coatings.⁸⁵
7. It seems that Mn from AA3005 together with Zr from ZrCC are able to trigger a self-sealing and active corrosion protection within the coating by incorporation in the bottom part of the conversion coating. This is very promising results and we suggest that future formulas of ZrCC should include Mn.

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Supplementary Information

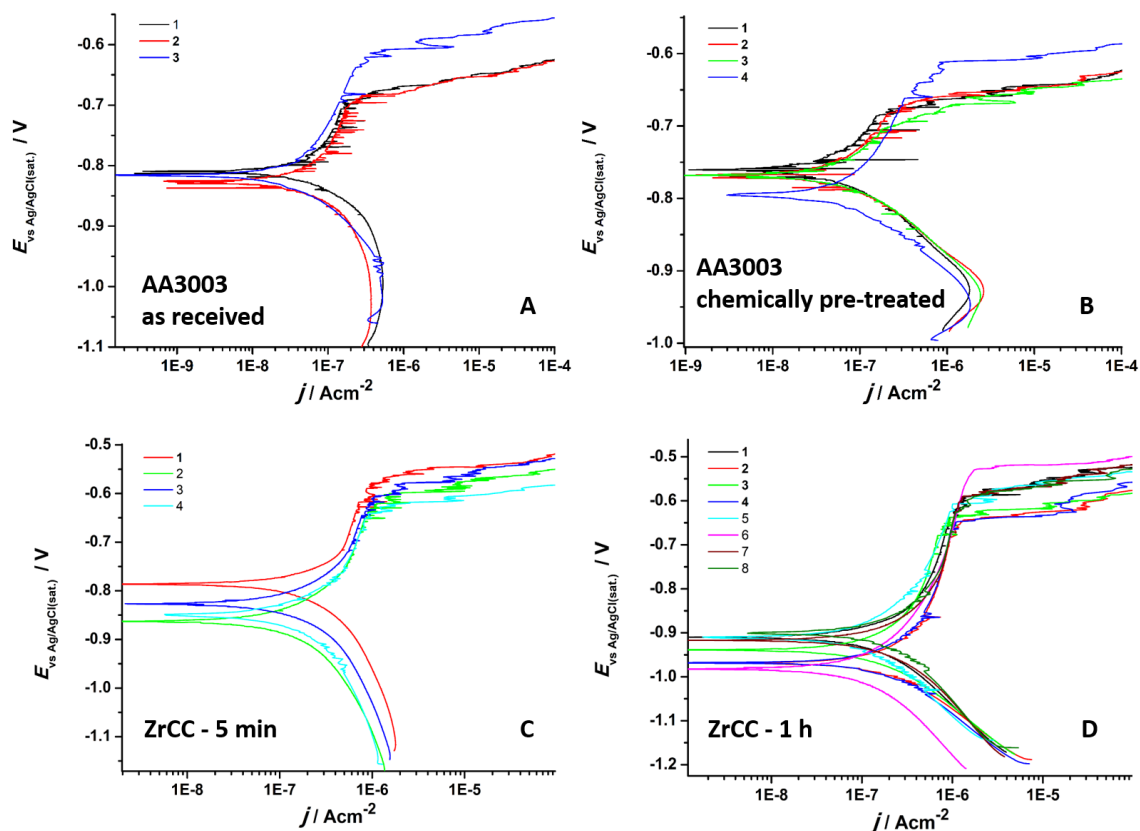


Figure S1: Potentiodynamic polarization curves recorded in 0.5 M NaCl for (a) as-received and (b) chemically pre-treated AA3003 after a 1-h immersion, and for zirconium conversion coated AA3003 after (c) 5 minutes and (d) 1 hour immersion at OCP prior to electrochemical measurement. Numbers of curves are repetitions for each condition.

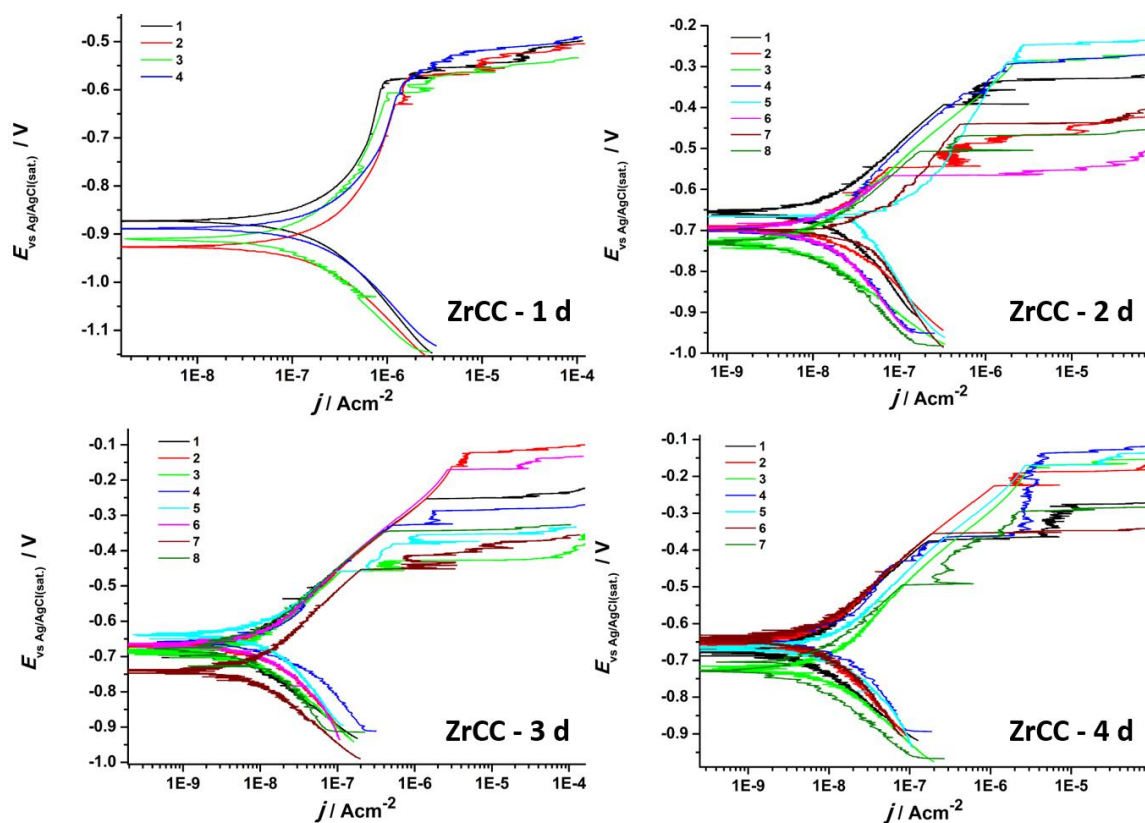


Figure S2: Potentiodynamic polarization curves recorded in 0.5 M NaCl for zirconium conversion coatings on AA3003 after a (a) 1-day, (b) 2-day, (c) 3-day and (d) 4-day immersion at OCP prior to electrochemical measurement. Numbers of curves are repetitions for each condition.

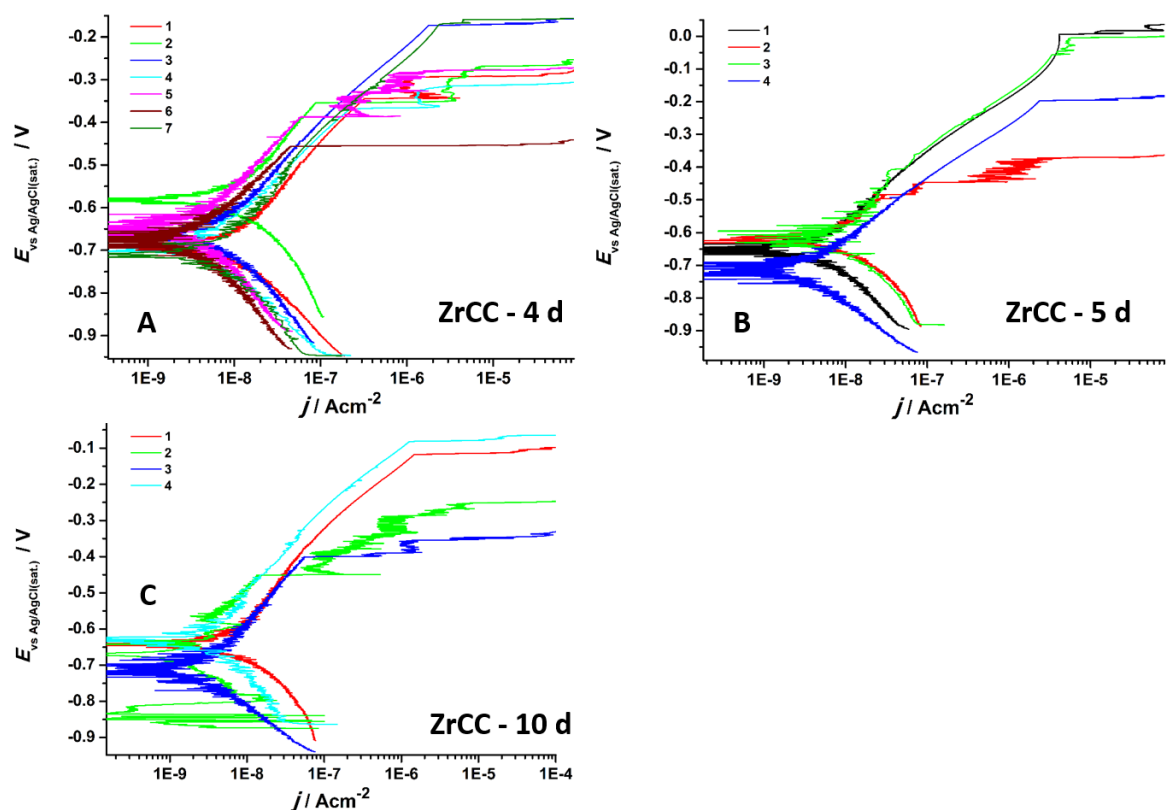


Figure S3: Potentiodynamic polarization curves recorded in 0.5 M NaCl for zirconium conversion coatings on AA3003 after a (a) 4-day, (b) 5-day and (c) 10-day immersion at OCP prior to electrochemical measurement. Numbers of curves are repetitions for each condition.

Table S1: Electrochemical data deduced from potentiodynamic polarization measurements (Figures S1-S3) for as-received, chemically pre-treated and zirconium conversion coated AA3005 immersed in 0.5 M NaCl for different periods of time at OCP prior to electrochemical measurements. In the table, all repetitions on different samples are given together with the average and standard deviation (SD). * $\Delta E = |E_{\text{pit}} - E_{\text{corr}}|$. Representative curves taken for figures in the article are shaded yellow.

Sample	J_{corr} A cm ⁻²	OCP V	E_{corr} V	E_{pit} V	ΔE^* V	β_a mV/d ec	$-\beta_c$ mV/de c	$R_{\text{P, LPR}}$ Ω cm ²	$R_{\text{P, Tafel}}$ Ω cm ²
Bare-1h-1	5.2E-08	-	-	-	0.12	212	86	9.1E+05	5.1E+05
Bare-1h-2	3.5E-08	-	-	-	0.18	200	130	9.7E+05	9.8E+05
Bare-1h-3	2.4E-08	-	-	-	0.11	194	132	6.1E+05	1.4E+06
Bare-1h-4	4.6E-08	-	-	-	0.20	254	130	9.5E+05	8.1E+05
Bare-1h-mean	3.9E-08	-	-	-	0.15	220	116	8.6E+05	9.3E+05
SD	1.1E-08	0.02	0.03	0.03	0.04	23	19	1.5E+05	3.2E+05
Meta-1h-1	5.9E-08	-	-	-	0.09	147	106	6.5E+05	4.5E+05
Meta-1h-2	7.9E-08	-	-	-	0.09	195	96	4.8E+05	3.6E+05
Meta-1h-3	7.0E-08	-	-	-	0.06	124	103	1.4E+05	3.5E+05
Meta-1h-4	9.1E-08	-	-	-	0.13	239	101	5.8E+05	3.4E+05
Meta-1h-mean	7.5E-08	-	-	-	0.10	176	102	4.6E+05	3.8E+05
SD	1.2E-08	0.01	0.01	0.02	0.02	44	4	2.0E+05	4.4E+04
5min-1	2.7E-07	-	-	-	0.20	412	381	1.9E+05	3.2E+05
5min-2	3.0E-07	-	-	-	0.21	461	297	1.6E+05	2.6E+05
5min-3	1.8E-07	-	-	-	0.26	300	265	1.9E+05	3.4E+05
5min-4	2.3E-07	-	-	-	0.22	295	335	1.9E+05	2.9E+05
5min-mean	2.4E-07	-	-	-	0.22	367	320	1.8E+05	3.0E+05
SD	4.5E-08	0.02	0.03	0.02	0.02	72	43	1.3E+04	3.0E+04
1h-1	1.9E-07	-	-	-	0.32	347	184	3.0E+05	2.7E+05
1h-2	2.8E-07	-	-	-	0.32	494	152	2.2E+05	1.8E+05
1h-3	1.7E-07	-	-	-	0.30	366	157	2.9E+05	2.8E+05
1h-4	2.5E-07	-	-	-	0.34	465	161	2.3E+05	2.1E+05
1h-5	2.7E-07	-	-	-	0.27	408	233	2.8E+05	2.4E+05
1h-mean	2.3E-07	-	-	-	0.31	416	177	2.6E+05	2.4E+05
SD	4.4E-08	0.01	0.03	0.02	0.02	56	30	3.3E+04	3.7E+04

2h-1	1.5E-07	—	—	—	0.30	313	205	4.6E+05	3.6E+05
2h-2	1.7E-07	—	—	—	0.30	240	188	3.1E+05	2.7E+05
2h-3	1.8E-07	—	—	—	0.35	304	182	2.9E+05	2.8E+05
2h-4	1.6E-07	—	—	—	0.39	282	201	3.8E+05	3.1E+05
2h-mean	1.6E-07	—	—	—	0.34	285	194	3.6E+05	3.1E+05
SD	1.1E-08	0.02	0.02	0.01	0.04	28	9	6.7E+04	3.5E+04
1d-1	1.3E-08	—	—	—	0.31	183	217	2.5E+06	3.4E+06
1d-2	1.2E-08	—	—	—	0.15	164	176	2.2E+06	3.1E+06
1d-3	7.3E-09	—	—	—	0.44	176	150	2.4E+06	4.8E+06
1d-4	1.4E-08	—	—	—	0.40	229	260	4.6E+06	3.8E+06
1d-5	3.3E-08	—	—	—	0.42	114	282	1.5E+06	1.1E+06
1d-6	4.7E-09	—	—	—	0.13	72	97	1.9E+06	3.9E+06
1d-7	1.5E-08	—	—	—	0.26	87	103	2.4E+06	1.4E+06
1d-8	1.0E-08	—	—	—	0.22	175	221	4.9E+06	4.3E+06
1d-mean	1.4E-08	—	—	—	0.29	150	188	2.8E+06	3.2E+06
SD	8.1E-09	0.02	0.02	0.12	0.11	50	64	1.2E+06	1.2E+06
2d-1	3.9E-09	—	—	—	0.44	147	135	2.3E+06	7.8E+06
2d-2	7.2E-09	—	—	—	0.55	175	159	2.7E+06	5.0E+06
2d-3	5.3E-09	—	—	—	0.23	174	127	2.4E+06	6.0E+06
2d-4	1.6E-08	—	—	—	0.31	237	219	4.4E+06	3.1E+06
2d-5	9.2E-09	—	—	—	0.19	153	233	1.7E+06	4.4E+06
2d-6	9.6E-09	—	—	—	0.28	169	231	2.1E+06	4.4E+06
2d-7	6.1E-09	—	—	—	0.29	170	162	2.5E+06	5.9E+06
2d-8	7.0E-09	—	—	—	0.33	184	241	6.4E+06	6.5E+06
2d-mean	8.0E-09	—	—	—	0.33	176	188	3.0E+06	5.4E+06
SD	3.5E-09	0.03	0.03	0.11	0.11	26	44	1.5E+06	1.4E+06
3d-1	3.9E-09	—	—	—	0.31	182	155	2.7E+06	9.4E+06
3d-2	5.7E-09	—	—	—	0.43	198	188	2.9E+06	7.3E+06
3d-3	8.2E-09	—	—	—	0.55	226	181	1.9E+06	5.3E+06
3d-4	1.2E-08	—	—	—	0.50	314	256	2.0E+07	5.1E+06
3d-5	8.3E-09	—	—	—	0.50	198	177	3.9E+06	4.9E+06

3d-6	5.3E -09	- 0.66	- 0.65	- 0.36	0.30	168	191	2.3E +06	7.3E +06
3d-7	5.0E -09	- 0.72	- 0.73	- 0.30	0.43	179	176	6.7E +06	7.7E +06
3d-mean	6.9E -09	- 0.69	- 0.68	- 0.25	0.43	209	189	5.8E +06	6.7E +06
SD	2.6E -09	0.03	0.03	0.09	0.09	46	29	5.6E +06	1.5E +06
4d-1	7.9E -09	- 0.70	- 0.70	- 0.35	0.35	224	166	2.9E +06	5.3E +06
4d-2	8.2E -09	- 0.61	- 0.58	- 0.36	0.23	197	191	3.0E +06	5.1E +06
4d-3	5.4E -09	- 0.67	- 0.67	- 0.17	0.50	219	167	2.1E +06	7.6E +06
4d-4	4.0E -09	- 0.70	- 0.69	- 0.37	0.32	187	186	9.1E +06	1.0E +07
4d-5	3.1E -09	- 0.65	- 0.65	- 0.39	0.27	186	210	1.5E +06	1.4E +07
4d-6	2.9E -09	- 0.69	- 0.69	- 0.46	0.23	167	213	2.1E +06	1.4E +07
4d-7	7.0E -09	- 0.70	- 0.71	- 0.17	0.54	238	249	7.8E +06	7.6E +06
4d-mean	5.5E -09	- 0.67	- 0.67	- 0.32	0.35	203	197	4.1E +06	9.1E +06
SD	2.1E -09	0.03	0.04	0.10	0.12	23	27	2.8E +06	3.5E +06
5d-1	4.6E -09	- 0.65	- 0.67	- 0.01	0.66	218	240	8.9E +05	1.1E +07
5d-2	5.5E -09	- 0.64	- 0.63	- 0.49	0.15	175	148	3.1E +06	6.4E +06
5d-3	8.0E -09	- 0.64	- 0.63	- 0.00	0.63	310	204	9.8E +06	6.7E +06
5d-4	2.4E -09	- 0.72	- 0.73	- 0.20	0.53	175	142	2.2E +06	1.4E +07
5d-mean	5.1E -09	- 0.66	- 0.67	- 0.17	0.49	220	184	4.0E +06	9.6E +06
SD	2.0E -09	0.03	0.04	0.20	0.20	55	41	3.4E +06	3.2E +06
10d-1	6.1E -09	- 0.66	- 0.65	- 0.12	0.53	227	196	2.5E +06	7.5E +06
10d-2	1.6E -09	- 0.63	- 0.67	- 0.29	0.38	268	107	1.7E +06	2.1E +07
10d-3	2.0E -09	- 0.70	- 0.73	- 0.40	0.33	191	141	3.2E +06	1.8E +07
10d-4	3.0E -09	- 0.62	- 0.63	- 0.08	0.54	252	249	1.4E +07	1.8E +07
10d-mean	3.2E -09	- 0.65	- 0.67	- 0.22	0.45	235	173	5.3E +06	1.6E +07
SD	1.8E -09	0.03	0.04	0.13	0.09	29	54	5.0E +06	5.1E +06

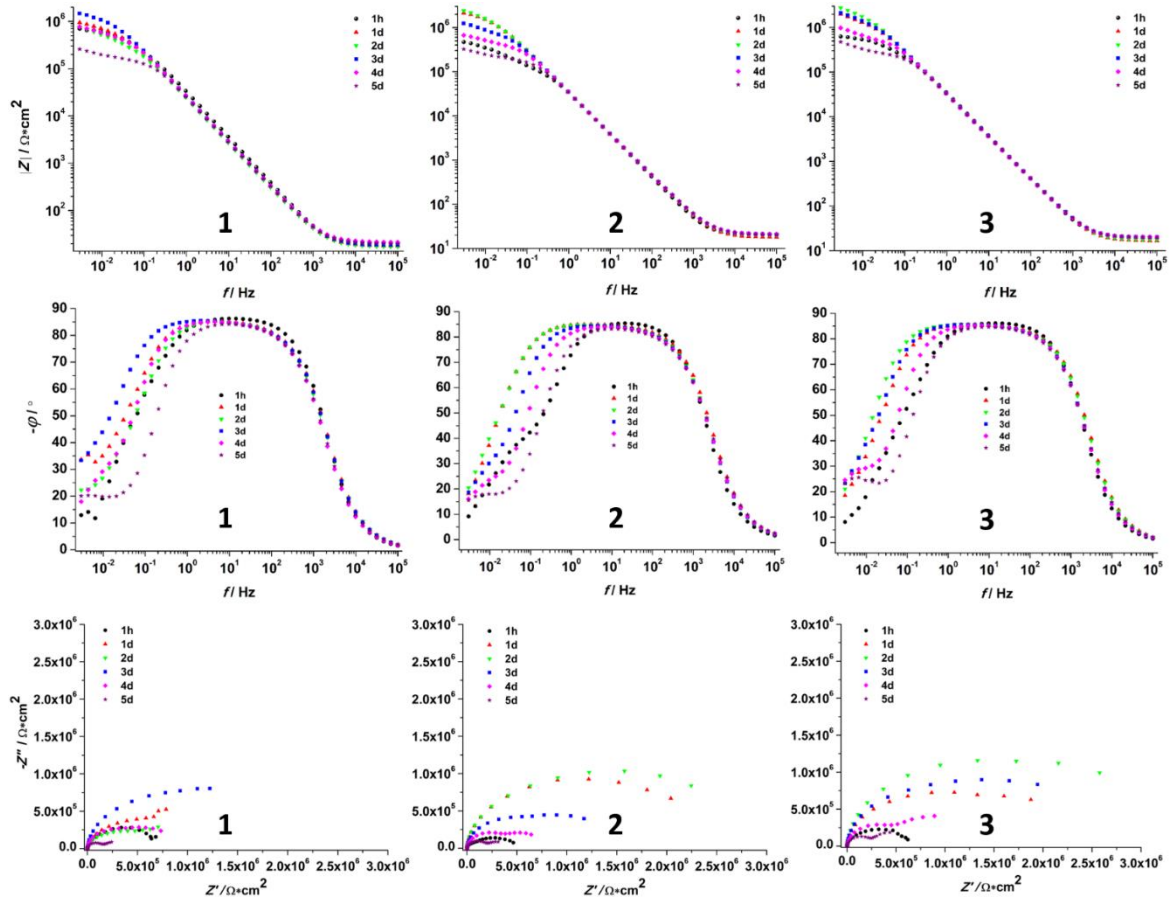


Figure S4: Bode and Nyquist diagrams for as-received (bare) AA3005 immersed in 0.5 M NaCl solution for different periods of time. 1, 2 and 3 are three repetitions of each condition on different samples.

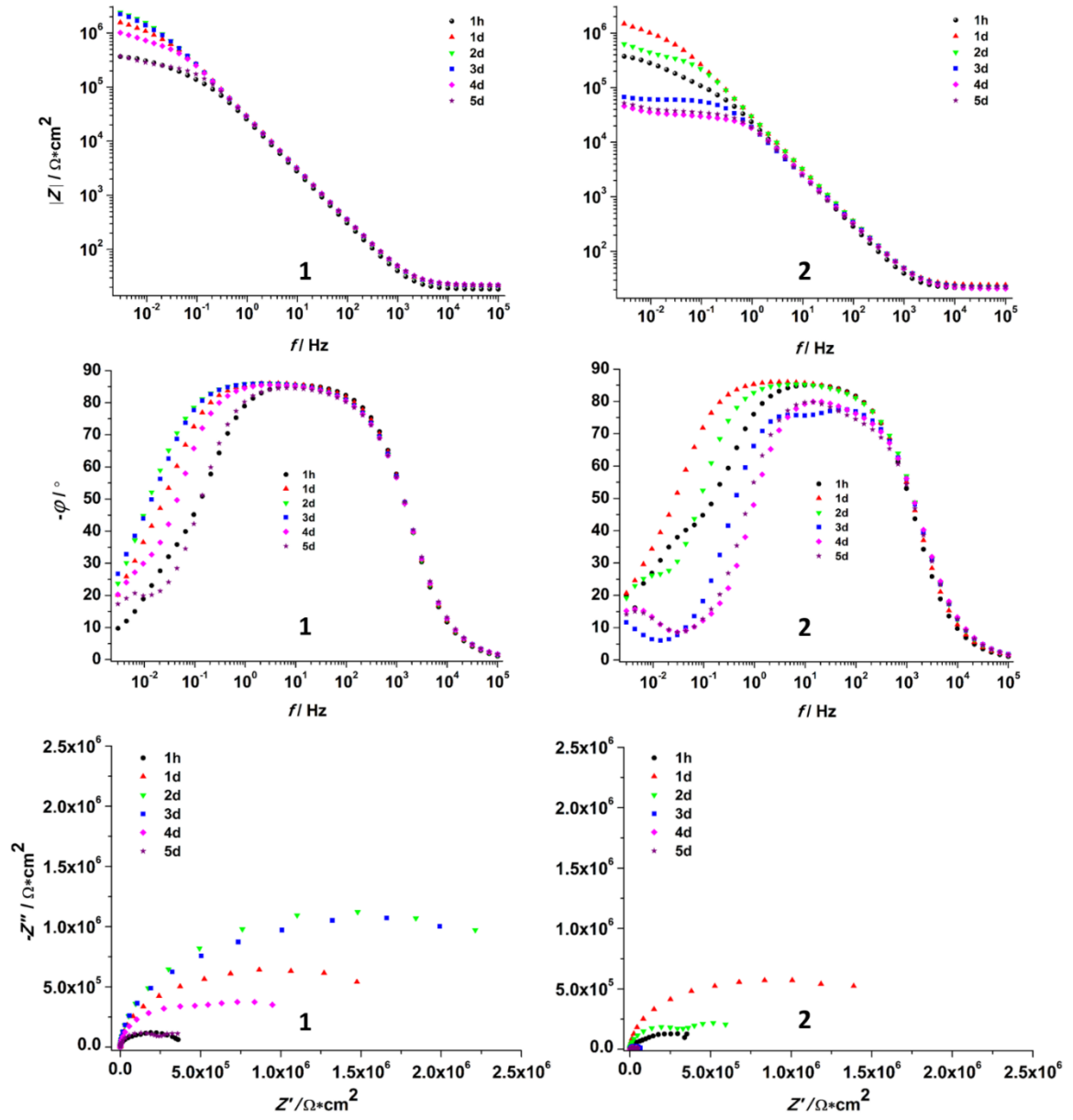


Figure S5: Bode and Nyquist diagrams for chemically pre-treated AA3005 immersed in 0.5 M NaCl solution for different periods of time. 1 and 2 are two repetitions of each condition on different samples.

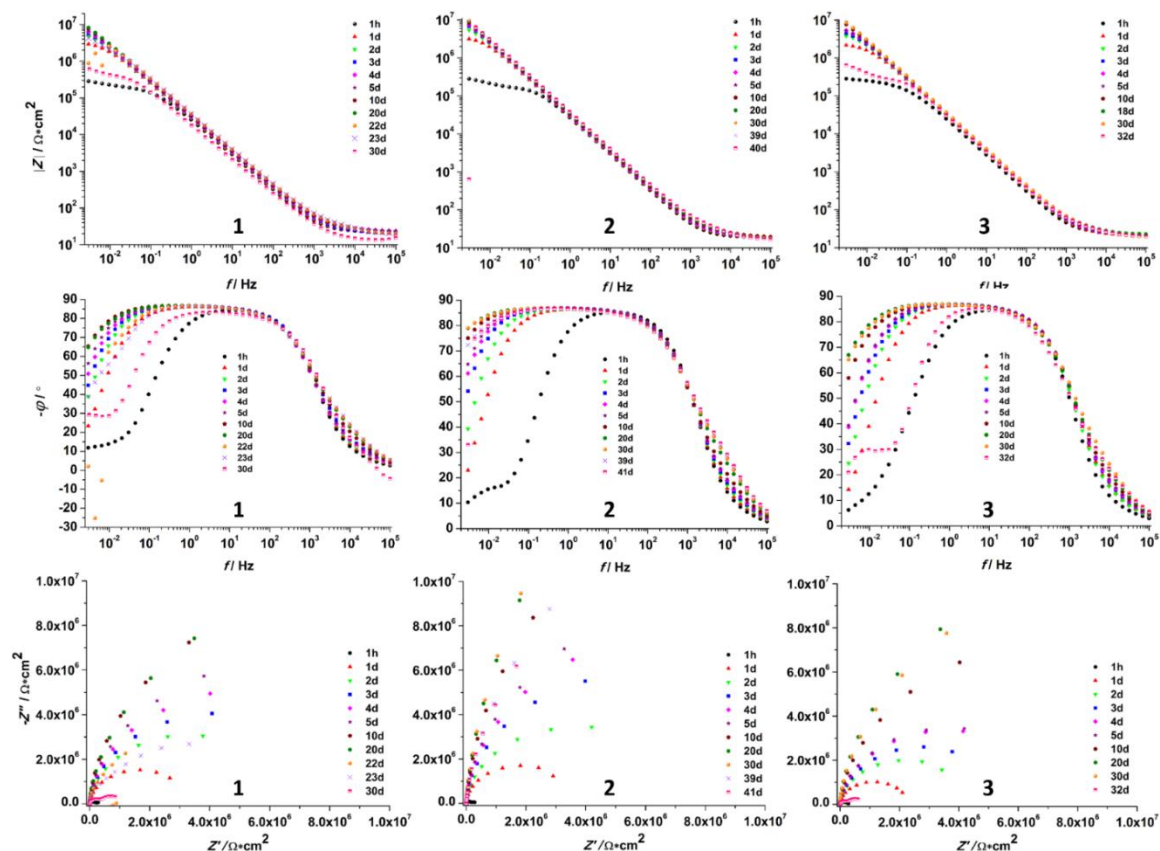


Figure S6: Bode and Nyquist diagrams for zirconium conversion coatings on AA3005 immersed in 0.5 M NaCl solution for different periods of time. 1, 2 and 3 are three repetitions of each condition on different samples.

Table S2: EDS analysis of as-prepared zirconium conversion coatings on AA3005 (Figure 7b); electron beam voltage was 3 kV (denoted 1, 2, 3, 4, 5) or 11 kV (denoted 1*, 2*, 3*, 4*, 5*).

Spot	Al	Zr	O	F	Mn	Mg
1	55.4	12.7	25.5	6.4	–	–
2	54.9	11.3	27.0	6.9	–	–
3	22.3	23.9	45.1	8.7	–	–
4	–	33.5	56.2	10.3	–	–
5	74.9	7.6	13.9	3.6	–	–
1*	91.4	1.5	5.4	1.0	0.3	0.4
2*	91.1	0.6	3.4	0.6	0.4	0.5
3*	27.1	17.4	47.1	8.4	–	–
4*	8.1	22.3	57.1	11.5	–	–
5*	96.6	0.4	2.1	0.2	0.3	0.4

Table S3: EDS analysis of zirconium conversion coatings on AA3005 immersed in 0.5 M NaCl solution for 2 days (Figure 7c); electron beam voltage was 3 kV (denoted 1, 2, 3, 4, 5, 6) or 11 kV (denoted 1*, 2*, 3*, 4*, 5*, 6*).

Spot	at.% Al	at.% Zr	at.% O	at.% F	at.% Mn	at.% Mg	at.% Cl
1	53.1	10.9	34.6	1.4	–	–	–
2	58.6	10.4	29.7	1.3	–	–	–
3	33.0	17.8	47.8	1.5	–	–	–
4	–	27.1	72.9	–	–	–	–
5	30.7	0.7	65.8	2.8	–	–	–
6	30.3	5.0	62.1	2.6	–	–	–
1*	86.4	1.7	10.8	0.3	0.3	0.4	–
2*	93.5	0.6	5.5	–	–	0.4	–
3*	62.8	9.0	27.3	0.5	–	0.4	–
4*	4.0	22.3	73.7	–	–	–	–
5*	51.2	0.9	46.0	1.5	–	–	0.4
6*	61.6	2.4	34.3	1.2	–	0.2	0.2

Table S4: EDS analysis of zirconium conversion coatings on AA3005 immersed in 0.5 M NaCl solution for 5 days (Figure 7d); electron beam voltage was 3 kV (denoted 1, 2, 3, 4, 5, 6) or 11 kV (denoted 1*, 2*, 3*, 4*, 5*, 6*).

Spot	at.% Al	at.% Zr	at.% O	at.% F	at.% Mn	at.% Fe	at.% Mg
1	53.9	11.0	33.7	1.4	–	–	–
2	54.5	10.6	33.4	1.5	–	–	–
3	9.4	23.5	67.2	–	–	–	–
4	–	24.0	76.0	–	–	–	–
5	57.7	10.2	31.0	1.1	–	–	–
6	35.2	18.7	45.0	1.1	–	–	–
1*	90.0	1.2	7.4	–	0.7	0.4	0.4
2*	92.5	0.5	6.1	–	0.4	–	0.4
3*	69.8	6.8	23.4	–	–	–	–
4*	2.6	22.3	75.1	0.5	–	–	0.4
5*	90.8	0.6	7.5	0.6	–	–	0.5
6*	68.6	6.7	23.6	0.4	0.2	0.1	–

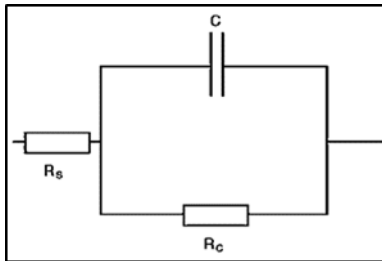
Table S5: EDS analysis of the cross section of as-prepared ZrCC at MnFe intermetallic particle (Figure 10b); electron beam voltage was 3 kV (denoted 1, 2, 3) or 11 kV (denoted 1*, 2*, 3*).

Spot	at.% Al	at.% Zr	at.% O	at.% F	at.% Mn	at.% Fe	At.% Mg
1	11.7	34.7	45.6	8.1	–	–	–
2	95.6	–	4.5	–	–	–	–
3	95.8	–	3.4	–	–	–	0.8
1*	26.0	36.3	32.9	4.8	–	–	–
2*	78.8	0.3	1.8	0.3	7.4	11.4	–
3*	97.8	–	1.6	–	–	–	0.6

Table S6: EDS analysis of the cross section of ZrCC at MnFe intermetallic particle after 5 days of immersion in 0.5 M NaCl solution (Figure 11c); electron beam voltage was 3 kV (denoted 1, 2, 3, 4, 5, 6, 7) or 11 kV (denoted 1*, 2*, 3*, 4*, 5*, 6*, 7*).

Spot	at.% Al	at.% Zr	at.% O	at.% F	at.% Mn	at.% Fe	At.% Cu
1	9.4	37.3	52.5	0.8	–	–	–
2	74.6	–	4.1	–	9.1	12.2	–
3	76.4	–	3.4	–	12.2	8.6	–
4	44.2	8.3	46.7	0.8	–	–	–
5	27.1	0.9	53.8	0.4	–	17.8	–
6	50.9	–	40.1	0.9	1.4	3.1	3.5
7	41.8	0.5	48.9	4.0	–	4.7	–
1*	28.1	40.5	30.8	0.7	–	–	–
2*	86.8	0.6	3.2	–	4.8	4.6	–
3*	84.1	1.0	5.9	–	5.0	3.9	–
4*	83	1.7	14.9	0.4	–	–	–
5*	56.3	2.1	33.1	–	–	8.6	–
6*	72.2	1.0	22.4	0.3	0.8	3.3	–
7*	81.0	0.6	16.6	1.1	–	0.7	–

Table S7: Fitting of EIS parameters according to the procedure proposed by Buchheit et al. [85]. Buchheit et al. used a simplified equivalent electric circuit to fit EIS data $R_s(R_cC)$ measured from 10^{-2} Hz to 10^4 Hz. In this work, we used $3 \cdot 10^{-3}$ Hz to 10^5 Hz and the values reported in the manuscript refer to Z at 3 mHz, i.e. lower frequency than used by Buchheit et al. We herein used the same model as Buchheit et al. to fit the data at 1 mHz and obtained values are presented in the table for three different samples together with average values after a 4-day (96 h) and a 7-day (168 h) immersion in 0.5 M NaCl.

Immersion time	4 days		7 days	
Sample	1			
Element	Value	Error (%)	Value	Error (%)
Rs, Ω·cm ²	15		15	
Rc, Ω·cm ²	1.21E+07	1.08	1.48E+07	1.27
C, F/cm ²	6.29E-06	0.57	6.14E-06	0.58
χ ²	0.102		0.110	
Sample	2			
Rs, Ω·cm ²	15		15	
Rc, Ω·cm ²	1.76E+07	1.05	2.38E+07	1.46
C, F/cm ²	6.17E-06	0.41	6.00E-06	0.44
χ ²	0.057		0.069	
Sample	3			
	Value	Error (%)	Value	Error (%)
Rs, Ω·cm ²	15		15	
Rc, Ω·cm ²	6.86E+06	0.84	9.66E+06	1.01
C, F/cm ²	6.05E-06	0.71	5.88E-06	0.68
χ ²	0.116		0.126	
	Mean value			
Rc, Ω·cm ²	1.2·10 ⁷		1.61·10 ⁷	
Equivalent electric circuit used to fit EIS data same as in reference [111].				
				

Chapter 4

Prolonged Protection of AlSi7Mg0.3 Aluminium Alloy in Chloride Solution by Zirconium Conversion Coatings

This chapter presents the study of the formation and electrochemical behaviour of zirconium conversion coatings applied to AlSi7Mg0.3 aluminium alloy. Electrochemical behaviour was studied with open-circuit potential vs. time curves, linear polarization resistance, potentiodynamic polarization curves and electrochemical impedance spectroscopy techniques. Microstructural and surface characterization was performed with FIB-SEM-EDX, TEM, XPS and ToF-SIMS techniques. In this study, we optimized the formation of zirconium conversion coatings applied to AlSi7Mg0.3 aluminium alloy. Optimally prepared zirconium conversion coatings showed self-sealing and active corrosion protection properties. The mechanism of self-sealing of conversion coating during the course of immersion was proposed, as well as the mechanism of initiation of corrosion at Zn-rich sites.

This chapter addresses thesis Objective 2) from Chapter 1, Section 1.6.

Regarding my contribution: I made a literature overview of the topic, planned and performed the experiments and jointly prepared the manuscript with co-authors.



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Prolonged protection, by zirconium conversion coatings, of AlSi7Mg0.3 aluminium alloy in chloride solution


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ABSTRACT

Zirconium conversion coatings (ZrCC) were prepared on aluminium alloy AlSi7Mg0.3 by immersion of the latter in 100–500 ppm baths of H_2ZrF_6 . Their electrochemical characterization was carried out while immersed in 0.5 M NaCl for up to 10 days. Immersion tests were performed for up to 28 days. Detailed microstructure characterization of the coatings was carried out prior to and following immersion. The ZrCC-200 coating had a bi-layer structure that was thicker round the intermetallic particles (130–150 nm) than at the matrix (50–60 nm). The corrosion resistance of the ZrCC-200 coating improved during immersion, which was ascribed to transformation of ZrF_4/ZrO_3F_2 to $ZrO_2 \cdot xH_2O(s)$ and to formation of $Al(OH)_3$ in the outermost part of the coating.

1. Introduction

Pre-treatment of a metal surface during its preparation for industrial applications is a very important step. It should improve the adhesion of top paints and improve the corrosion resistance of the substrate. Chemical conversion coatings have been used for such purposes for many years in the appliance, automotive, architectural, defence and space industries. Chemical conversion coating is the preferred choice in the industry for surface pre-treatment because of the simplicity of its preparation. The most widely known conversion coatings are chromate and phosphate coatings. However, the latter have already been banned in the EU and USA, based on health and environmental issues, while phosphate coatings are being replaced on the basis of environmental and economic issues [1]. There is, therefore, a quest in industry, involving an opportunity for scientific research, to find green alternatives for such coatings. The most viable replacements, already introduced into the industry, are zirconium conversion coatings (ZrCCs) and trivalent chromium processing (TCP). Appropriate zirconium conversion coating baths are usually composed of H_2ZrF_6 and various organic/inorganic additives [2,3].

Conversion coating with zirconium is an electrochemical process driven by the difference in Volta potential between local anodes and cathodes [2]. It starts by thinning natural oxide layers by the attack of free fluoride ions that exposes cathodic sites for coating formation.

Oxygen reduction and hydrogen evolution take place at cathodic sites. This causes a local increase of pH of up to 8.5 at or near cathodic sites, leading to precipitation of zirconium oxide and, eventually, to the formation of the desired coating. ZrCCs are much thicker at/or near intermetallic particles (IMPs) due to the nature of the ZrCC process. There have been many studies of the effect of ZrCCs on aluminium alloys [4–32], magnesium alloys [33,34], zinc [35–38] and steel [3,39–44]. Addition of small amounts of additives affects the conversion coating process and its performance: Cu increases the speed of forming coating by introducing additional cathodic sites; F increases the speed of the activation step; Si increases coating thickness while Ce, V and Mo add active corrosion protection and improve coating performance. Surface pre-treatment affects the conversion coating process as well as its performance [2]. ZrCCs with the best performances have been obtained by pre-treatments that produce a hydroxylated surface [17].

AlSi7Mg0.3 belongs to the 3xx.x (Al-Si-Cu and/or Mg) series of aluminium cast alloys. It has excellent mechanical properties and corrosion resistance and is therefore used for light metal castings for engine constructs, vehicle and aeroplane constructs, shipbuilding, electrical engineering and engine constructions, constructions for food handling, car wheels, etc. There is, however, a lack of studies concerning the formation and corrosion properties of ZrCCs applied to the 3xx.x series of cast alloys or 4xxx series of wrought aluminium alloys which are alloys based on Si. On the other hand, several studies

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on ZrCCs have been applied on the 6xxx wrought (Al-Si-Mg) series [5–7,17,19,24] that have alloying elements in common with those of the 3xxx cast and 4xxx wrought series but in lower contents. Andreatta et al. studied the mechanism of ZrCC formation on AA6061, using scanning Kelvin probe force microscopy (SKPFM) and electron microscopy allied to chemical analysis [7]. Coating formation is an electrochemically driven process caused by the difference in Volta potential between IMPs and Al matrix. Schoukens et al. investigated the formation of titanium conversion coatings (TiCCs) on aluminized steel, with and without the addition of Si [20]. The coating was two-fold thicker for a Si containing coating than that for a Si-free aluminium coated steel. The reason for this may be the higher cathodic activity of Si eutectic particles. On Al metal, coating started to form at AlFe₃ IMPs while, on Si-rich alloy, it was formed on Si precipitates and at the eutectic Si-Al phase (grain boundaries) [20]. Lunder et al. studied the formation of a zirconium-titanium conversion coating (ZrTiCC) on AA6060 and found that the coating was much thicker at and around α -Al(FeMn)Si cathodic IMPs [6]. The stirring and the pH of the bath affected the coating formation; medium stirring and pH = 4 were both beneficial.

It is a widely accepted opinion that ZrCCs act only as barrier coatings and will deteriorate if there are cracks or pores in the coating. In none of the previous studies improvement of corrosion resistance with immersion time in chloride containing solution was observed or even considered as a possibility. In fact, only Smit et al. noticed an improvement of corrosion resistance of TiCCs with time of immersion in NaCl solution, but they have not elaborated this phenomenon further [45]. In our previous work we reported the extraordinary ability of ZrCC to self-seal when deposited on manganese containing aluminium alloy 3005 [27]. Electrochemical measurements showed that the passivity and corrosion resistance of ZrCC on AA3005 improved during immersion in 0.5 M NaCl solution. Microstructural and compositional characterization showed that this behaviour is related to changes in composition and structure of conversion coating including, respectively transformation of ZrF₄/ZrO_xF_y to ZrO₂·xH₂O_(s) and formation of Al(OH)₃ in the top layer of ZrCC, accompanied by change in thickness of individual layers within the coating. It appeared that Mn from AA3005, together with Zr from ZrCC, was able to trigger self-sealing and active corrosion protection within the coating by their incorporation in the bottom part of the conversion coating [27]. Improvement of corrosion protection with time was also observed for a TCP (Cr(III)- and Zr(IV)-containing) coating on AA3003 in chloride and for simulated acid rain solutions [28]. In the present study we elaborated further the phenomenon of self-sealing of ZrCC and report, for the first time, self-sealing on Al-Si7Mg0.3 aluminium alloy. The results suggest that ZrCCs provide active corrosion protection or self-sealing of coating on alloys of the 3xxx series.

The formation and electrochemical behaviour of ZrCCs prepared by immersion of AlSi7Mg0.3 in a conversion bath of hexafluorozirconic acid (H₂ZrF₆) were investigated. The microstructure of the coated substrate was characterized using scanning electrochemical microscopy equipped with energy X-ray dispersive spectrometry (SEM/EDS), cross-section focus ion beam microscopy (FIB), X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS). Electrochemical characterization of samples was carried out in 0.5 M NaCl solution by measuring open circuit potential (OCP) vs. time, potentiodynamic polarization curves and electrochemical impedance spectra (EIS). Additionally, we performed a long term immersion test in 0.5 M NaCl solution to check the corrosion resistance of the coatings on the macroscale. The interesting behaviour of the improvement of the corrosion characteristics of coated samples with time was confirmed and a mechanism of self-sealing /active protection was proposed.

2. Experimental procedure

2.1. Materials, sample preparation and chemicals

The aluminium alloy EN AC¹ 42100 / ENAC AlSi7Mg0.3, with a nominal composition of Si 6.5–7.5 wt.%, Fe 0.15 wt.%, Cu 0.03 wt.%, Mn 0.10 wt.%, Mg 0.30–0.45 wt.%, Zn 0.07 wt.%, Ti 0.18 wt.%, was produced by TALUM d.d. (Kidričevo, Slovenia), was used as a substrate. The composition, provided by the supplier and determined by EDS analysis at a beam voltage of 20 kV was: 7.6 at. % Si, 0.1 at. % Fe, 0.4 at. % Mg, 0.2 at. % Ti and 91.8 at. % Al.

This is the alloy used for castings and corresponds to the following standards: International ISO–AlSi7Mg0.3, Germany–3.2371, UNSA13560, A356.0 and USA–A356.0. The alloy was subjected to T6 heat treatment. Samples used in experiments were cut in a rectangular shape with dimensions of 2.5 cm × 4 cm × 0.3 cm.

The following chemicals were used for experiments: NaCl (for analysis, Fischer Scientific, Leicestershire), H₂ZrF₆ (50 wt.% in water, Sigma-Aldrich, Saint Louis, USA), NH₄HCO₃ (reagent grade, Sigma-Aldrich, Steinheim, Germany) and Metaclean® (alkaline cleaner, Amity international, Barnsely, United Kingdom). Milli-Q Direct water, with a resistivity of 18.2 MΩ·cm at 25 °C (Merck, Darmstadt, Germany), was used for rinsing and for solution preparation.

pH was measured using a pH meter 827 pH-lab equipped with a Unitorde/Pt1000 (Metrohm AG, Herisau, Switzerland). Teflon beakers (V = 1 L) were used for conversion baths, and glass beakers (V = 600 mL) for alkaline cleaner and rinsing baths. Sample holders were made of Teflon. Conversion coating solutions were stored in polyethylene bottles.

2.2. Preparation of conversion coatings

Prior to immersion in a conversion coating bath, samples were ground on SiC papers ranging from 320- to 4000-grit, using a grinding/polishing machine LaboPol-20 (Struers, Ballerup, Denmark). Immediately after grinding, samples were ultrasonicated in absolute ethanol for 5 min using an ultrasonic bath Elmasonic P (Elma, Germany) at 37 KHz and 100% power. After cleaning, samples were dried with N₂ and kept in a desiccator until the chemical cleaning step. Samples were chemically cleaned by immersion for 3 min in 5 wt.% Metaclean solution (T = 57 °C, stirring rate 150 rpm). Immediately afterwards, they were washed with Milli-Q Direct water, then dipped in a Milli-Q Direct water bath for 45 s. Samples were then dipped immediately in a conversion coating bath (T = 25 °C, stirring rate 450 rpm). Conversion baths of different concentrations were used, containing 100, 150, 175, 200, 300 and 500 ppm of H₂ZrF₆. The pH was set to 4.8 with 15 wt. % NH₄HCO₃. The following conversion times: 1.5, 3, 6 and 10 min: were explored. Following the conversion bath step, samples were immediately rinsed with Milli-Q Direct water, then dipped in a Milli-Q Direct water bath for 1 min. Samples were then dried in an N₂ stream and left to dry in air for 24 h.

Mechanically ground/polished samples are denoted by MP, mechanically ground/polished and chemically pre-treated samples by CP, and zirconium conversion coated CP samples by ZrCC-x, where x represents the concentration of conversion bath in ppm.

2.3. Immersion test

MP, CP and ZrCC-200 samples were immersed in 500 mL 0.5 M NaCl solution for 28 days in accordance with the NACE TM0169/G31 - 12a standard procedure [46]. Samples were placed in polyethylene bottles (V = 550 mL) and sealed with perforated para-film. Digital images of the samples during the course of immersion were recorded using the digital camera with a resolution of 13 MP.

¹ EN = European standard, AC = component cast in aluminium

2.4. Electrochemical characterization

Electrochemical experiments were carried out with a Multi Autolab/M204 (Metrohm Autolab, Utrecht, Netherlands) potentiostat/galvanostat controlled by Nova 2.1 software. Measurements were conducted in a standard three-electrode flat cell with a volume of 250 mL. The sample was the working electrode, the carbon rod the counter electrode, and a saturated Ag/AgCl_(sat) electrode was the reference electrode ($E_{\text{SHE}} = 0.198 \text{ V}$). All potentials in the text refer to the Ag/AgCl_(sat) scale. The electrolyte was freshly prepared 0.5 M NaCl. The area of the working electrode was 1 cm^2 and the temperature of the electrolyte, 25°C .

Prior to electrochemical measurements each sample was allowed to rest at open circuit potential (OCP) for 5 min, 1 h, 2 h, 1 day, 2 days, 3 days and 4 days. Electrochemical measurements were conducted in the following sequence from least destructive to more destructive: (i) measurement of the OCP as a function of resting time, (ii) recording of linear polarization resistance curves, and (iii) recording of potentiodynamic polarization curves. The system was allowed to rest for 10 s before switching to the next electrochemical technique.

Linear polarization resistance curves (LPR) were recorded in the range of -10 to 10 mV vs. OCP using a 0.1 mV/s scan rate. Polarization resistance ($R_{\text{p, LPR}}$) was determined as the slope of the fitted potential (E) vs. current density (j) curve using Nova 2.1 software.

Potentiodynamic polarization curves were recorded in the range of potential starting at -250 mV vs. OCP in the anodic direction until current density reached 0.1 mA/cm^2 . The scan rate was 1 mV/s .

Corrosion current density and corrosion potential were determined using Nova 2.1 software based on the Tafel extrapolation method [47]. Polarization resistance was calculated from parameters obtained with the Tafel extrapolation ($R_{\text{p, Tafel}}$) method using Nova 2.1 software based on Eq. (1), in accordance with standard ASTM G59-97 [48],

$$R_{\text{p, Tafel}} = \frac{B}{j_{\text{corr}}} \quad (1)$$

where B is the Stern-Geary constant.

Electrochemical impedance spectroscopy (EIS) spectra were recorded from 100 kHz to 3 mHz frequency using an AC potential amplitude of 10 mV . Spectra were recorded every day at the OCP up to 10 days of immersion or until samples were pitted.

Electrochemical measurements were repeated for each condition for at least three different samples. Representative measurements are presented in plots and average values with standard deviation are given. When indicated, average values are also given in plots (i.e. for $|Z|_{3\text{mHz}}$ and OCP).

2.5. Microstructure characterization

Surfaces were characterized using scanning electron microscopy combined with energy dispersive X-ray spectrometry (SEM/EDS), focused ion beam microscopy (FIB), time of flight - secondary ion mass spectrometry (ToF-SIMS) and X-ray photoelectron spectroscopy (XPS).

SEM images were taken in secondary electron (SE) and back-scattered (BSE) modes, using an FEI Helios Nanolab 650 microscope. EDS spectra were recorded using an Oxford Instruments AZtec system with an X-max SDD (50 mm^2) detector. The analysed area was 100 nm^2 with an analysis depth of 100 nm (near surface condition) at 3 kV beam energy and ca. $3 \mu\text{m}$ at 20 kV . EDS mapping was recorded with a 3 kV beam energy and a resolution of 1024 lines. Prior to analysis, samples were coated with a thin carbon layer to reduce the charging effect.

FIB was used to determine the cross-section of conversion coatings. An FEI Helios Nanolab 650, equipped with EDS, was used to deposit a $1 \mu\text{m}$ thick Pt protective layer. A relatively large cross-section was then made by rough removal of material with Ga ions ($30 \text{ keV}/48 \text{ nA}$) followed by rough polishing ($30 \text{ keV}/22 \text{ nA}$) then fine polishing ($30 \text{ keV}/9 \text{ nA}$). EDS maps of the cross-section were recorded with a resolution of

1024 lines. The average thickness of the oxide layers was evaluated using the ImageJ programme.

ToF-SIMS ion depth profiles were determined using a ToF-SIMS V spectrometer (ION TOF GmbH – Munster, Germany). The analysis chamber was operated at a pressure less than $\sim 10^{-9}$ mbar. Depth profiles for negative ions were recorded by interlacing a pulsed 30 keV Bi^+ primary ion source delivering 1.2 pA of target current over a $100 \times 100 \mu\text{m}^2$ area with sputtering, using a 2 keV Cs^+ source beam delivering 523 nA target current over a $400 \times 400 \mu\text{m}^2$ area. The sputtering rate for ToF-SIMS depth profiling was determined by depth profiling of a thin film of Al_2O_3 of known thickness (50 nm) on an Si substrate under the same conditions as those applied for other samples. The sputtering rate was 0.30 nm/s ($\pm 0.02 \text{ nm/s}$).

XPS was carried out using a PHI-TFA XPS spectrometer (Physical Electronic Inc.). The vacuum during the XPS analysis was in the range of 10^{-9} mbar. The analysed area was 0.4 mm in diameter and the depth approximately $3\text{--}5 \text{ nm}$. X-rays were provided from a monochromatic Al $K\alpha$ source at a photon energy of 1486.6 eV . XPS spectrometer was operated at a nominal energy resolution of 0.6 eV measured on the Ag $3d_{5/2}$ peak. XPS spectra were analysed by Multipack software, version 8.0 (Physical Electronics Inc.). Spectra were normalized relative to the position of the C 1s peak at 284.8 eV .

3. Results and discussion

3.1. Characterization of as-prepared conversion coatings

3.1.1. OCP measurements made during the formation of conversion coating

The formation of ZrCC was followed by measuring the open circuit potential during immersion of AlSi7Mg0.3 in H_2ZrF_6 baths at various concentrations. OCP vs. time curves, obtained as means of five measurements, are represented in Fig. 1; repetitions are given in Fig. S1. There are three distinct phases of coating formation [2,27,28]. (i) In phase I, the natural aluminium oxide film is thinned by attack by F^- ions and the surface is activated for coating formation [2,16,49,50]. The OCP dropped to more negative values within the first 100 s. (ii) The levelling of the OCP represents the beginning of phase II where the OCP gradually shifted to more positive values with respect to the minimum in phase I. In phase II, insoluble $\text{Zr}(\text{OH})_2 \cdot x\text{H}_2\text{O}_{(\text{s})}$ / ZrF_4 , together with AlO_xF_y is precipitated at the substrate surface due to the increase of local alkalinity up to $\text{pH} = 8.5$ [21]. ZrCC starts to form on cathodic areas of the substrate (IMPs and Si-crystallites), afterwards growing in a lateral direction until completely covering the substrate [6,7]. (iii) Phase III marks the complete formation of ZrCC when the potential plateau is established; at longer conversion times the coating continues to grow but usually cracks due to internal stress [38,51].

The position of the minimum value of OCP varied with the concentration of H_2ZrF_6 which is more negative in more concentrated baths. The position of the OCP maximum in the region III was also dependent on the concentration of the H_2ZrF_6 bath and was positioned at 500 s, 550 s, 600 s, 650 s, 700 s and 800 s for 500 ppm, 300 ppm, 200 ppm, 175 ppm, 150 ppm and 100 ppm H_2ZrF_6 bath concentration, respectively. This implies that a higher concentration of H_2ZrF_6 in the conversion bath speeds up the conversion coating process. The conversion time of 10 min, which is optimal for 200 ppm, was then taken for the preparation of ZrCC in further experiments. It should be borne in mind, however, that the optimum conversion time is dependent on the bath concentration and should be determined for each concentration separately.

3.1.2. SEM/EDS characterization of the bare and coated substrates

Microstructural characterization of chemically pre-treated AlSi7Mg0.3 alloy was carried out using SEM-EDS mapping and spot analysis at a 20 kV electron beam voltage (Fig. 2). A typical microstructure of AlSi7Mg0.3 alloy is observed consisting of an α -Al matrix (grains) and eutectic Si solution (grain boundaries) in the form of

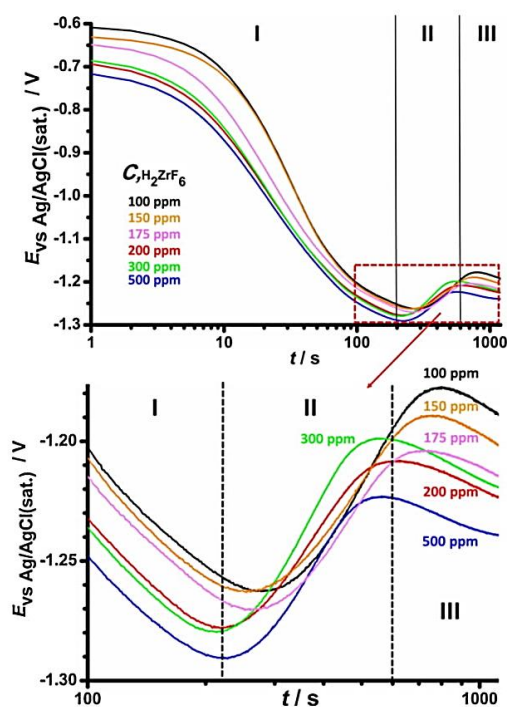


Fig. 1. Open circuit potential measurement during the formation of ZrCC on AlSi7Mg0.3 in 100, 150, 175, 200, 300 and 500 ppm H_2ZrF_6 conversion bath. Numerals I, II and III denote the regions of surface activation, initial coating formation and growth, respectively. The curves presented are mean values of five measurements. Note that the x-scale is logarithmic from 1 to 1000s (upper panel) and from 100 to 1000s (17 min) (lower panel). Repeat measurements are presented in Fig. S1 for all H_2ZrF_6 concentrations.

dendrites. The white dots, barely visible under this magnification, represent IMPs. EDS spot analysis was performed at 30 different IMPs and, in all of them, Al, Si, Mg and Fe were detected (Table S1), in accordance with the literature [52–60]. Ti was dissolved in the α -Al matrix. The IMPs and Si-crystallites are more noble than the Al matrix and represent spots where the zirconium conversion coating first starts to form [55].

The effect of conversion time on the formation of coating was checked for ZrCC-200 (Fig. 3 and Table 1). The high magnification SE

and low magnification BSE images are presented; the former better represents the morphology of the coating and the latter the lateral formation of the coating at the surface. For a conversion time of 1.5 min, only an etched, activated surface was seen in the SE images, implying that coating formation did not start (or cannot be observed using these images). However, in the BSE image, some small, bright spots were noted, indicating the initiation of coating formation in some areas (FeMg-rich IMPs). The initiation of coating formation was confirmed by EDS (Fig. 3, Table 1): after 1.5 min conversion, the concentrations of Zr and F amounted to ca. 3 at. % each (Table 1). After 3 min conversion, the formation of some spots could be observed, but etched structure was still visible. In BSE mode the spread of bright and white areas was observed, indicating progressive coverage of the substrate with conversion coating. Thus, bright spots indicate areas where formation of the coating started and then proceeded to grow in the lateral direction. After 6 min, a nodular coating structure was observed in the SE images while, in the BSE mode, the amount of bright areas increased further. The concentrations of Zr and F reached ca. 14 and 7 at. %. According to OCP measurements, the conversion time of 10 min should be optimal (Fig. 1). Indeed, the nodular structure was fused into a single structure, with only a few nano-pores visible. In BSE mode the proportion of bright areas indicates complete formation of conversion coating containing ca. 15 and 7 at. % (Table 1). The concentration of O is ca. 40 at. %. When the conversion process lasted 12 min, however, the coating was due to overgrowth, as indicated by a mud-crack structure at some areas.

EDS mapping analysis was carried out for the ZrCC-200 coating prepared for a conversion time of 10 min (Fig. 3, lower panel). The largest amounts of Zr, F and O were detected in the areas of the coating that were the brightest in the SEM BSE image; at these spots the conversion coating was much thicker than in the surrounding areas. These spots are related to the FeMg-rich IMPs in the AlSi7Mg0.3 alloy.

High magnification SE and low magnification BSE SEM images of ZrCCs prepared from 100, 150, 175, 200, 300 and 500 ppm H_2ZrF_6 baths for 10 min are shown in Fig. 4. The corresponding EDS analysis is presented in Table 2. There was no significant difference between coatings when inspected at high magnification: ZrCC-100 and ZrCC-150 exhibited a nodular morphology, suggesting that the coating was not completely formed due to the short conversion time. Nodular morphology was also noted for ZrCC-175, but it appeared to be more compact. For ZrCC-200, the morphology was more homogeneous, with some nano-sized pores. ZrCC-300 and ZrCC-500 looked almost the same as ZrCC-200 at high magnification images. In BSE mode the differences between coatings were clearly visible. Bright spots and areas indicate areas of coating formation. ZrCC-100 and ZrCC-150 samples had lower coverage, with bright areas and visible pits structure indicating

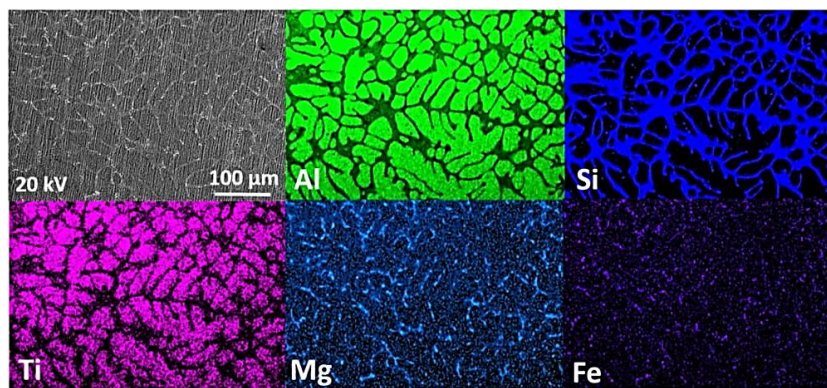


Fig. 2. SEM BSE images and EDS mapping of chemically pre-treated AlSi7Mg0.3. The point EDS analysis carried out on individual intermetallic particles at the surface is presented in Table S1.

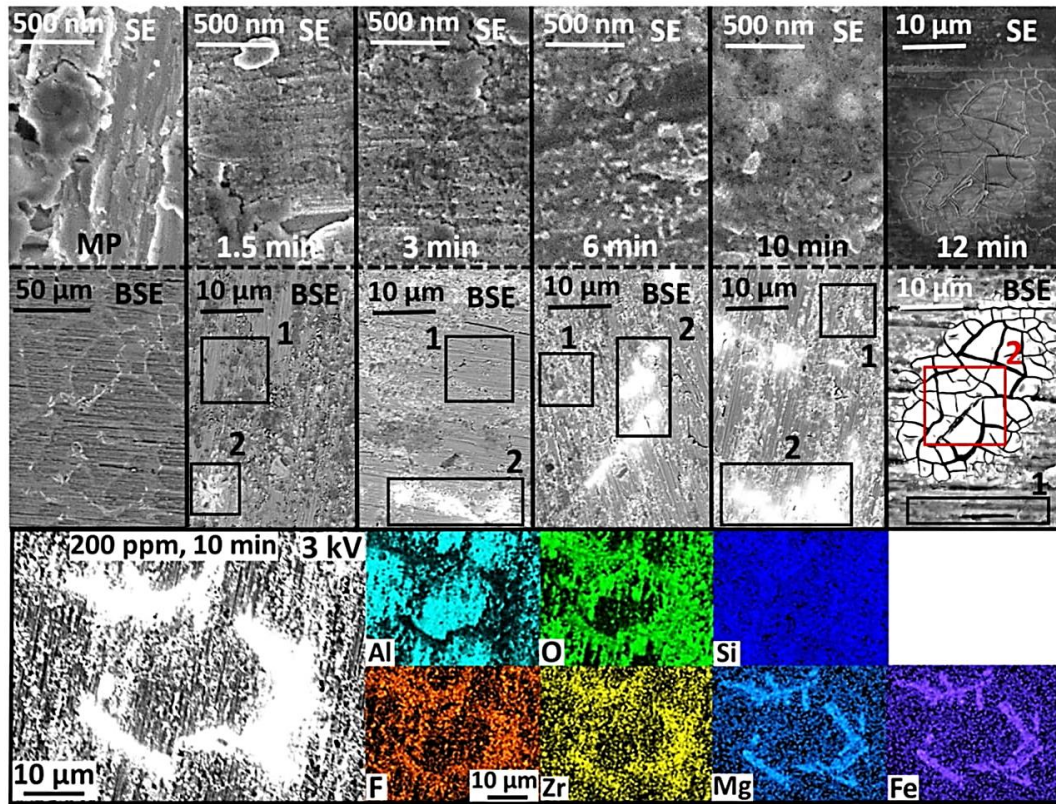


Fig. 3. SEM images (upper panel: SE images at higher magnification; middle panel: BSE images at lower magnification) of ZrCC on AlSi7Mg0.3 prepared in a 200 ppm H_2ZrF_6 bath for different conversion times: 1.5 min; 3 min, 6 min, 10 min and 12 min. Middle panel: EDS analysis was carried out over the whole area (average) and at enumerated spots (1, 2); the results are given in Table 1. Lower panel: SEM BSE image and corresponding EDS mapping for ZrCC-200 prepared for 10 min.

Table 1

EDS analysis of zirconium conversion coatings on AlSi7Mg0.3 from a 200 ppm H_2ZrF_6 conversion bath for conversion times of: 1.5, 3, 6, 10 and 12 min. The analysis was performed at enumerated spots (1, 2) and the whole area (average) in SEM BSE images in Fig. 3 (middle panel). The electron beam voltage of the analysed spots was 3 kV, corresponding to an analysis depth of ca. 100 nm.

spot	at. % Al	at. % O	at. % Zr	at. % F	at. % Mg	at. % Si
ZrCC-1.5 min						
Average	56.2	31.2	3.4	3.1	0.4	6.6
1	63.0	27.0	3.1	2.1	0.1	4.6
2	48.0	31.1	4.5	3.0	2.9	10.5
ZrCC-3 min						
Average	47.9	32.0	8.6	3.7	0.4	7.4
1	67.6	20.2	7.6	3.1	/	1.5
2	39.5	33.7	10.9	4.4	1.3	10.2
ZrCC-6 min						
Average	40.1	31.2	14.8	7.5	0.3	/
1	52.9	24.2	14.2	6.6	/	/
2	26.6	36.2	18.6	8.7	0.9	/
ZrCC-10 min						
Average	39.8	33.2	15.3	7.1	0.3	4.3
1	56.5	20.6	14.9	5.9	/	2.1
2	22.3	36.2	22.2	9.0	2.4	8.0
ZrCC-12 min						
Average	31.5	40.2	17.9	7.1	0.1	3.2
1	39.6	37.3	14.3	5.7	/	3.1
2	15.4	51.5	22.5	9.2	/	1.4

incomplete formation of conversion coating and etched structure. ZrCC-175 and ZrCC-200 featured the highest coverage, with bright areas and non-etched structures indicating optimal coating formation. The ZrCC-500 sample had an etched structure, indicating an overlong conversion time and coating overgrowth.

EDS analysis showed that the amount of Zr and F increased with bath concentration (Table 2) and correlates well with the effect of conversion time on the content of Zr and F (Table 1). The same amount of Zr and F could be obtained with lower H_2ZrF_6 concentration and extended conversion time (Fig. 1). The thickness and morphology of the conversion coatings are related directly to the concentration of the conversion bath and to the time of conversion, indicating that the concentration of H_2ZrF_6 in the conversion bath determines the kinetics of the conversion coating process.

3.1.3. SEM/EDS characterization at the coating cross-section

SEM images of cross-section and related EDS mapping of as-prepared ZrCC-200 were taken in the region near the Si-crystallites and IMPs of the AlSi7Mg0.3 sample (Fig. 5, Table 3). The as-prepared coating was thicker and scaled up at the areas of IMPs and Si crystallites, as is evident at the top-view and side-view SEM images (Figs. 5a,b). The EDS analysis of the cross-section above Si-crystallites and IMPs (Fig. 5b) is presented in Table 3. Crystallites were composed of Si (Table 3, spot 2); IMPs were composed of Al, Si and Mg (spot 4). It

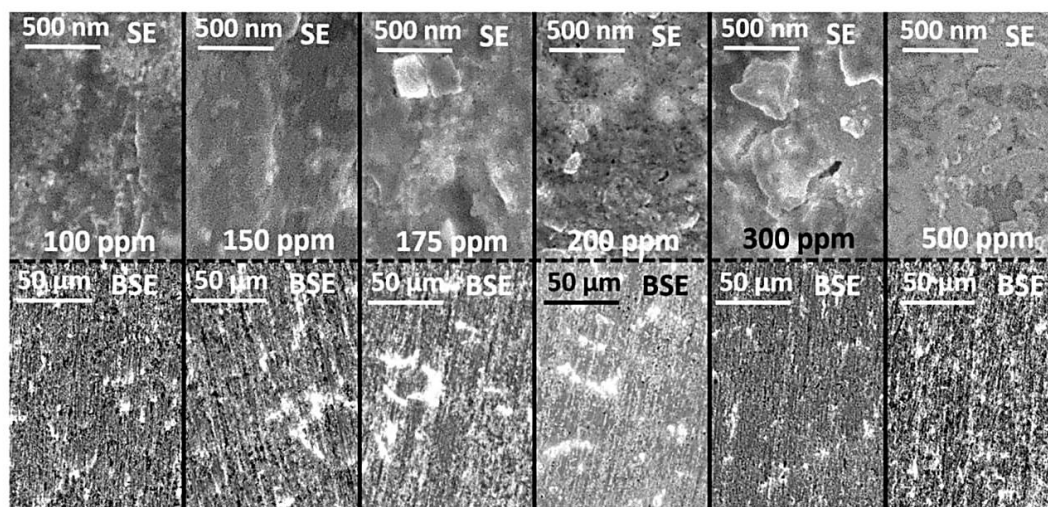


Fig. 4. SEM (SE and BSE) images of ZrCC on AlSi7Mg0.3 prepared in 100, 150, 175, 200, 300 and 500 ppm H_2ZrF_6 bath at conversion times of 10 min. EDS analysis was carried out over the whole area. The results of EDS analysis are given in Table 2.

Table 2

EDS analysis of zirconium conversion coatings on AlSi7Mg0.3 prepared in 100, 150, 175, 200, 300 and 500 ppm H_2ZrF_6 conversion bath for conversion times of 10 min. The analysis was performed at the whole area in SEM images in Fig. 4. The electron beam voltage of analysed spots was 3 kV corresponding to an analysis depth of ca. 100 nm.

Concentration of H_2ZrF_6	at. % Al	at. % O	at. % Zr	at. % F	at. % Mg	at. % Si
100 ppm	44.7	32.3	12.2	5.4	0.5	5.0
150 ppm	43.3	29.8	14.2	6.9	0.3	4.5
175 ppm	39.8	31.3	14.8	7.5	0.1	6.5
200 ppm	39.8	33.2	15.3	7.1	0.3	4.3
300 ppm	39.1	29.3	16.0	7.4	0.7	7.5
500 ppm	36.9	32.9	17.0	8.2	0.2	4.8

appears that some Mg-containing IMPs at the surface of the alloy were also covered by conversion coating (spot 3).

The thickness of the as-prepared coating was between 130 and 150 nm (Fig. 5c). The coating had a bi-layer structure, as shown by EDS mapping (Fig. 5d). In the as-prepared coating, Zr was concentrated in its top layer; F and O were equally distributed across the whole coating, while Al, Si and Mg were concentrated in the bottom layer of the coating (Fig. 5d). Instead of using EDS mapping (Fig. 5d), the structure of ZrCC-200 can be better described using atomic ratios of elements for the enumerated spots (Fig. 5c and Table 3)². Atomic ratios O/Zr, Al/Zr, Mg/Zr and Si/Zr increased from the upper to the inner part of the coating, showing the enrichment of the inner part with Al, O, F, Si and Mg.

3.2. Behaviour of conversion coatings in 0.5 M NaCl

3.2.1. Electrochemical impedance spectra and open circuit potential

To check the effect of H_2ZrF_6 bath concentration on the performance of conversion coatings, EIS spectra were measured at OCP for MP, CP and ZrCC coated AlSi7Mg0.3 samples. The EIS spectra shown in

Figs. S2 to S9 for MP, CP and ZrCCs were measured at different concentrations of the H_2ZrF_6 conversion bath. The polarization resistance of the coating is proportional to its corrosion resistance and can be approximated with a modulus at low frequencies [61,62]. The dependence on the immersion time of the average values of the impedance modulus at 3 mHz ($|Z|_{3\text{mHz}}$) in 0.5 M NaCl is presented for different concentrations of ZrCCs (Fig. 6a). The magnitude of $|Z|_{3\text{mHz}}$ decreased in the following order: ZrCC-200 > ZrCC-175 > ZrCC-300 > ZrCC-500 > ZrCC-150 $\approx$ ZrCC-100 > CP $\approx$ MP. Average values of $|Z|_{3\text{mHz}}$ together with the standard deviations, are given in Table S2. For ZrCC-200, the average impedance modulus after 1 h of immersion was $2 \cdot 10^5 \Omega\text{cm}^2$; it increased during the first three days of immersion, reaching $2.6 \cdot 10^6 \Omega\text{cm}^2$. This increase with time of the impedance modulus indicates that self-sealing and active corrosion protection processes are both taking place. At longer immersion times, the value of $|Z|_{3\text{mHz}}$ started to decrease slowly up to the 6th day of immersion, reaching $1.2 \cdot 10^6 \Omega\text{cm}^2$, then recovered up to $1.6 \cdot 10^6 \Omega\text{cm}^2$ and remained constant up to the 10th day. The drop in $|Z|_{3\text{mHz}}$ from the 4th to the 6th day is related to pitting, but the recovery at longer immersion times indicates self-sealing and the closure of pits.

It is noteworthy that the average value of $|Z|_{3\text{mHz}}$ for ZrCC-175 also increased, reaching a value of $1.8 \cdot 10^6 \Omega\text{cm}^2$ after two days of immersion (Fig. 6, Table S2). After longer immersion, it dropped to $1.2 \cdot 10^6 \Omega\text{cm}^2$. The average values of $|Z|_{3\text{mHz}}$ for ZrCC-100, ZrCC-150, ZrCC-300 and ZrCC-500 samples also increased after 1 day of immersion but then decreased. In contrast, the values for ZrCC-300 and ZrCC-500 samples recovered up to $7 \cdot 10^5 \Omega\text{cm}^2$ after the 5th day of immersion, while those for ZrCC-100 and ZrCC-150 continued to decrease with no recovery at all. These findings suggest that the self-sealing mechanism operates for all concentrations of H_2ZrF_6 but that it depends on the conversion time, i.e. the coating thickness. This effect will be most pronounced for the optimal conversion time, i.e. for 10 min for ZrCC-200 and ZrCC-175. On the other hand, for 150 ppm and 100 ppm H_2ZrF_6 concentrations, the conversion time of 10 min was too short to allow complete formation of coating (Fig. 4), resulting in a poor self-sealing effect (Fig. 6). Conversely, this conversion time was too long for 300 and 500 ppm concentrations, resulting in overgrowth and cracking of the coating (Fig. 4). If the conversion coating is not completely formed, it cannot be properly sealed; conversely, if the coating is overgrown and only sporadically cracked, it can eventually be sealed but not as effectively as the coating prepared for the optimized

² Note that the atom concentrations at spots 1 and 2 were reconstructed from EDS maps on which the analysis spot is larger than the analysed spot. The relative error is therefore always similar and allows for relative comparison of concentrations.

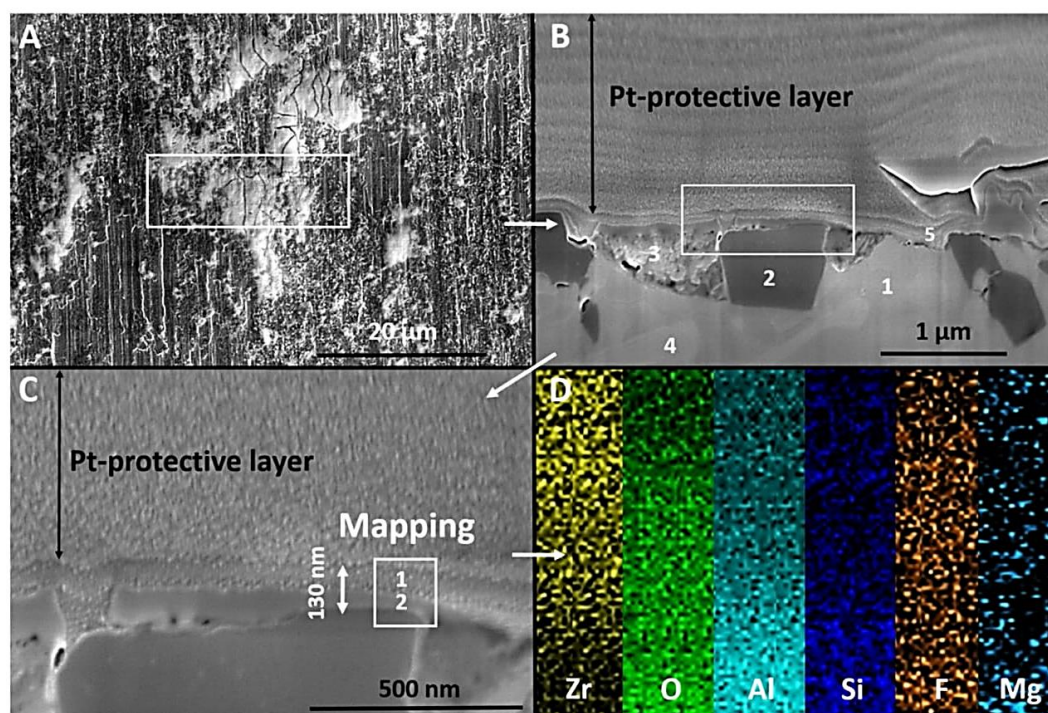


Fig. 5. SEM images of a cross-section of ZrCC-200 on AlSi7Mg0.3 prepared for a conversion time of 10 min: (a) top view, (b) side view, and (c) cross-section of coating in the proximity of Si-crystallites and IMPs. (a) White rectangles denote areas where a cross-section was made and zoomed in (b) and (c). EDS analysis was carried out at enumerated spots in (b) and (c) and the results are given in Table 3; average concentration relates to white rectangle. (d) EDS mapping of a cross-section of the coating presented in (c, white rectangle).

conversion time (i.e. 200 ppm and 10 min, Fig. 3).

This observation is corroborated by the fact that the time dependences of $|Z|_{3\text{mHz}}$ and OCP follow similar trends (Fig. 6b). Average values of OCP, together with standard deviations, are given in Table S3. Depending on the sample, the average OCP shifted from ca. -1.10 V after 1 h of immersion to ca. -0.65 V after 4 days (Fig. 6b). Trends in OCP and $|Z|_{3\text{mHz}}$ were correlated as a function of immersion time and reflect the development of pitting corrosion and its subsequent recovery, indicating active corrosion protection of ZrCCs. The same trend is evident on Bode phase angle diagrams (Fig. S7), where the phase angle at low frequencies increased continually up to 3, 4 and 5 days, then dropped, indicating the occurrence of pitting followed by recovery to ca. -40° .

To further explore the time dependence of the OCP of uncoated and coated samples, the OCP was measured continuously over 5 days of immersion in 0.5 M NaCl for MP, CP and ZrCC-200 AlSi7Mg0.3 samples (Fig. 7). During the first 0.5 to 1 h (depending on sample) of immersion, OCP of the ZrCC-200 sample shifted to more negative. Such a trend suggests the penetration of Cl^- ions and water through ZrCC and the initiation of a corrosion process at IMPs. Afterwards, the OCP value recovered and, during the next 12 h, moved towards more positive values, indicating active corrosion protection / self-sealing of conversion coatings. After 12 h, electrochemical noise appeared in the OCP curves for all ZrCC coated samples, probably originating from metastable pitting (Fig. 7). The OCP for MP and CP samples, given for comparison, did not decrease at all during immersion in 0.5 M NaCl,

Table 3

EDS analysis of the cross-section of the as-prepared zirconium conversion coatings prepared in a 200 ppm H_2ZrF_6 conversion bath for 10 min on AlSi7Mg0.3. Point analysis was performed at enumerated spots (Figs. 5b and 5c). The average concentration in Fig. 5c was measured within the white rectangle. The electron beam voltage of analysed spots was 3 kV (ca. 100 nm).

spot	Atomic ratio					Atomic percent					
	Al/Zr	O/Zr	F/Zr	Mg/Zr	Si/Zr	at. % Al	at. % O	at. % Zr	at. % F	at. % Mg	at. % Si
ZrCC-as-prepared (Fig. 11b)											
1						95.7	3.1	/	/	0.5	0.7
2						7.2	2.1	/	/	/	90.7
3						64.9	22.7	1.1	1.6	0.9	8.8
4						54.7	3.2	/	1.5	15.6	25.0
5						20.6	23.4	36.6	3.2	2.7	13.5
ZrCC-as-prepared (Fig. 11c)											
1	0.44	0.39	0.048	/	0.052	22.9	20.3	51.6	2.5	/	2.7
2	2.55	1.42	0.16	0.12	0.37	45.4	25.2	17.8	2.9	2.2	6.6
Avg.	1.18	0.76	0.088	0.055	0.16	36.4	23.5	30.8	2.7	1.7	5.0

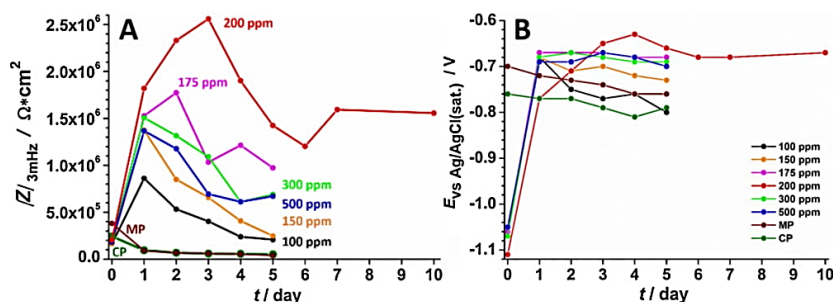


Fig. 6. (a) Average impedance modulus at 3 mHz ($|Z|_{3\text{mHz}}$) and (b) open circuit potential (OCP) as a function of immersion time in 0.5 M NaCl solution for: mechanically pre-treated (MP), chemically pre-treated (CP) and zirconium conversion coated AlSi7Mg0.3. ZrCCs were prepared in 100–500 ppm H_2ZrF_6 conversion bath for 10 min. Lines were drawn to guide the eye. Repetitions of all measurements are presented in Table S2 for $|Z|_{3\text{mHz}}$ and in Table S3 for OCP.

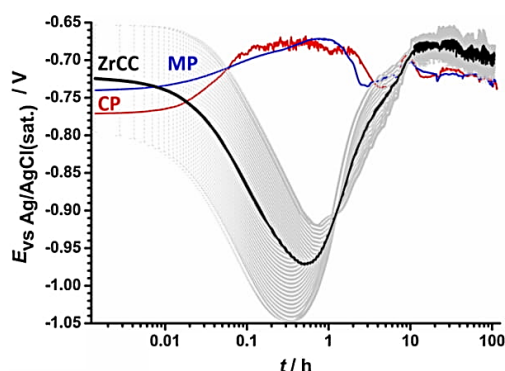


Fig. 7. Open circuit potential measured continuously as a function of immersion time in 0.5 M NaCl (5 days) for mechanically pre-treated (MP), chemically pre-treated (CP) and ZrCC-200 coated AlSi7Mg0.3 samples. Note that the x-scale is logarithmic. The mean value of 3 repetitions on different ZrCC samples is presented by a solid curve and the standard deviation (SD); values of impedance modulus, measured after 5 days immersion (120 h), are given in Table 4.

Table 4

Impedance modulus at 3 mHz measured after 5 days at the OCP in 0.5 M NaCl solution (Fig. 7) for: zirconium conversion coated in a 200 ppm H_2ZrF_6 conversion bath (mean value of 3 different samples with standard deviation (SD)); mechanically pre-treated (MP) and chemically pre-treated (CP) AlSi7Mg0.3.

Sample	ZrCC-mean	ZrCC-SD*	MP	CP
$ Z _{3\text{mHz}} / \Omega \cdot \text{cm}^2$	$1.91\text{E}+06$	$3.18\text{E}+05$	$8.06\text{E}+04$	$1.16\text{E}+05$

indicating that the active corrosion protection/self-sealing occurred only for ZrCC coated samples.

Following these continuous OCP measurements for 5 days, EIS spectra were measured again on the same samples. The resulting values of $|Z|_{3\text{mHz}}$ are presented in Table 4. ZrCC coated samples exhibited a mean value of $1.91 \cdot 10^6 \Omega \cdot \text{cm}^2$ with a standard deviation of $3.18 \cdot 10^5 \Omega \cdot \text{cm}^2$. These results confirm the high corrosion resistance of ZrCC-200 AlSi7Mg0.3 samples after 5 days of immersion in 0.5 M NaCl. At the same time, MP and CP AlSi7Mg0.3 samples exhibited values one and two orders of magnitude smaller at $8.1 \cdot 10^4 \Omega \cdot \text{cm}^2$ and $1.2 \cdot 10^5 \Omega \cdot \text{cm}^2$, respectively.

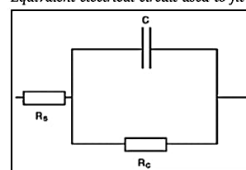
3.2.1.1. Comparison of EIS with standard methods. Experimental data obtained from EIS measurements for ZrCC-200 were used to correlate with the salt spray testing results. According to Buchheit et al. and Kelly et al., if a conversion coating applied to aluminium alloy AA356 (Al-Si-Mg alloy) exhibits an R_c (defined as apparent integrated pitting resistance) of $4.6 \cdot 10^6 \Omega \cdot \text{cm}^2$ (range $1.5 \cdot 10^6$ to $1.5 \cdot 10^7 \Omega \cdot \text{cm}^2$) after 24 h immersion in 0.5 M NaCl, it will pass the 168 h NSST test with a

Table 5

Fitting of EIS parameters according to the procedure proposed by Buchheit et al. [63]. The authors used a simplified equivalent electrical circuit to fit EIS data R_c (R_cC) measured from 10^{-2} Hz to 10^4 Hz. In this work, EIS spectra were measured from $3 \cdot 10^{-3}$ Hz to 10^5 Hz, i.e. the low frequency limit was lower than that used by Buchheit et al. To align with the model proposed, we use our experimental data measured at 1 mHz to fit the data. The fitted values are presented for three different samples, together with average values after 1 days' (24 h) and 3 days' (72 h) immersion in 0.5 M NaCl. (SD*-standard deviation).

Immersion time	1 day		3 days	
Sample 1	Value	Error (%)	Value	Error (%)
Element	10		10	
$R_s, \Omega \cdot \text{cm}^2$				
$R_c, \Omega \cdot \text{cm}^2$	$2.59\text{E}+06$	1.56	$6.2\text{E}+06$	2.16
$C, \text{F}/\text{cm}^2$	$1.85\text{E}-05$	1.19	$1.7\text{E}-05$	0.88
χ^2	0.353		0.261	
Sample 2	Value	Error (%)	Value	Error (%)
Element	10		10	
$R_s, \Omega \cdot \text{cm}^2$				
$R_c, \Omega \cdot \text{cm}^2$	$2.25\text{E}+06$	1.52	$4.70\text{E}+06$	2.29
$C, \text{F}/\text{cm}^2$	$1.97\text{E}-05$	1.23	$1.80\text{E}-05$	1.11
χ^2	0.359		0.392	
Sample 3	Value	Error (%)	Value	Error (%)
Element	10		10	
$R_s, \Omega \cdot \text{cm}^2$				
$R_c, \Omega \cdot \text{cm}^2$	$2.54\text{E}+06$	1.80	$4.81\text{E}+06$	2.51
$C, \text{F}/\text{cm}^2$	$2.10\text{E}-05$	1.27	$1.92\text{E}-05$	1.13
χ^2	0.424		0.419	
Mean value				
$R_c, \Omega \cdot \text{cm}^2$	$2.46 \cdot 10^6$		$5.24 \cdot 10^6$	
$SD^*, \Omega \cdot \text{cm}^2$	$1.50 \cdot 10^5$		$6.83 \cdot 10^5$	

Equivalent electrical circuit used to fit EIS data same as in reference [63].



probability of > 80% [63,64]. Buchheit et al. used a simplified equivalent electrical circuit to fit EIS data $R_c(R_cC)$ measured from 10^{-2} Hz to 10^4 Hz [63]. In the present work, the spectra were measured from $3 \cdot 10^{-3}$ Hz to 10^5 Hz. The values reported in Figs. 6a, 7 and Table 4 refer to $|Z|$ at 3 mHz, i.e. a lower frequency than that used in [63].

Here we have used the same model as that proposed in [63] to fit experimental data obtained at 1 mHz in the present study. The values obtained after immersion for 1 day (24 h) and 3 days (72 h) in 0.5 M NaCl are presented in Table 5 as mean values of three different samples. The mean experimental $|Z|_{3\text{mHz}}$ values were $1.82 \cdot 10^6 \Omega \cdot \text{cm}^2$ and $2.56 \cdot 10^6 \Omega \cdot \text{cm}^2$ after 1 and 3 days of immersion, respectively (Table S2). The fitted mean values of EIS parameters are R_c (24 h) = $2.46 \cdot 10^6 \Omega \cdot \text{cm}^2$ and R_c (72 h) = $5.24 \cdot 10^6 \Omega \cdot \text{cm}^2$. Based on these results which, after 24 h and 72 h, fit within the proposed threshold range between $1.5 \cdot 10^6$

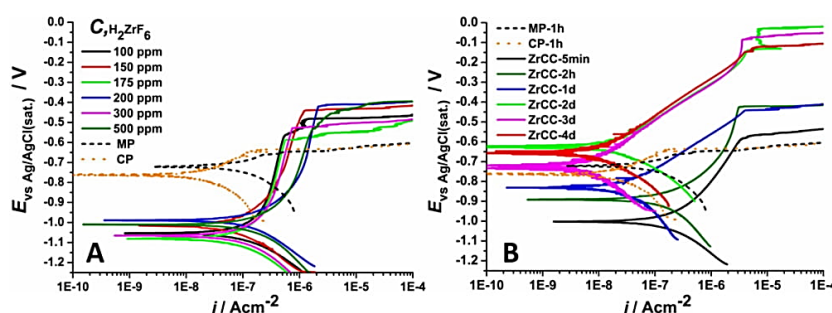


Fig. 8. Potentiodynamic polarization curves recorded in 0.5 M NaCl for mechanically pre-treated (MP), chemically pre-treated (CP) and ZrCC-coated AlSi7Mg0.3 alloy. (a) Zr coatings were prepared in conversion baths of different concentrations (100 to 500 ppm) for 10 min. Samples were rested at the OCP for 1 h OCP prior to measurement. Electrochemical data deduced from polarization curves are given in Table S4. (b) ZrCC-200 coated AlSi7Mg0.3 samples were rested at the OCP for 5 min up to 4 days prior to measurement. Electrochemical data deduced from polarization curves are given in Table 6.

to $1.5 \cdot 10^{-7} \Omega \text{cm}^2$, the coating has > 80% probability of passing the 168 h NSSM mark [63].

3.2.2. Electrochemical potentiodynamic curves

Potentiodynamic polarization curves were measured for MP and CP AlSi7Mg0.3 and for ZrCC samples prepared at different concentrations of conversion baths (Fig. 8a). Electrochemical parameters are presented in Table S4. Before making measurements, samples were allowed to rest at the OCP for 1 h. The shapes of potentiodynamic polarization curves for MP and CP AlSi7Mg0.3 samples are common to those of aluminium alloys in chloride containing solutions [52]. AlSi7Mg0.3 alloy showed strong corrosion resistance, with a range ΔE ($\Delta E = |E_{\text{pit}} - E_{\text{corr}}|$) of ca. 60–120 mV before breakdown at the pitting potential (E_{pit}). The value of ΔE reflects the protective nature of the coating, the broader the ΔE , the broader being the passive range. This suggests that the alloy is more resistant in a chloride environment than are copper- or zinc-containing Al alloys [65]. Chemically pre-treated AlSi7Mg0.3 exhibited a 2-fold lower corrosion current density than the MP sample (Fig. 8a, Table S4). Chemical pre-treatment cleaned and passivated the substrate surface by removing organic contaminants, producing a more uniform aluminium oxide at the surface, thus resulting in smaller current densities. The curves recorded for coated samples after 1 h at the OCP all had similar shapes (Fig. 8a): the value of E_{corr} became more negative by ca. 300 mV, giving average values of ΔE between 0.49 V and 0.53 V, and average corrosion current densities of between $8.8 \cdot 10^{-8} \text{ A cm}^{-2}$ and $1.6 \cdot 10^{-7} \text{ A cm}^{-2}$. It is evident that the formation of ZrCC improves the corrosion properties of uncoated substrate (i.e. smaller j_{corr} and broader ΔE); however, based on the polarization curves measured after only 1 h immersion in 0.5 M NaCl solution, it is difficult to classify the performance of ZrCCs of different concentrations. It is also noteworthy that the main effect of the coating is the establishment of a broad ΔE window, indicating that ZrCCs acted as cathodic inhibitors. The reduction in j_{corr} , compared to that for uncoated samples, was not particularly large, being within a half order of magnitude, but the shifts of E_{corr} and E_{pit} in negative and positive directions were large.

In the following experiment we focused on the ZrCC-200, which shows the most optimal corrosion performance (Fig. 6), investigating the effect of a period of immersion at the OCP of up to 4 days. After 2 h immersion in 0.5 M NaCl solution, j_{corr} for ZrCC were similar as those measured for MP and CP (Fig. 8b), although the ΔE window was broader. The electrochemical parameters are presented in Table 6. These results could indicate that ZrCC did not provide significant protection for AlSi7Mg0.3, although the behaviour changed at longer resting periods at the OCP. The values of j_{corr} for ZrCC-200 samples decreased continuously, E_{corr} shifting towards more positive values and ΔE increasing with immersion time. After 1 day of immersion, j_{corr} was smaller by one order of magnitude, while OCP shifted towards more positive values, reaching -0.71 V . This indicated a significant improvement in the performance of ZrCC-200 compared with that after a short immersion of only 1 h. The trend of decreasing corrosion current densities continued up to 3 days, reaching an OCP of -0.70 V , j_{corr} of

$4.85 \cdot 10^{-9} \text{ A cm}^{-2}$ and ΔE of 0.53 V. After 4 days, the corrosion parameters indicate weakening of the ZrCC-200 coating (Table 6). This kind of electrochemical behaviour suggests that ZrCC, on AlSi7Mg0.3, changes its behaviour from acting as a cathodic inhibitor at short immersion times (e.g. 1 h) to a prevailing anodic inhibitor at prolonged immersion (e.g. 2 days). This change may be related to the occurrence of some kind of self-sealing/active corrosion protection.

3.2.3. Immersion test

The corrosion performance of ZrCC-200 on AlSi7Mg0.3 was visualized by carrying out the immersion test for MP, CP and ZrCC-200 samples in 0.5 M NaCl for up to 28 days, in accordance with [46] (Fig. 9). The results of this immersion test were in accordance with the electrochemical behaviour of MP, CP and ZrCC-200 samples (Figs. 6–8): for MP, severe corrosion damage but only a few pits appeared after only 1 day; CP showed greater corrosion resistance, with visible corrosion products appearing after 2 days, but at a smaller severity than for MP. For the ZrCC-200 sample, one pit appeared near the edge after 5 days although the rest of the sample was undamaged. This situation remained the same after 28 days.

3.2.4. SEM/EDS characterization

SEM SE and BSE images for ZrCC-200 before and after immersion in 0.5 M NaCl for 1, 2 and 5 days are shown in Fig. 10. Images were recorded at 3 kV in SE and BSE modes and at 20 kV in BSE mode; the combination of different voltages and modes allows the coating formation and degradation to be followed in more detail, namely in SE images at 3 kV it was almost impossible to observe the coating until large cracks appeared (Fig. 10d). The BSE images are most suitable for observing, not only the coating, but also its degradation. After 1 day of immersion there was no visible damage; after 2 days some small cracks appeared which, after 5 days, progressed to a larger cracks in the middle of the sample; few corrosion spots formed around the cracked area. However, corrosion damage was discrete and the rest of the coating remained undamaged after 5 days of immersion.

A more detailed insight into the course of the degradation process is presented in Fig. 11. BSE images (Figs. 11a, d, e, h) are accompanied by EDS analysis in Table 7; SE images (Figs. 11b, c, f, g) present the morphology of the surface at high magnification (as compared to that of low magnification given in Fig. 10). The homogeneous morphology of the as-prepared coating is evident at high magnification, with some nano-pores present that are impossible to avoid during coating formation. No significant changes can be observed in SE images (Figs. 11c, f, g) during the course of immersion. However, when observing the BSE images at low magnification, degradation due to corrosion was easier to follow (Figs. 11d, e, h). Additional SEM images, recorded at different magnifications, are presented in Figs. S10 and S11. EDS analysis showed that the average composition of ZrCC-200 changed over time (Table 7): the concentration of O increased; that of F decreased 7.5-fold; the concentration of Al decreased and those of Si and Zr remained similar at ca. 5 at. %, with cracked spots where the corrosion process

Table 6

Electrochemical data deduced from measurements of potentiodynamic polarization (Fig. 8b) recorded in 0.5 M NaCl for mechanically pretreated (MP), chemically pre-treated (CP) and zirconium conversion coated AlSi7Mg0.3 (ZrCC-200). Samples were allowed to rest at OCP for different periods of time prior to electrochemical measurements (MP and CP for 1 h and ZrCC-200 from 5 min to 4 days). In the Table, average values deduced from several repetitions at different samples are given (SD*-standard deviation).

Sample	j_{corr} , A cm ⁻²	E_{ocp} , V	E_{corr} , V	E_{pit} , V	ΔE , V	β_a , mV/dec	$-\beta_c$, mV/dec	$R_{p,\text{LPR}}$, Ω cm ²	$R_{p,\text{Tafel}}$, Ω cm ²
MP	1.21E-07	-0.69	-0.72	-0.65	0.07	107	205	1.70E+05	2.50E+05
SD*	2.95E-08	0.02	0.02	0.01	0.02	42	1	9.31E+04	5.27E+04
CP	6.07E-08	-0.70	-0.71	-0.66	0.05	116	180	4.62E+05	5.15E+05
SD	1.39E-08	0.03	0.02	0.02	0.03	19	43	8.70E+04	7.76E+04
5 min	1.41E-07	-0.98	-1.01	-0.59	0.42	213	176	1.47E+05	3.05E+05
SD	2.62E-08	0.03	0.02	0.03	0.02	12	12	9.26E+03	4.43E+04
1 h	7.25E-08	-0.98	-0.99	-0.55	0.44	264	206	5.92E+05	6.59E+05
SD	8.76E-09	0.11	0.10	0.08	0.12	24	13	1.66E+05	9.71E+04
2 h	1.29E-07	-0.94	-0.95	-0.50	0.45	190	210	3.04E+05	3.36E+05
SD	1.57E-08	0.06	0.06	0.06	0.07	11	28	2.53E+04	2.33E+04
1 d	3.10E-08	-0.71	-0.68	-0.24	0.44	164	228	2.28E+06	1.65E+06
SD	1.29E-08	0.09	0.103	0.138	0.10	10	48	1.62E+06	7.98E+05
2 d	1.16E-08	-0.68	-0.68	-0.20	0.48	165	191	1.70E+06	3.87E+06
SD	4.74E-09	0.05	0.06	0.19	0.22	13	48	8.99E+04	1.40E+06
3 d	4.85E-09	-0.70	-0.73	-0.20	0.53	188	178	1.57E+06	8.94E+06
SD	1.29E-09	0.03	0.05	0.14	0.13	9	16	3.90E+05	3.27E+06
4 d	1.13E-08	-0.65	-0.64	-0.09	0.55	188	154	2.59E+06	4.32E+06
SD	6.06E-09	0.04	0.09	0.04	0.05	11	16	1.35E+06	2.14E+06

initiated after 2 and 5 days. Cracks were composed of: Al, O, Zr, Zn, Si (Fig. 11e, spot 4, Table 7) and Al, O, Zr, Zn, Si, F (Fig. 11h, spot 4, Table 7). It appears that the corrosion process started around spots in the alloy where Zn was present; these spots acted as local cathodes for hydrogen and oxygen evolution reactions and caused dissolution of nearby Al and cracking of ZrCC-200 coating. Dark circle areas are composed of Al and O (Fig. 11h, spot 6, Table 7). Apparently, corrosion occurred at these spots as well but a dense layer of aluminium oxide was formed and terminated the pit growth. This correlates well with the progressive disappearance of nano-pores under prolonged immersion, namely after 5 and 10 days, when nano-pores appear to be overlaid with the formed Al-oxide layer (Fig. 11g). These findings are in accordance with the EIS results, where pitting of ZrCC took place after 4–6 days of immersion in 0.5 M NaCl. Coating recovered afterwards, probably due to the formation of dense aluminium oxide that stopped further pitting (Fig. 6).

To summarize, EDS findings showed that, during immersion of ZrCC-200 in 0.5 M NaCl solution, the concentration of F decreased and that of O increased, leading to the closure of nano-pores and the self-sealing of coating that resulted in improved corrosion resistance during

the first 3 to 4 days of immersion. Afterwards, Zn-rich spots in the alloy, beneath the ZrCC, apparently acted as weak spots where the corrosion process was initiated, resulting in the appearance of cracks and pits. At the same time, the surrounding Al matrix dissolved but, eventually, as confirmed by EIS data and polarization curves (Figs. 6a and 8b), even these cracks/pits become covered with aluminium oxide and pit growth stopped. The role of Zn-rich spots in the initiation of corrosion, as well as the role of Si from the substrate in the self-sealing/active corrosion protection will be elaborated further in the next section.

3.2.5. SEM/EDS characterization at the coating cross-section

After 5 days of immersion in 0.5 M NaCl, the morphology and composition at the coating/substrate cross-section changed (Fig. 12). SEM images and EDS mapping were recorded in the proximity of the IMPs (i.e. at the matrix) (Fig. 12 and Table 8) and above the IMPs (Fig. 13 and Table 8). The coating was undamaged in the proximity of IMPs but the distribution of elements changed from that in the as-prepared coating (Fig. 5, Table 3). The concentration of F decreased 10-fold but was still distributed evenly across the coating. The concentrations of Si and Al increased, while that of O decreased and was

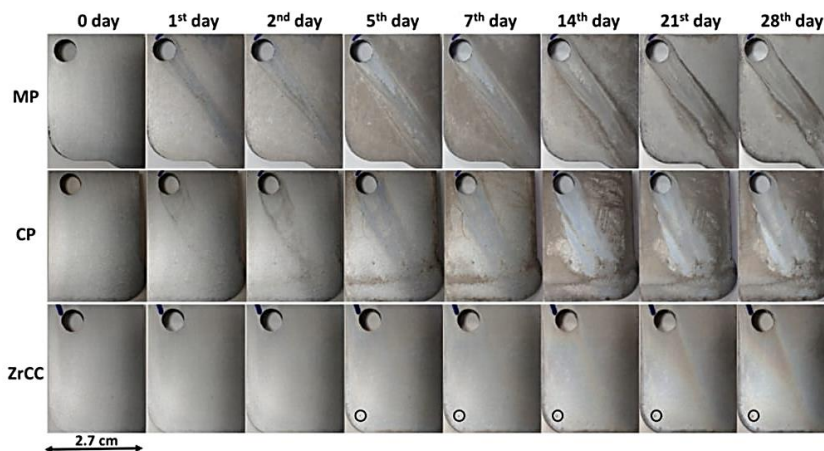


Fig. 9. Images of samples during immersion tests for mechanically pre-treated (MP), chemically pre-treated (CP) and ZrCC-200 coated AlSi7Mg0.3 samples. Black circles on the ZrCC samples denote sites of pitting. Immersion test were carried out in 0.5 M NaCl in accordance with NACE TM0169/G3-12a standard [46].

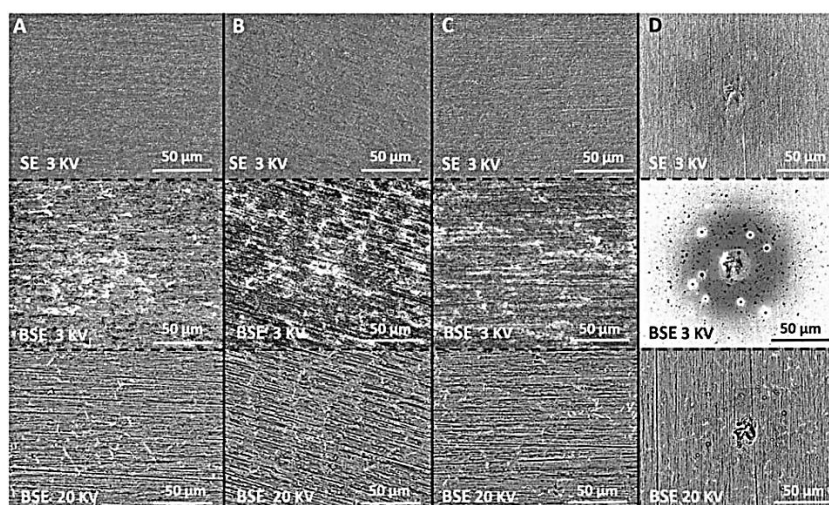


Fig. 10. SEM (SE and BSE) images of ZrCC on AlSi7Mg0.3 prepared in a 200 ppm H_2ZrF_6 for a conversion time of 10 min and then immersed in 0.5 M NaCl solution for different immersion periods: (a) as prepared (0 day), (b) 1 day, (c) 2 days and (d) 5 days.

segregated in the bottom layer of coating. The most important changes were the increased atomic ratio Si/Zr throughout the coating, especially in the bottom layer, and the decreased atomic ratios F/Zr and O/Zr

(Table 8). These findings indicate that Si and Al became incorporated in the ZrCC-200 structure with increasing immersion time.

At the top of the damaged areas, the corrosion products, in the

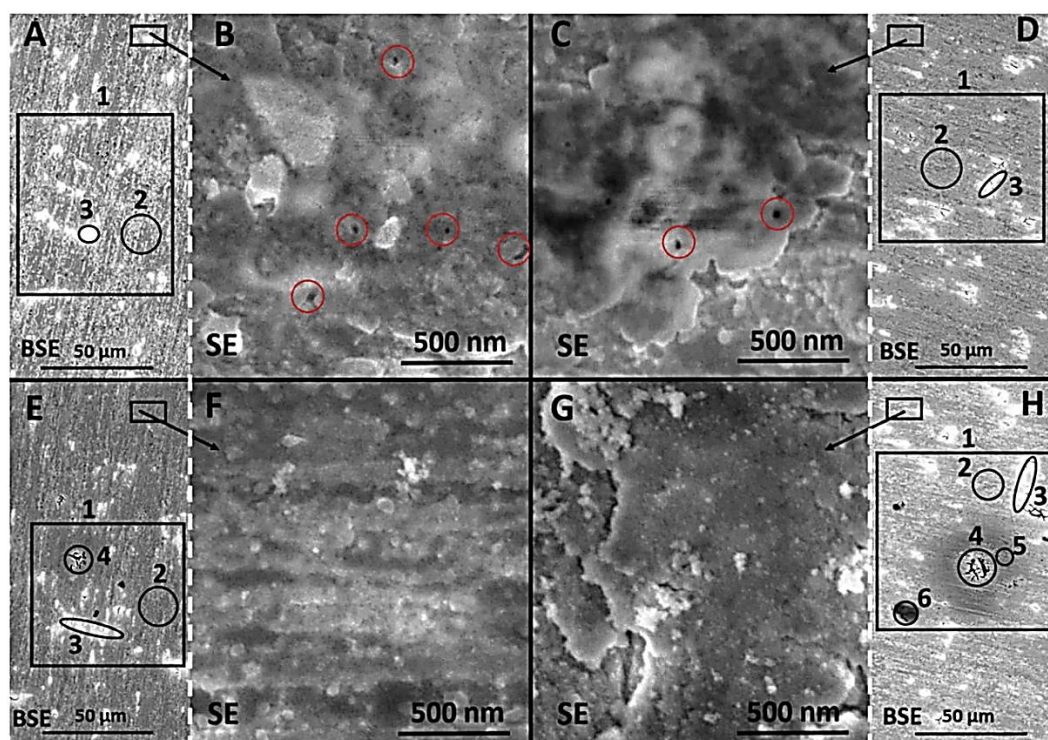


Fig. 11. SEM (a, d, e, h) BSE and (b, c, f, g) SE images of ZrCC on AlSi7Mg0.3 prepared in a 200 ppm H_2ZrF_6 bath for a conversion time of 10 min and then immersed in 0.5 M NaCl solution for different immersion periods: (a) as prepared (0 day), (b) 1 day, (c) 2 days and (d) 5 days. BSE images were recorded at lower magnification; rectangles with arrows denote the locations where SE images at high magnification were recorded. EDS analysis was carried out at enumerated spots in the BSE images (a, d, e, h) and the results are given in Table 7 (1 is the average concentration within the rectangle and 2–6 concentrations at the denoted points). Red circles in SE images indicate the nano-pores in the coatings (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

Table 7

EDS analysis of AlSi7Mg0.3 coated with ZrCC-200 prepared in a 200 ppm H_2ZrF_6 conversion bath for 10 min: as-prepared sample and samples immersed in 0.5 M NaCl solution for 1, 2 and 5 days. The analysis was performed at enumerated spots denoted in SEM images in Fig. 11. The electron beam voltage of analysed spots was 3 kV, corresponding to an analysis depth of ca. 100 nm.

spot	at. % Al	at. % O	at. % Zr	at. % F	at. % Zn	at. % Si
ZrCC-as prepared (Fig. 11a)						
1	39.0	34.7	13.8	7.5	/	5.0
2	43.6	32.8	12.2	7.3	/	4.0
3	14.6	58.6	15.0	8.5	/	3.4
ZrCC-1d (Fig. 11d)						
1	28.1	52.9	12.8	1.4	/	4.8
2	28.7	52.2	12.1	1.4	/	5.5
3	15.1	64.2	19.0	/	/	1.7
ZrCC-2d (Fig. 11e)						
1	33.3	47.6	12.9	1.2	/	5.0
2	38.3	44.8	10.8	1.0	/	5.0
3	20.3	57.0	19.2	/	/	3.4
4	14.8	64.0	9.3	/	0.7	11.3
ZrCC-5d (Fig. 11h)						
1	31.4	51.9	11.6	1.0	/	4.1
2	32.7	50.8	11.8	1.1	/	3.7
3	18.3	58.2	20.2	/	/	3.2
4	62.2	20.7	10.6	0.8	1.3	4.4
5	30.2	61.0	7.8	1.0	/	/
6	27.1	72.9	/	/	/	/

shapes of roses, were composed mainly of $\text{Zn}(\text{OH})_2$ (Fig. 13a, spot 1, Table 8). EDS mapping confirmed that pitting and cracking of ZrCC occurred at Zn-rich IMPs, where a small amount of Cu was also detected (Fig. 13a). The cross-section shows almost perfect trenching around a ball-like structure in the middle of the pit (Fig. 13b, Table 8). The latter structure was composed mainly of Al and O but also contained Si and Zr (spot 1). The point EDS analysis of the enumerated spots in Fig. 13a, and given in Table S5, confirms a large concentration of Zn at the rose-shaped product. These results suggest that the corrosion process initiated in this area leads to the de-alloying of Zn, Mg and Al and to a reduction of hydrogen evolution/oxygen reaction. This process eventually induces cracking of the ZrCC. Dealloyed Zn is redeposited at the top of the crack area, forming a rose-like structure composed of $\text{Zn}(\text{OH})_2$ and Al. The area above the pit was covered with a cracked, porous layer composed of Si, Al, O and minor amounts of Zr and F (Fig. 13b, spot 6, Table 8). EDS mapping/analysis proved that the interior of the pit walls was composed of a dense layer of aluminium oxide with small amounts of Zr and Si (spot 2). This newly formed layer appears to stop pit growth and further corrosion. In the proximity of these cracked areas, the coating was undamaged, even after 5 days of immersion in 0.5 M NaCl.

The fact that, at the site of corrosion damage, the concentration of Zn was increased was investigated further. According to the EN AC^a standard, the AlSi7Mg0.3 alloy contains max. 0.07 wt. % Zn. No Zn was detected by EDS analysis of the alloy (Section 2.1), nor was Zn

identified in any of the 30 individual IMPs (Table S1). Despite that, Zn was identified unambiguously at the corrosion site (Fig. 13). The presence of Zn was further checked at other corrosion sites. It is noteworthy that only a few corrosion sites were detected in the samples; the majority of the surface was protected. An example where SEM BSE images, accompanied by EDS mapping and EDS point analysis, is presented in Fig. 14 and Table S6. Two different voltages were used to achieve increased surface sensitivity. Zn was identified at the corrosion site (Figs. 14g, h) although, in this case, the corrosion products were not in the form of a rose, as in Fig. 13a. It appears that this site is related to the presence of Mg, Fe and Si, leading to the conclusion that Zn is present in one of the IMPs rich in these elements. Further, even more detailed analysis would be necessary to establish the presence of Zn in these IMPs, since it appears that, although Zn is present in small amounts in the alloy, Zn-rich sites constitute weak spots for the long-term corrosion resistance of ZrCCs on AlSi7Mg0.3 alloy. We denote these IMPs/spots with a general notation Al-Mg-Zn*.

3.2.6. XPS characterization of the coating surface

Chemically pre-treated AlSi7Mg0.3, as-prepared ZrCC-200, and ZrCC-200 immersed in 0.5 M NaCl solution for 2 and 5 days were all characterized with XPS. The XPS method, that enables a depth of analysis of ca. 10 nm, provides information from the top-most surface of the ZrCC. The composition of the surface obtained from the XPS survey spectra is presented in Table 9. The surface of the CP sample was composed of Al, O, Si and P. The phosphorus could result from the Metaclean alkaline cleaner that contains NaSiO_3 and, probably, some P-based corrosion inhibitor/surfactant. The aluminium and the oxygen originate from the aluminium oxide/hydroxide. Zr and F appeared after immersion in the H_2ZrF_6 bath, while Al disappeared due to the substrate being covered with ZrCC.

After 2 days immersion in NaCl solution, the fluorine was leached out from the coating while, at the same time, Al appeared. On prolonged immersion, the Al concentration increased and that of Zr decreased. Silicon, originating from AlSi7Mg0.3 substrate, appeared after one day and its concentration then increased continuously during immersion. Chlorine appeared after 1 day, after which its concentration decreased.

High energy resolution XPS spectra for the elements of interest are presented in Fig. 15. Two peaks appeared in the Al 2p spectrum for CP AlSi7Mg0.3 at binding energies (E_b) of 72.7 eV and 74.8 eV (Fig. 15a), corresponding to Al metal and $\text{Al}(\text{OH})_3$ respectively [66,67]. This result suggests that the surface of the alloy, after chemical pre-treatment, was covered by a few nanometres thick layer of $\text{Al}(\text{OH})_3$ which allows detection of the Al metal underneath.

Peaks for Al were not observed for as-prepared ZrCC-200, proving the complete covering of AlSi7Mg0.3 with coating. The peak at 74.8 eV appeared again after immersion for 2 days, indicating formation of $\text{Al}(\text{OH})_3$ in the top layer of coating. The intensity of this peak increased with time of immersion.

The O 1s spectra are presented in Fig. 15b. For the CP sample, the

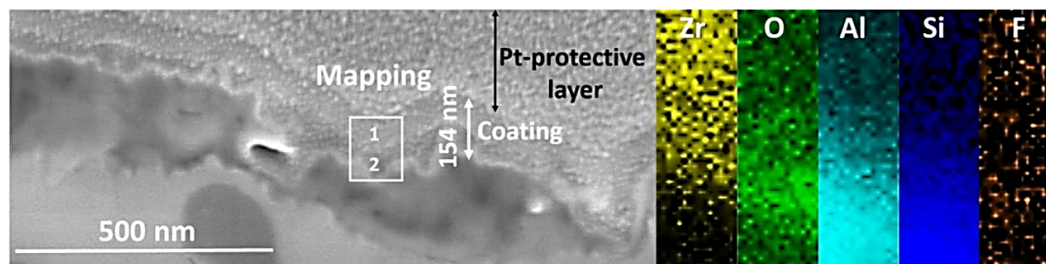


Fig. 12. SEM image and EDS mapping of a cross-section of ZrCC-200 on AlSi7Mg0.3 prepared for a conversion time of 10 min after 5 days of immersion in 0.5 M NaCl. The area where the mapping was recorded is denoted by the white rectangle, numbers 1 and 2 denote the spots where EDS analysis was carried out (Table 8).

Table 8

EDS analysis of the cross-section of zirconium conversion coatings prepared in a 200 ppm H_2ZrF_6 conversion bath for 10 min on AlSi7Mg0.3 in the proximity of IMPs (Fig. 12) and above Si-crystallites/ IMPs (Fig. 13) after 5 days of immersion in 0.5 M NaCl. Point analysis was performed at enumerated spots, whereas the average concentration in Fig. 12 was obtained within the white rectangle. The electron beam voltage of analysed spots was 3 kV (ca. 100 nm).

spot	Atomic ratio					Atomic percent						
	Al/Zr	O/Zr	F/Zr	Mg/Zr	Si/Zr	at. % Al	at. % O	at. % Zr	at. % F	at. % Mg	at. % Si	at. % Zn
ZrCC-5d (Fig. 12)												
1	0.71	0.25	0.006	/	0.14	33.7	11.8	47.5	0.3	/	6.8	/
2	2.76	0.58	0.012	/	1.43	47.7	10.1	17.3	0.2	/	24.7	/
Avg.	1.26	0.34	0.006	/	0.49	40.7	10.9	32.4	0.2	/	15.8	/
ZrCC-5d (Fig. 13b)												
1						75.3	18.3	0.9	/	/	5.5	/
2						45.0	49.4	1.4	/	/	4.2	/
3						50.5	8.5	0.9	1.2	13.5	25.4	/
4						24.4	36.4	8.2	0.3	/	/	30.7
5						36.0	33.9	21.8	0.3	/	5.5	2.5
6						15.2	13.0	0.4	0.2	/	71.1	/
7						80.3	10.3	0.9	0.4	/	8.2	/
8						89.7	3.6	1.7	/	/	5.0	/
9						97.2	2.8	/	/	/	/	/
10						48.2	1.8	/	/	/	50.0	/

peak was centred at 531.7 eV, suggesting a higher concentration of hydroxide than of oxide. Qualitatively, in this spectrum, three peaks for bound H_2O , $\text{Al}(\text{OH})_3$ and $\text{ZrO}_2 \cdot 2\text{H}_2\text{O}$ were identified with binding energies of 533, 532 (531.9) and 530.5 eV, respectively [67,68]. After the formation of ZrCC, the O 1s peak shifted to 531.2 eV, and exhibited a shoulder at 530.5 eV, suggesting the predomination of hydrated Zr oxide and/or oxyfluoride ($\text{ZrO}_2 \cdot x\text{H}_2\text{O}$ / ZrF_xO_y). After both, 2 and 5 days immersion of ZrCC in NaCl solution, the centre of the O 1s peak moved back to a slightly higher E_b of 531.7 eV, related to $\text{ZrO}_2 \cdot 2\text{H}_2\text{O}$ and $\text{Al}(\text{OH})_3$.

The F 1s peak was centred at an E_b of 684.8 eV and was present only for the as-prepared ZrCC, suggesting the presence of $\text{ZrF}_4/\text{ZrF}_x\text{O}_y$ in the

top layer (Fig. 15d). The F 1s peak was not detected after 2 and 5 days immersion, suggesting leaching of fluorine from the coating and transformation of $\text{ZrF}_4/\text{ZrF}_x\text{O}_y$ to $\text{ZrO}_2 \cdot x\text{H}_2\text{O}$, in accordance with the O 1s peak (Fig. 15b).

High energy resolution Zr 3d spectra were detected after the formation of ZrCC-200 (Fig. 15c). The Zr 3d_{5/2} and 3d_{3/2} peaks for the as-prepared coating were centred at 185.1 eV and 182.8 eV, respectively. Taking into account the relatively high fluorine and oxygen concentrations, this spectrum correlated with that for a mixture of $\text{ZrF}_4/\text{ZrF}_x\text{O}_y$ and $\text{ZrO}_2 \cdot x\text{H}_2\text{O}$ [69]. After 2 and 5 days immersion in 0.5 M NaCl solution, however, the peaks were shifted to lower E_b values of 184.9 eV and 182.5 eV, respectively, suggesting the continuous

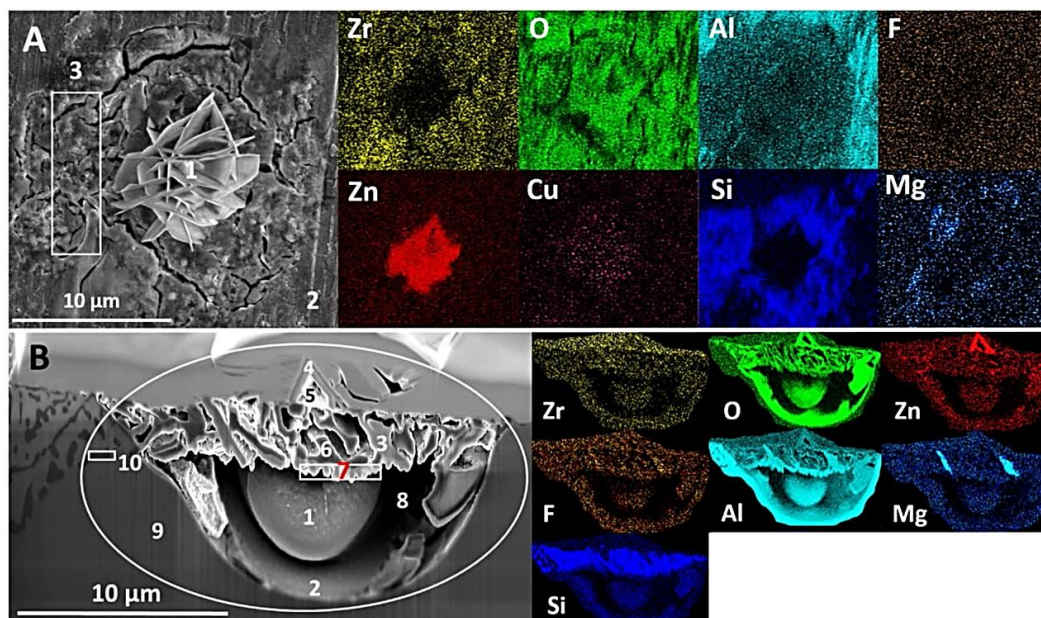


Fig. 13. (a) Top view and (b) side view SEM images (left) with EDS mapping (right) of a cross-section of ZrCC-200 on AlSi7Mg0.3 prepared for a conversion time of 10 min after 5 days of immersion in 0.5 M NaCl solution. (a) EDS analysis was carried out at enumerated spots with results given in Table S5. EDS mapping (right) was performed over the whole area in (a). (b) EDS analysis was carried out at enumerated spots with the results given in Table 8. EDS mapping (right) was performed at the area denoted by the white circle (left).

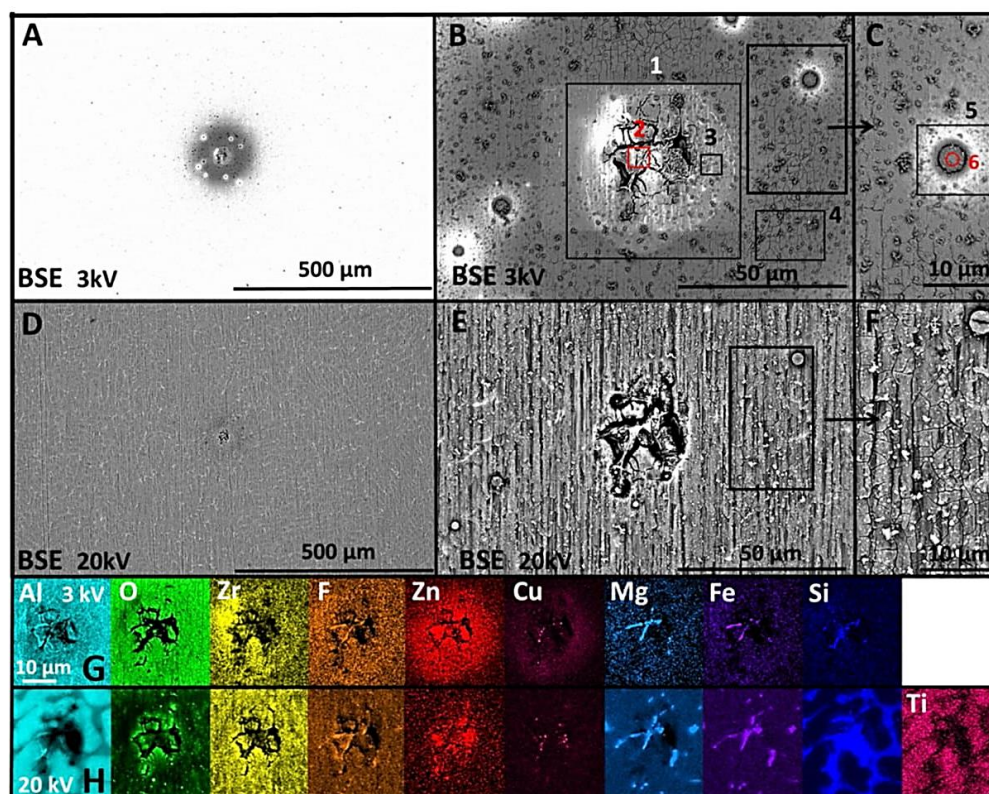


Fig. 14. SEM (BSE) images with EDS mapping of ZrCC on AlSi7Mg0.3 prepared from 200 ppm H_2ZrF_6 for a conversion time of 10 min, then immersed in 0.5 M NaCl solution for 5 days. Images were recorded at (a–c) 3 kV and (d–f) 20 kV energies at different magnifications. (g–h) EDS mapping was obtained at (g) 3 kV and (h) 20 kV in the area denoted by the square in (b). EDS point analysis was carried out also at enumerated spots in (b) and results are given in Table S6.

Table 9

Concentration of elements obtained by XPS analysis of chemically pre-treated (CP) and zirconium conversion coated AlSi7Mg0.3 samples: as-prepared and immersed in 0.5 M NaCl solution for 1, 2 and 5 days.

Sample	at.% Al	at.% O	at.% Zr	at.% F	at.% Si	at.% Cl	at.% P
CP	24.6	67.8	/	/	1.8	/	5.8
ZrCC-0d	/	64.4	24.4	11.3	/	/	/
ZrCC-1d	4.8	70.1	17.5	0.2	0.3	7.2	/
ZrCC-2d	9.6	70.6	11.7	1.6	0.8	5.6	/
ZrCC-5d	14.2	72.6	6.7	0.8	1.4	4.2	/

transformation of Zr-fluoride/oxyfluoride to $\text{ZrO}_2 \cdot x\text{H}_2\text{O}$. These results are in correlation with the disappearance of the fluorine peak in the F 1s spectrum.

The Si 2p spectra are presented in Fig. 15e. Two 2p peaks are present in the Si 2p spectrum for the CP sample, centred at 99.0 eV and 102.5 eV corresponding to Si metal and silicates/silanes, respectively. After the conversion coating process, however, peaks for Si diminished due to the covering of AlSi7Mg0.3 with ZrCC. After both, 2 and 5 days immersion in NaCl, a peak at 101.9 eV re-appeared suggesting the formation of silicates in the top layer of the coating.

3.2.7. ToF-SIMS characterization of the coating structure

ToF-SIMS negative ion profiles were recorded for as-prepared ZrCC-200 and for ZrCC-200 immersed for 5 days in 0.5 M NaCl solution (Fig. 16). The sputtering rate was 0.30 nm/s (± 0.02 nm/s). The

thickness of as-prepared ZrCC-200, determined based on depth profiles, was 50–60 nm. The coating showed a bi-layer structure with an outer layer with the highest concentration of ZrO^- (it could be $\text{ZrO}_2 \cdot x\text{H}_2\text{O}$ / ZrO_xF_y species) and a lower concentration of AlOF^- (region 1). A significant level of CuO^- ions was detected in the outer layer. The inner layer had the highest amount of AlOF^- ions accompanied by peaks for AlO^- , MgO^- and SiO^- ions (region 2). ZrO^- ions were detected in the inner layer but in a lesser amount than in the outer layer.

After 5 days of immersion in 0.5 M NaCl, the profile of ZrO^- ions was almost the same, with a maximum in the outer layer (Fig. 16, region 1). The time at which the ZrO^- intensity dropped to a half compared to surface value was taken as a boundary between the regions 1 and 2. The intensities of F^- and AlOF^- ions decreased significantly, while that of Cl^- ions increased significantly. The profile of Cl^- ions followed the same shape as that of F^- , AlO^- and AlOF^- ions. This suggests that Cl^- ions were exchanged with F^- ions and incorporated into the ZrCC structure. The intensity of the AlO^- profile was greater, exhibiting a maximum in the outer part and a plateau in the inner part of ZrCC. The Al_2^- profile reached that of a pristine coating at ca. 200 s which was taken as indicating that the inner interface with the substrate was reached. This point coincides with the drop of AlOF^- to that of half its maximum intensity and denotes the boundary between the regions 2 and 3. Based on these results it can be stated that Al_2O_3 was enriched in the inner layer at the interface of ZrCC. This could be one of the reasons for the improved corrosion resistance of the ZrCC coating, as shown previously in SEM/EDS analysis (Figs. 9–12). During the course of immersion in NaCl, the intensity profile related to CuO^- ions increased; copper is probably dissolved in the Al matrix and a certain

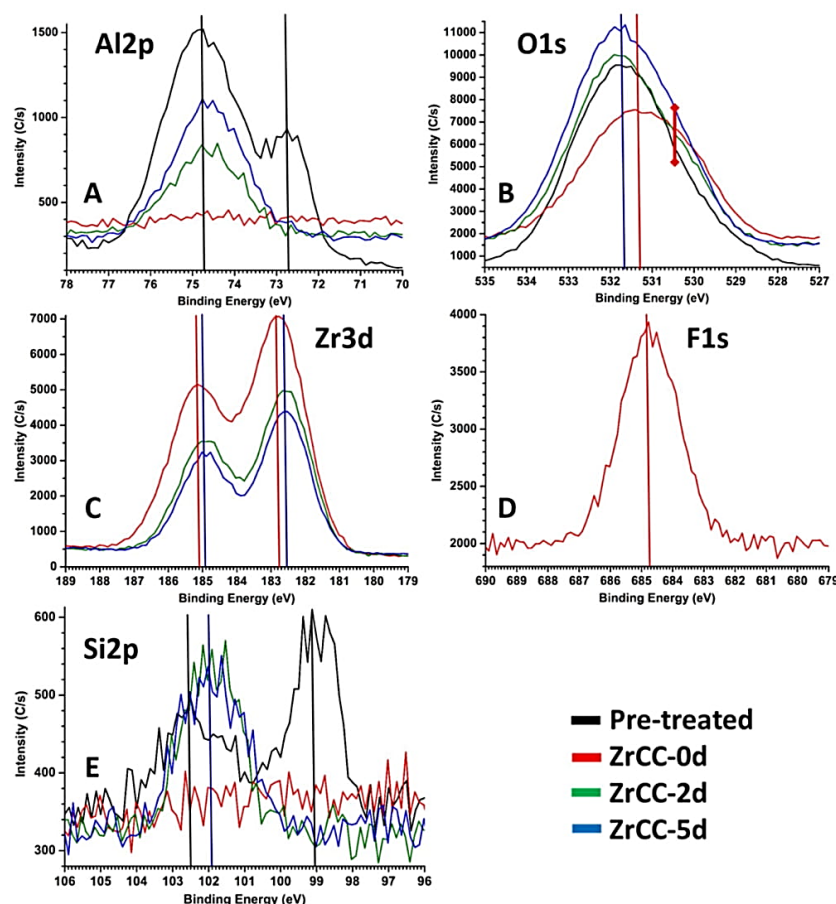


Fig. 15. High energy resolution XPS spectra (a) Al 2p, (b) O 1s, (c) Zr 3d, (d) F 1s and (e) Si 2p for chemically pre-treated AlSi7Mg0.3 and ZrCC-200 on AlSi7Mg0.3, as-prepared, then immersed in 0.5 M NaCl solution for 2 and 5 days. The conversion time was 10 min. Spectra were not normalized on the intensity scale.

Cu enrichment at the surface is probably a result of the de-alloying of aluminium.

The MgO^- profile decreased and shifted more deeply into the substrate as well, but this could be due to alloy heterogeneities. The intensity of the profile related to SiO^- ions remained unchanged, however it was shifted towards the surface, indicating incorporation of Si into the coating structure.

3.2.8. The mechanism of active corrosion protection / self-sealing

Electrochemical characterization demonstrated the improvement of corrosion resistance of AlSi7Mg0.3 during the first 4 days of immersion in 0.5 M NaCl. This is followed by the occurrence of pitting, as reflected in a drop of impedance modulus at 3 mHz. However, on longer immersion, the value of $|Z|_{3\text{mHz}}$ recovered up to $1.5 \cdot 10^6 \Omega\text{cm}^2$ and remained at that value until the end of immersion. This electrochemical behaviour suggests that active corrosion protection takes place for ZrCC applied on AlSi7Mg0.3.

XPS analysis showed the disappearance of fluorine from the top layer of ZrCC after 2 days in 0.5 M NaCl and the transformation of $\text{ZrF}_4/\text{ZrF}_x\text{O}_y$ into $\text{Zr}(\text{OH})_2 \cdot x\text{H}_2\text{O}$ and $\text{Al}(\text{OH})_3$. This was accompanied by increased concentrations of Al, Si and Cl in the top layer of ZrCC, suggesting incorporation of these elements into the coating structure.

SEM/EDS analysis showed that the concentration of F decreased and that of O increased during immersion. The concentration of Al decreased slightly due to the incorporation of other elements into ZrCC

and densification of the latter. ZrCC-200 was 130–150 nm thick in the proximity of Si-crystallites/IMPs. It was homogenous with a bi-layer structure according to cross-section analysis. ToF-SIMS analysis correlated well with XPS and SEM/EDS analyses. It showed that the concentrations of F^- and AlOF^- decreased, while those of AlO^- and Cl^- increased and had the same curve shape as AlOF^- , suggesting incorporation of these two elements into the ZrCC structure. The SiO^- profile intensified in the coating interior.

A study of SEM/EDS proved that pitting and cracking of ZrCC occurred at spots rich in Zn. Pits were ca. 10 μm deep with an almost perfect ball structure in the middle, composed mainly of Al and O with a minor amount of Si and traces of Zr and Zn. The pit was covered with a porous coating containing mainly Si, Al and O, with trace amounts of Zr and F. At the top of this coating, a cracked structure, sometimes in the form of a rose-shaped product was formed composed mainly of Zn, O and Al with a trace amount of Zr and F. This structure was probably pure $\text{Zn}(\text{OH})_2$, other elements originating from underlying layers. The most interesting fact is that the aluminium oxide layer with a minor amount of Si and Zr was formed at the pit wall. This oxide layer prevented further pit growth and corrosion and was responsible for recovery of the impedance modulus at 3 mHz after pitting up to $1.5 \cdot 10^6 \Omega\text{cm}^2$.

According to these results we propose the following mechanism of self-sealing/active corrosion protection in ZrCC applied to AlSi7Mg0.3 (Fig. 17).

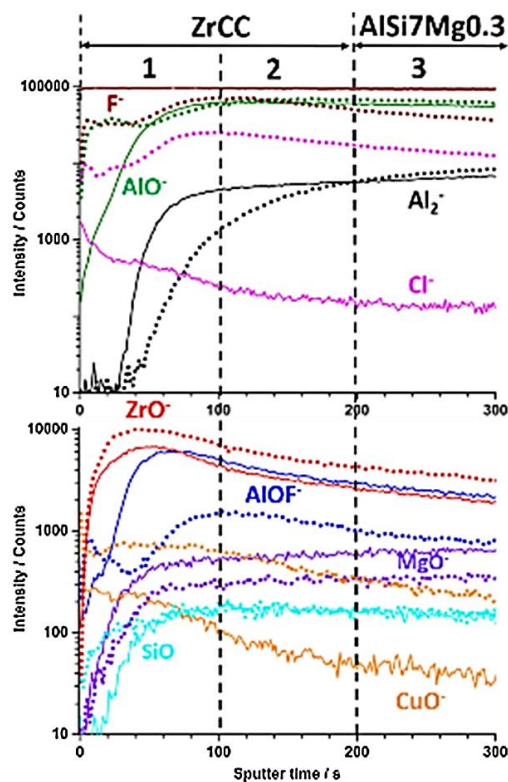


Fig. 16. ToF-SIMS negative ions depth profiles of ZrCC-200 applied on AlSi7Mg0.3. The conversion time was 10 min. Full lines – as-prepared ZrCC; dotted lines – ZrCC after 5 days of immersion in 0.5 M NaCl solution. 1-outer layer, 2-inner layer /or interface, 3-substrate.

Electrolyte penetrates into ZrCC through defects down to IMPs and Si-crystallites, where the corrosion process initiated. In these areas evolution of H_2 takes place and alkalinity increases (Eqs. 2,3). Weak spots under ZrCCs were Zn-rich. We assume that the spots may be Al-Mg-Zn* IMPs; at these spots the corrosion process was intense and led to de-alloying of Zn, Mg and Al (Eqs. 4,5). This process caused the cracking of ZrCCs at the surface. However, Zr and Si were apparently able to migrate to the pit walls and become incorporated into the dense conversion layer consisting mainly of aluminium oxide (Eq. 4). This leads to the conclusion that Si and Zr may play a role in stabilizing the aluminium oxide and preventing its dissolution.

The majority of the ZrCC coating was not subjected to pitting because of the self-sealing of ZrCCs. OH^- ions and $H_{2(g)}$ moved towards the outer interface with electrolyte, causing leaching of F^- ions from the coating. This causes the transformation of ZrF_4/ZrO_xF_y into $ZrO_2 \cdot xH_2O_{(s)}$ (Eq. 6). In electrolyte, F^- ions are equilibrated with Na^+ ions. ToF-SIMS analysis showed that F^- ions could be exchanged with Cl^- ions and incorporated into the coating structure (Eqs. 7,8). We believe that, simultaneously with the hydrogen evolution reaction, dissolution of Si/SiO₂ in the presence of F^- ions could take place at a low pH inside the pit; Si could be dissolved from Si-crystallites and/or IMPs (eqs. 9, 10) and play a role in improving the corrosion resistance of ZrCCs by the formation of $SiO_2 \cdot 2H_2O$ during the first 4 days of immersion in 0.5 M NaCl (Eq. 11).

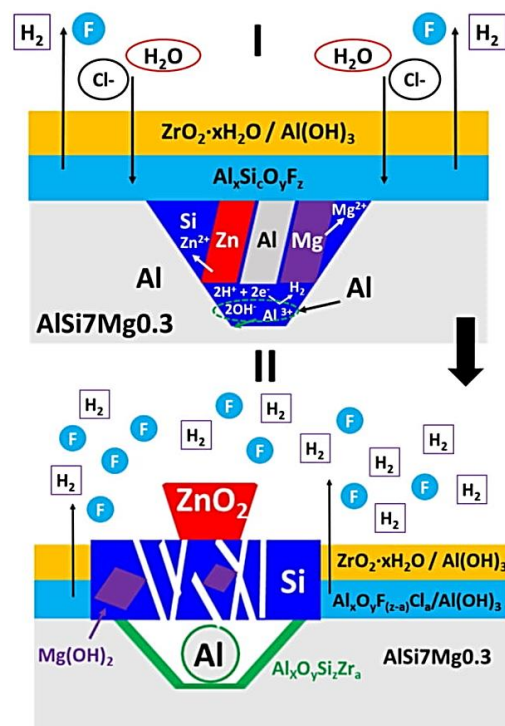
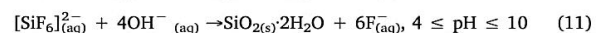
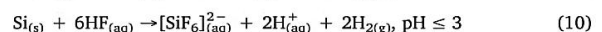
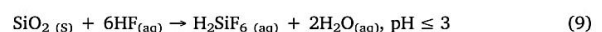
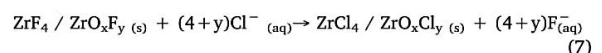
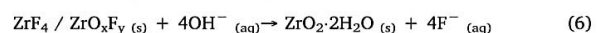
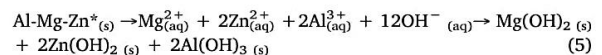


Fig. 17. Schematic presentation of the self-sealing mechanism of zirconium conversion coating applied on AlSi7Mg0.3 during its immersion in 0.5 M NaCl solution.



It appears that if the Zn-rich spots were removed by the pre-treatment, the ZrCC would be stable for a much longer period in 0.5 M NaCl solution and the self-sealing process would be even more pronounced. Based on the presented results it can be hypothesized that the leaching of fluorine ions from the coating would affect wet adhesion of organic coatings, primers and adhesives, as noted experimentally by fluoride-induced interfacial adhesion loss of post-treated anodized aluminium [70]. It would therefore be advisable to take this effect into account prior to application of an organic topcoat.

4. Conclusions

- 1 Zirconium conversion coatings formed from a 200 ppm H_2ZrF_6 bath at pH = 4.8 with a conversion time of 10 min at room temperature showed the best corrosion resistance when deposited on AlSi7Mg0.3.
- 2 The corrosion resistance of ZrCC was excellent. The Bode impedance modulus at 3 mHz increased 10 to 15-fold during immersion in 0.5 M NaCl solution and was sustained at $2.2 \cdot 10^6 \Omega \cdot \text{cm}^2$ to $3.0 \cdot 10^6 \Omega \cdot \text{cm}^2$ for at least 4 days with no observed pitting. The open circuit potential of ZrCC on AlSi7Mg0.3 shifted from -0.9 V to -0.65 V , indicating anodic inhibition behaviour of these coatings.
- 3 After 4 days of immersion in 0.5 M NaCl, the Bode impedance modulus at 3 mHz dropped but then recovered up to $1.5 \cdot 10^6 \Omega \cdot \text{cm}^2$ and remained constant for up to 10 days of immersion. This suggests that ZrCC deposited AlSi7Mg0.3 is gradually transformed in such a way as to enable increased corrosion protection at prolonged immersion time in chloride solution.
- 4 ZrCC-200 coating has a bi-layer structure with a thickness of 50–60 nm at the coating matrix and up to 130–150 nm at/around Si-crystallites/IMPs. Zr and O were concentrated in the top layer while Al, F, Si and Mg were concentrated in the bottom layer of the coating.
- 5 Fluorine then leached out of the coating, causing transformation of $\text{ZrF}_4/\text{ZrO}_x\text{F}_y$ to $\text{ZrO}_2 \cdot x\text{H}_2\text{O}_{(s)}$ during immersion in 0.5 M NaCl. The concentration of O increased significantly with immersion time.
- 6 After 5 days of immersion in 0.5 M NaCl solution the ZrCC was cracked/pitted. Pitting occurred at Zn-rich spots/IMPs, although a dense aluminium oxide layer containing a minor amount of Zr and Si formed at pit walls, prevented further pit growth.
- 7 It appears that Si from AlSi7Mg0.3, together with a Zr from ZrCC, play a role in self-sealing and active corrosion protection.
- 8 These results prove that ZrCC on AlSi7Mg0.3 alloy exhibits a self-sealing/active corrosion protection behaviour during immersion in 0.5 M NaCl solution [63].

Data availability statement

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations. They will be available on request.

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CRediT authorship contribution statement

Gavril Šekularac: Methodology, Formal analysis, Writing - original draft. **Janez Kovač:** Methodology, Writing - original draft. **Ingrid Milošev:** Conceptualization, Methodology, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.corsci.2020.108615>.

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Supplementary Information

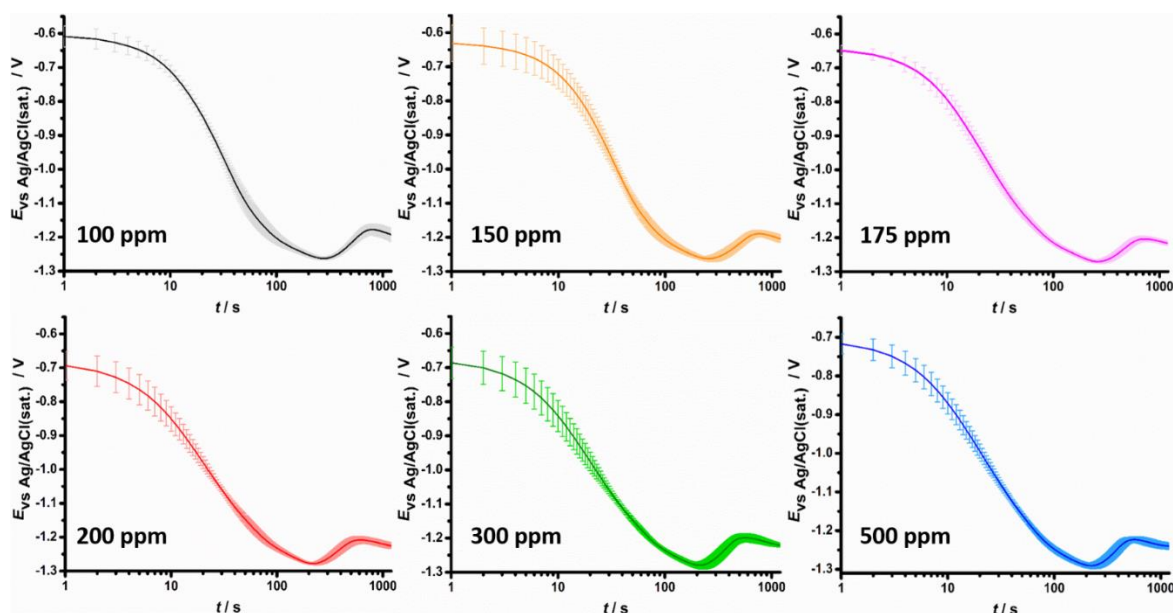


Figure S1: Open circuit potential measurements during the formation of zirconium conversion coating on AlSi7Mg0.3 in: 100, 150, 175, 200, 300 and 500 ppm H_2ZrF_6 conversion baths. The presented curves are mean values of 5 measurements and error bars represent standard deviations.

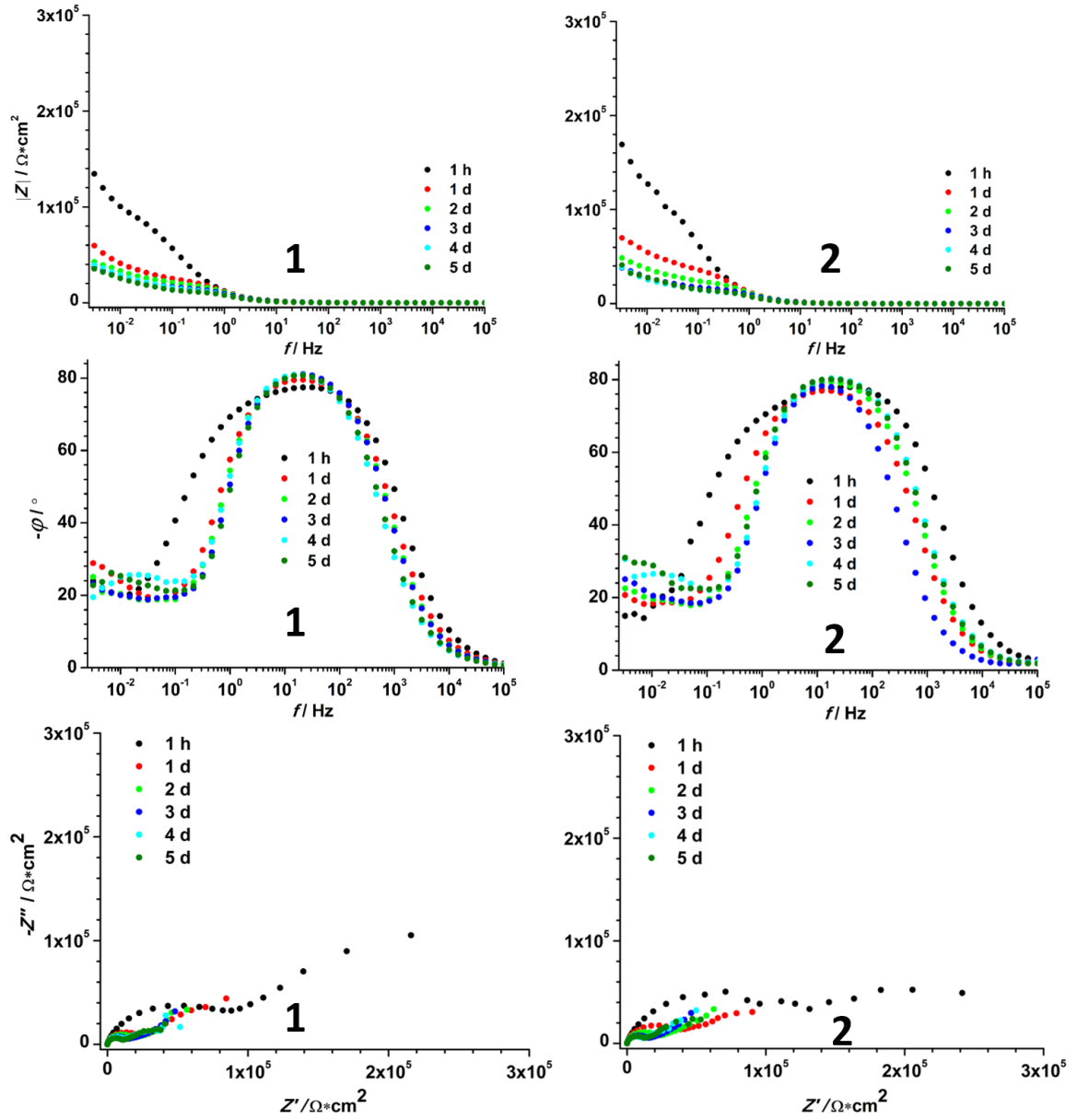


Figure S2: Bode and Nyquist diagrams for mechanically pre-treated AlSi7Mg0.3 immersed in 0.5 M NaCl solution for up to 5 days. 1 and 2 are two repetitions of each condition.

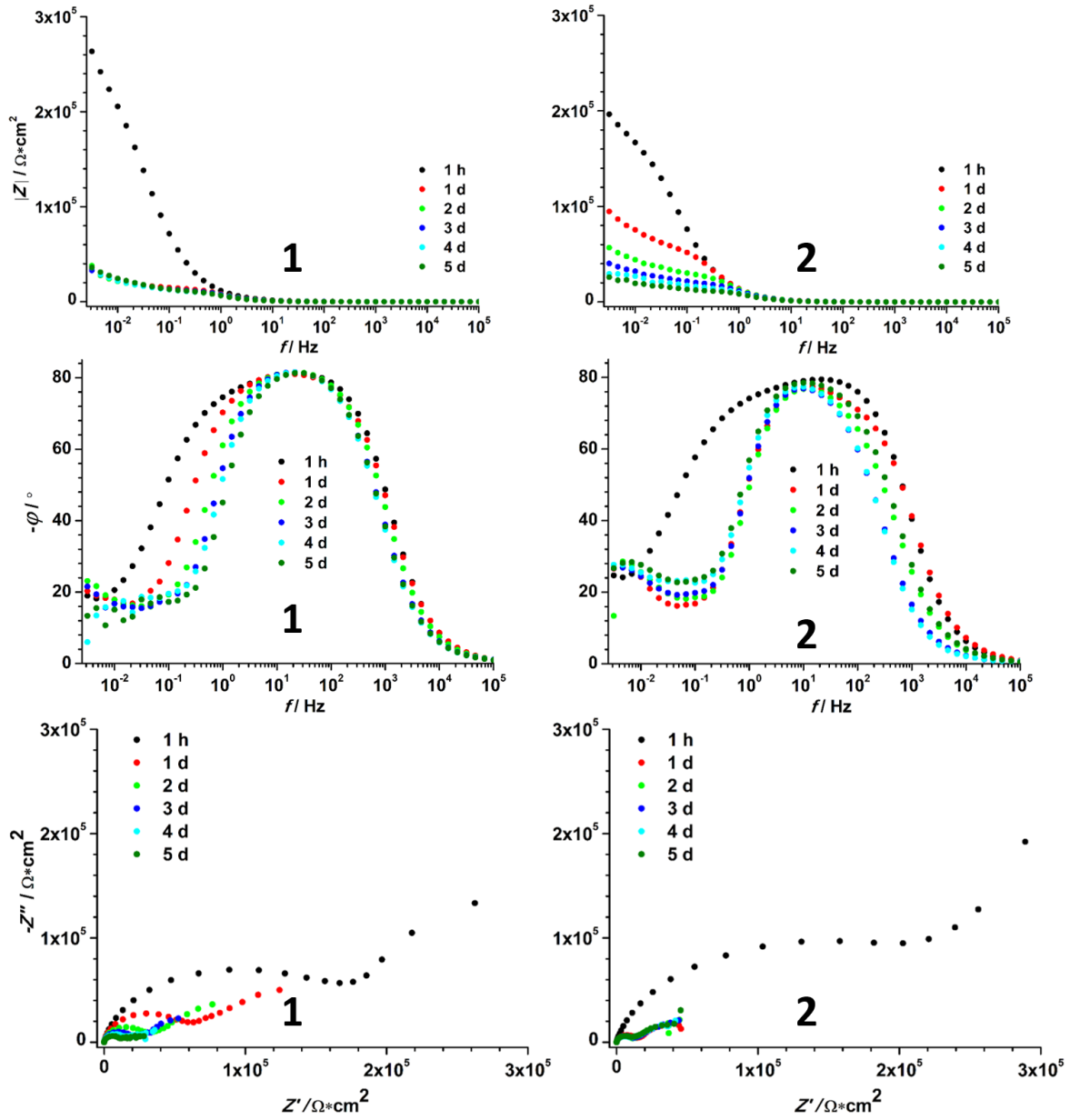


Figure S3: Bode and Nyquist diagrams for chemically pre-treated AlSi7Mg0.3 immersed in 0.5 M NaCl solution up to 5 days. 1 and 2 are two repetitions of each condition.

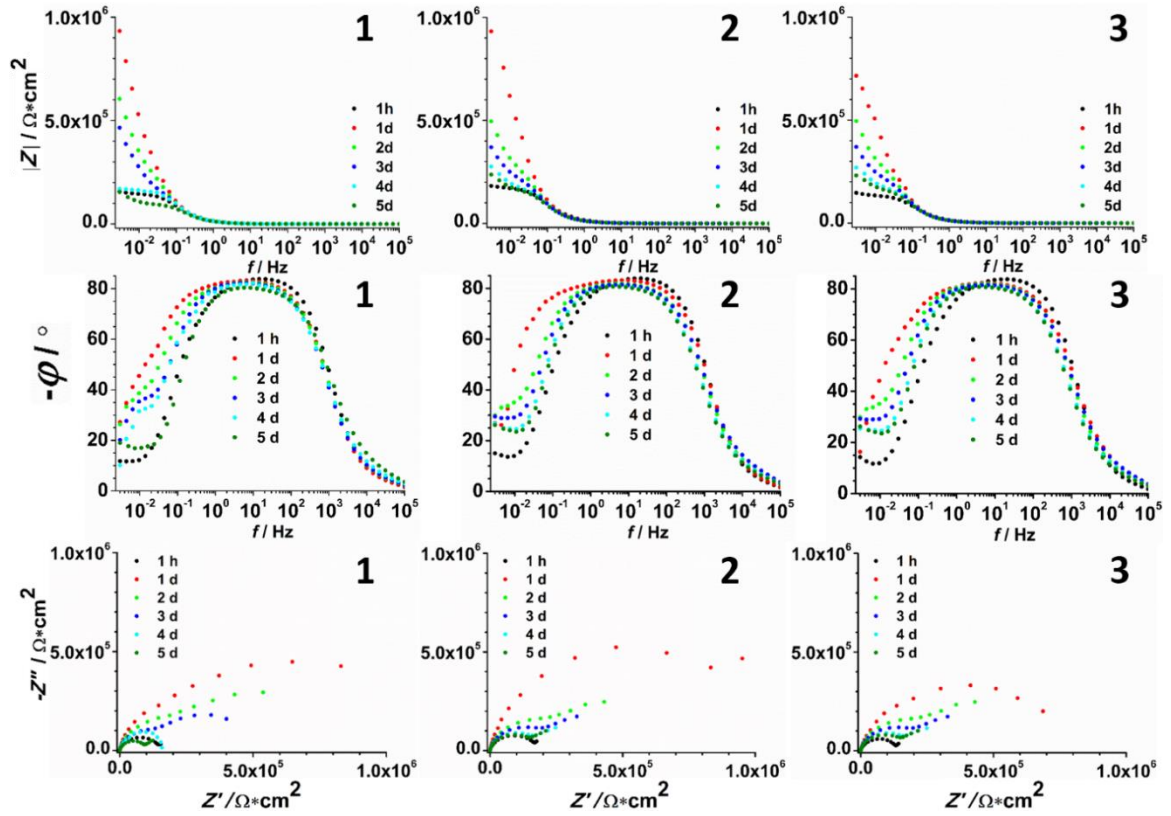


Figure S4: Bode and Nyquist diagrams for zirconium conversion coating prepared in a 100 ppm H_2ZrF_6 conversion bath for 10 minutes on AlSi7Mg0.3 immersed in 0.5 M NaCl solution for up to 10 days. 1, 2 and 3 are three repetitions of each condition.

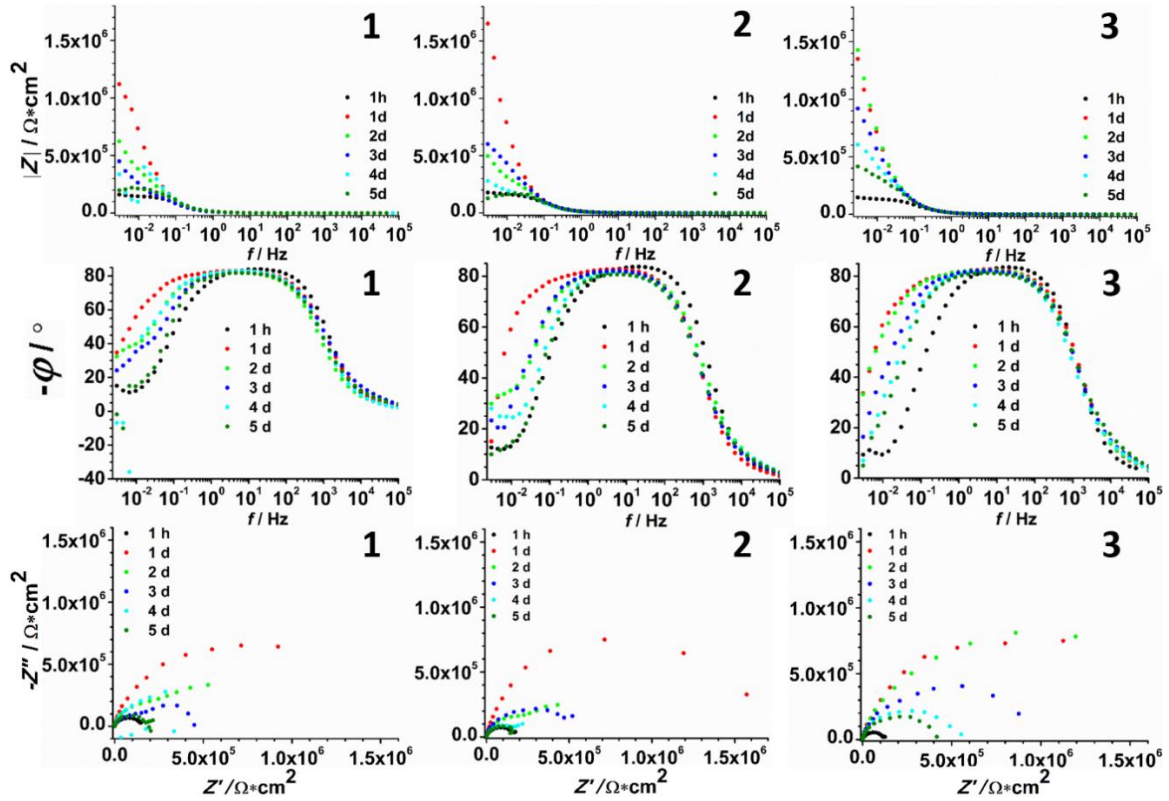


Figure S5: Bode and Nyquist diagrams for zirconium conversion coating prepared in a 150 ppm H_2ZrF_6 conversion bath for 10 minutes on AlSi7Mg0.3 immersed in 0.5 M NaCl solution for up to 10 days. 1, 2 and 3 are three repetitions of each condition.

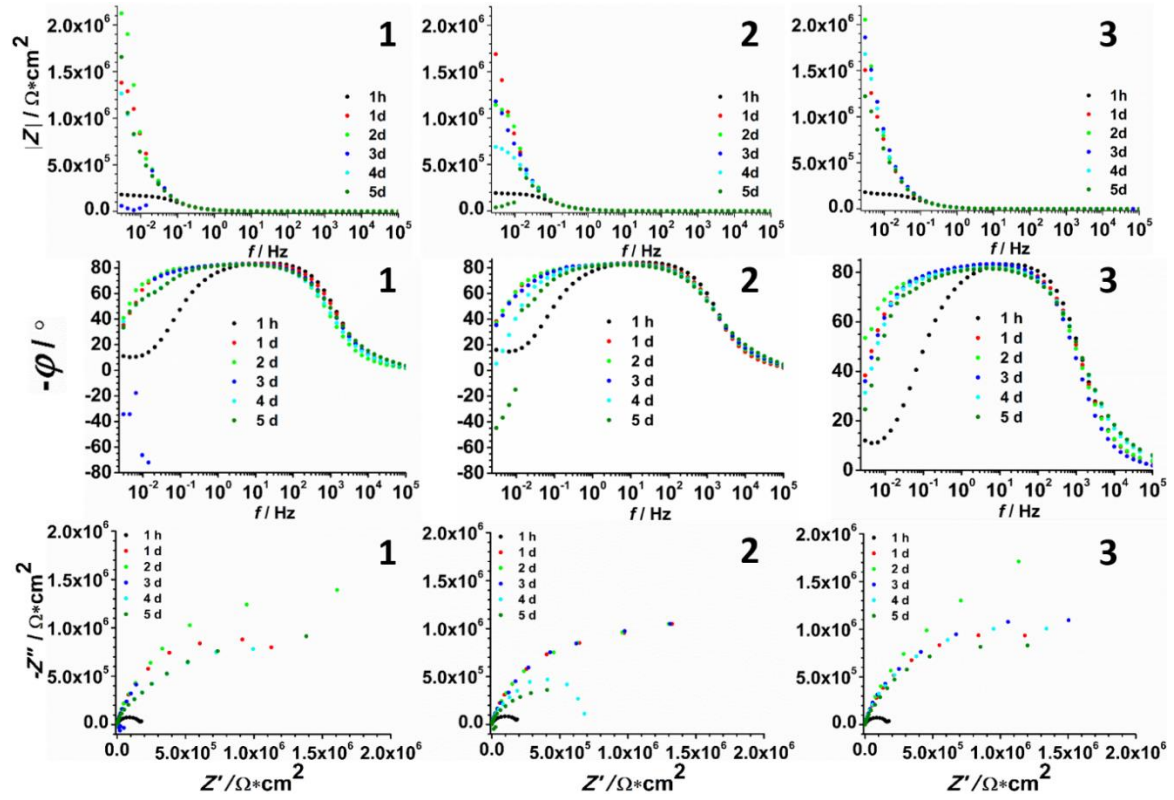


Figure S6: Bode and Nyquist diagrams for zirconium conversion coating prepared in a 175 ppm H_2ZrF_6 conversion bath for 10 minutes on AlSi7Mg0.3 immersed in 0.5 M NaCl solution for up to 10 days. 1, 2 and 3 are three repetitions of each condition.

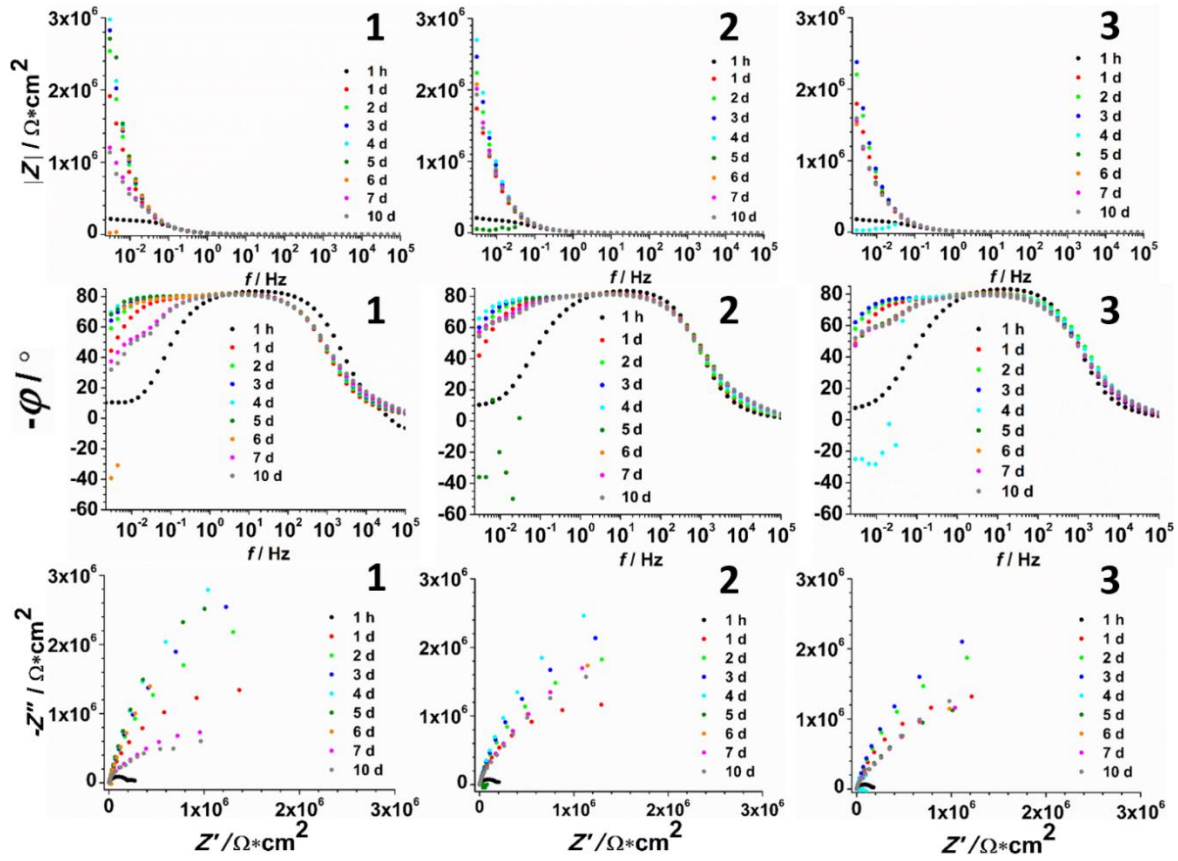


Figure S7: Bode and Nyquist diagrams for zirconium conversion coating prepared in a 200 ppm H_2ZrF_6 conversion bath for 10 minutes on AlSi7Mg0.3 immersed in 0.5 M NaCl solution for up to 10 days. 1, 2 and 3 are three repetitions of each condition.

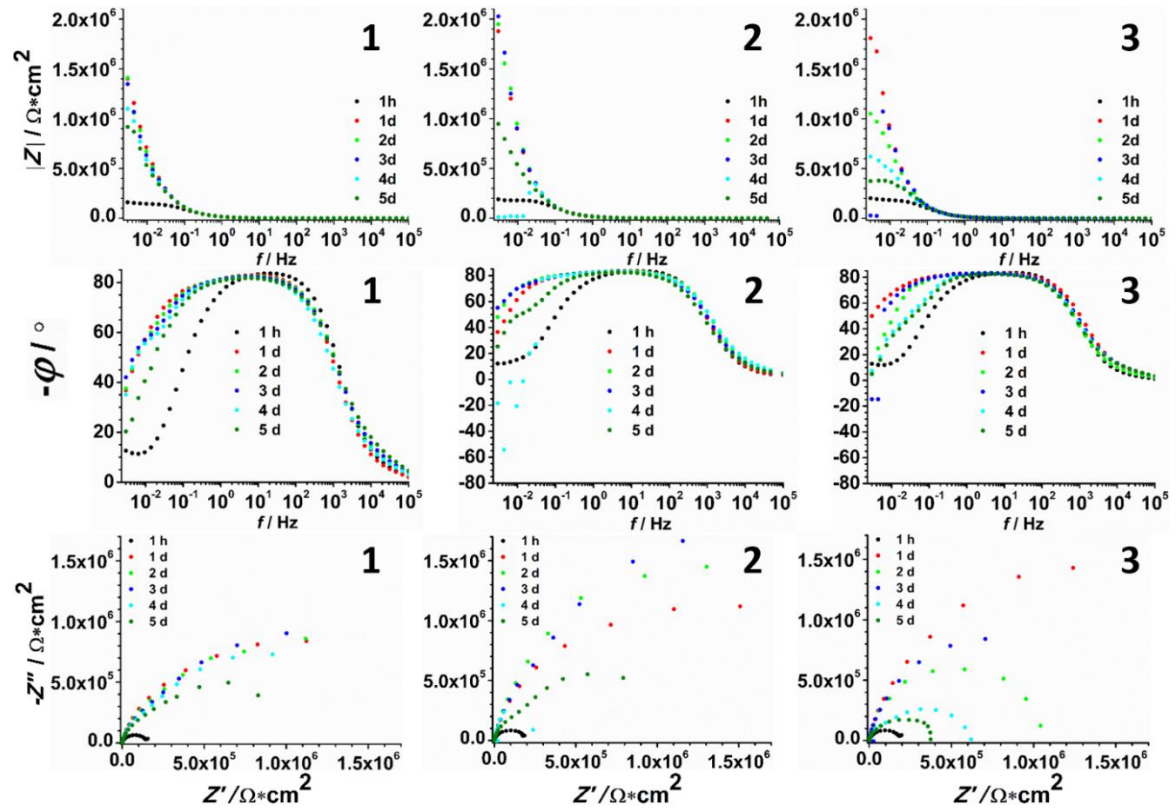


Figure S8: Bode and Nyquist diagrams for zirconium conversion coatings prepared in a 300 ppm H_2ZrF_6 conversion bath for 10 minutes on AlSi7Mg0.3 immersed in 0.5 M NaCl solution for up to 10 days. 1, 2 and 3 are three repetitions of each condition.

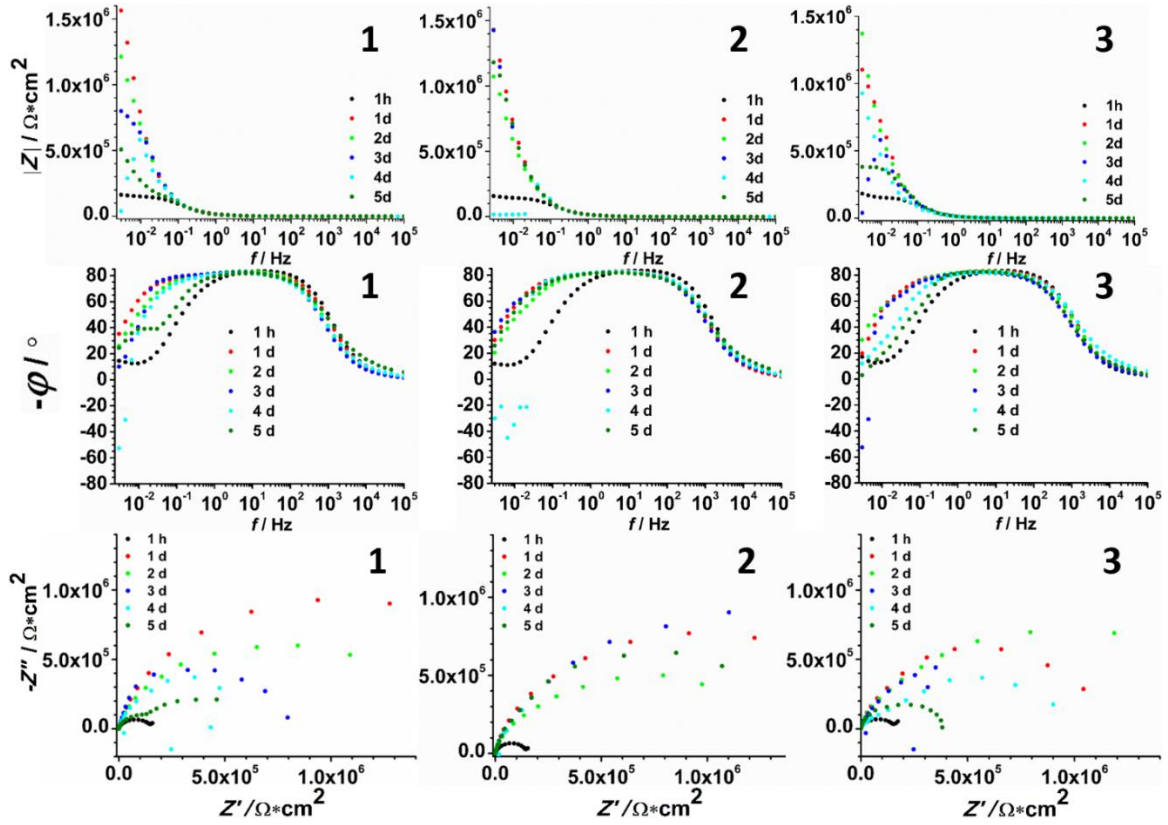


Figure S9: Bode and Nyquist diagrams for zirconium conversion coatings prepared in a 500 ppm H_2ZrF_6 conversion bath for 10 minutes on AlSi7Mg0.3 immersed in 0.5 M NaCl solution up to 10 days. 1, 2 and 3 are three repetitions of each condition.

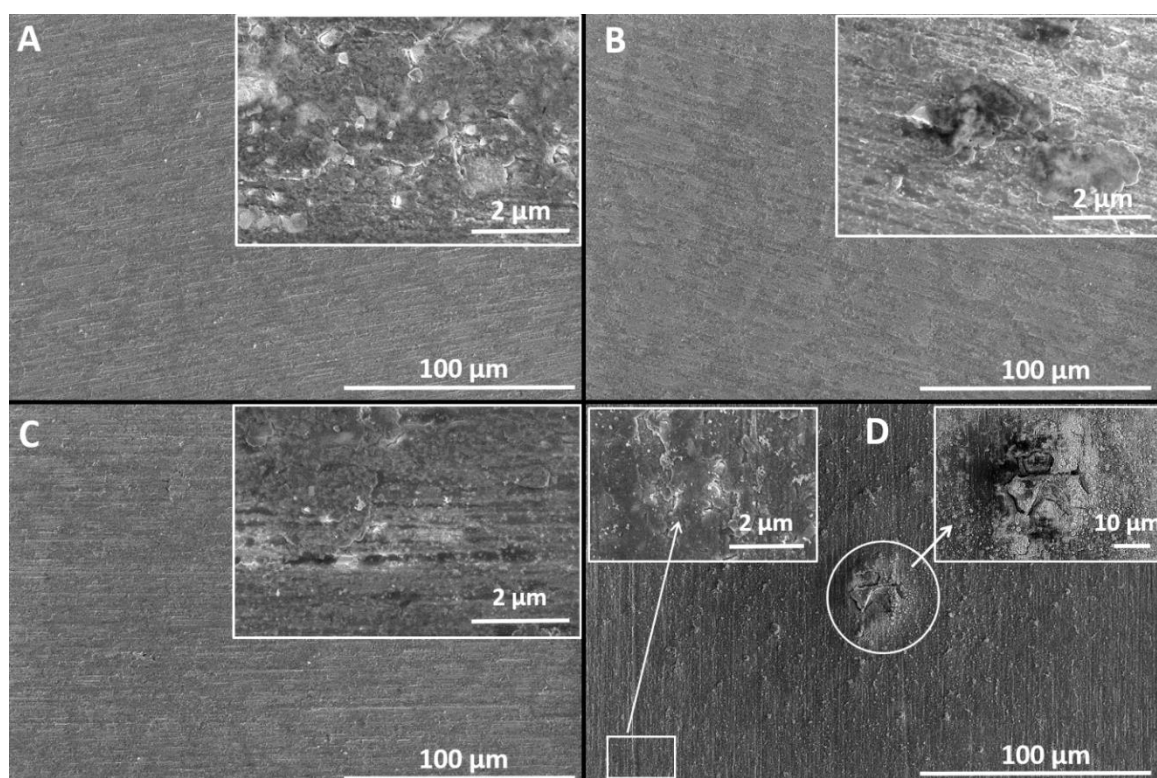


Figure S10: SEM (SE) images of ZrCC on AlSi7Mg0.3 prepared in a 200 ppm H_2ZrF_6 bath for a conversion time of 10 minutes and then immersed in 0.5 M NaCl solution for a different time: (a) as prepared, (b) 1 day, (c) 2 days and (d) 5 days.

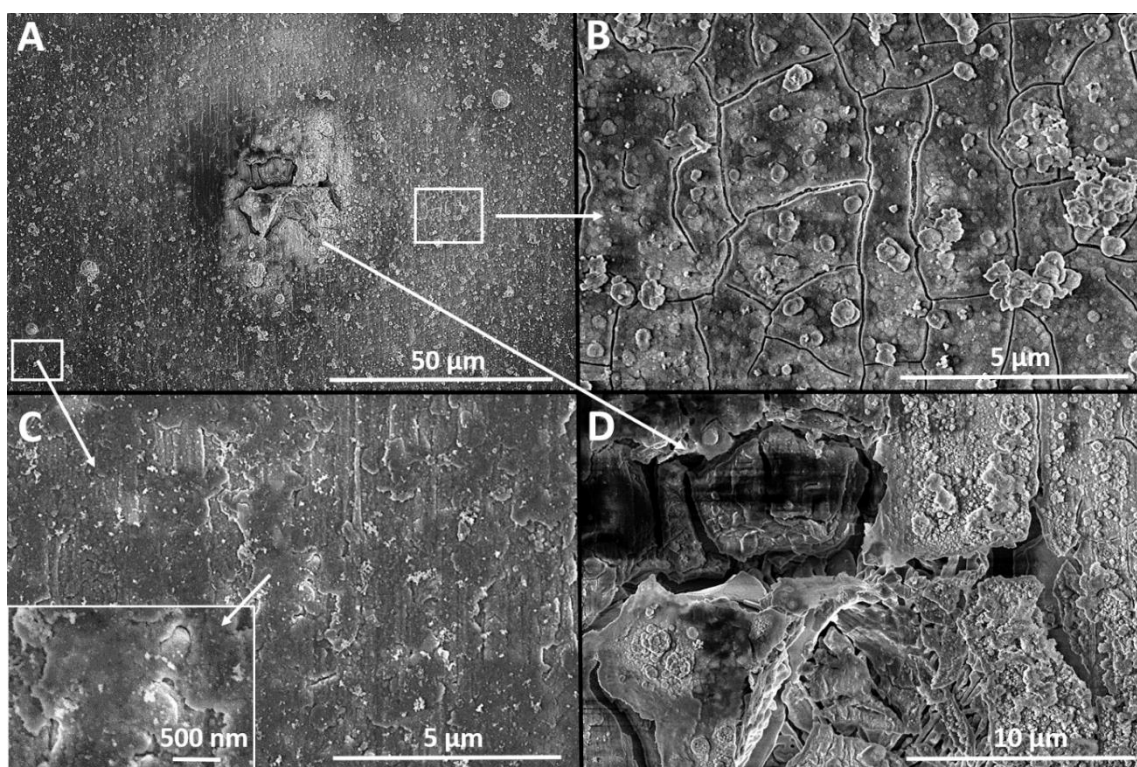


Figure S11: SEM (SE) images of ZrCC on AlSi7Mg0.3 prepared in a 200 ppm H_2ZrF_6 bath for a conversion time of 10 minutes and then immersed in 0.5 M NaCl solution for 5 days.

Table S1: EDS analysis of chemically pre-treated AlSi7Mg0.3 carried out at 30 spots. SEM and EDS mapping are presented in Fig. 2. The electron beam voltage of analysed spots was 20 kV (ca. 3 μm).

spot	at. % Al	at. % Si	at. % Mg	at. % Fe	at. % Ti
1	74.6	15.9	7.1	2.4	/
2	75.4	17.8	4.9	1.9	/
3	78.7	16.7	3.6	1.0	/
4	68.1	21.1	8.0	2.8	/
5	69.7	25.8	3.5	1.0	/
6	75.3	17.1	5.5	2.1	/
7	80.4	12.5	5.2	1.9	/
8	75.4	21.0	2.2	1.3	0.1
9	79.7	13.8	5.5	1.0	/
10	89.9	7.6	1.9	0.5	0.1
11	81.8	11.6	5.0	1.6	/
12	59.4	40.6	/	/	/
13	98.1	1.7	/	/	0.2
14	78.9	16.6	3.5	1.0	/
15	80.4	16.2	2.6	0.8	/
16	80.4	13.4	4.7	1.5	/
17	77.6	16.7	4.5	1.2	/
18	77.0	16.3	5.6	1.1	/
19	82.8	11.9	4.3	1.0	/
20	75.6	17.3	5.3	1.8	/
21	79.8	15.7	3.5	1.0	/
22	73.5	18.9	5.5	2.1	/
23	82.4	13.7	3.1	0.8	/
24	74.0	21.5	3.4	1.1	/
25	79.9	13.2	5.3	1.6	/
26	72.9	19.0	5.9	2.2	/
27	85.5	10.9	2.2	1.4	/
28	77.8	18.2	3.3	0.7	/
29	78.2	14.4	5.8	1.6	/
30	90.6	8.1	1.0	0.2	0.1

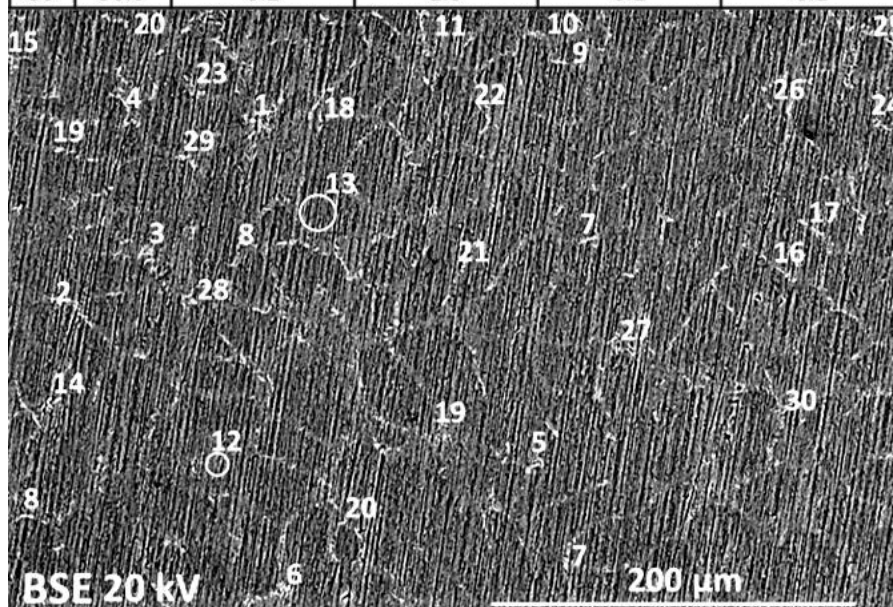


Table S2: The impedance modulus at 3 mHz ($\Omega \text{ cm}^2$) as a function of immersion time in 0.5 M NaCl solution for: mechanically pre-treated (MP) and chemically pre-treated (CP) and chemically pre-treated AlSi7Mg0.3 and zirconium conversion coated (100-500 ppm concentrations of H_2ZrF_6 in a conversion bath). (SD - standard deviation). Average values are presented in Fig. 5a.

$ Z _{3\text{mHz}} / \Omega \cdot \text{cm}^2$									
Sample	1 h	1 d	2 d	3 d	4 d	5 d	6 d	7 d	10 d
MP	2.4E+05	9.5E+04	6.8E+04	5.9E+04	5.6E+04	5.2E+04			
SD*	3.0E+03	5.0E+01	2.6E+03	7.5E+02	1.3E+03	6.4E+03			
CP	3.8E+05	9.1E+04	6.7E+04	6.0E+04	5.3E+04	4.1E+04			
SD	8.1E+04	4.33E+04	1.8E+04	9.40E+03	4.3E+03	1.4E+04			
100ppm	1.6E+05	8.6E+05	5.3E+05	4.0E+05	2.4E+05	2.1E+05			
SD	1.5E+04	1.0E+05	5.1E+04	4.5E+04	4.9E+04	3.6E+04			
150ppm	1.6E+05	1.4E+06	8.5E+05	6.6E+05	4.1E+05	2.5E+05			
SD	1.3E+04	2.2E+05	4.1E+05	2.0E+05	1.4E+05	1.2E+05			
175ppm	1.8E+05	1.5E+06	1.8E+06	1.0E+06	1.2E+06	9.7E+05			
SD	6.1E+03	1.3E+05	4.5E+05	7.4E+05	4.1E+05	6.9E+05			
200ppm	2.0E+05	1.82E+06	2.3E+06	2.6E+06	1.9E+06	1.4E+06	1.2E+06	1.6E+06	1.6E+06
SD	1.6E+04	7.5E+04	1.5E+05	1.9E+05	1.3E+05	1.1E+05	8.7E+05	3.4E+05	3.3E+05
300ppm	1.8E+05	1.51E+06	1.3E+06	1.1E+06	6.1E+05	6.9E+05			
SD	1.6E+04	3.8E+05	4.2E+05	7.2E+05	3.9E+05	2.5E+05			
500ppm	1.8E+05	1.4E+06	1.2E+06	6.9E+05	6.1E+05	6.7E+05			
SD	2.1E+04	2.5E+05	1.3E+05	5.2E+05	3.5E+05	2.6E+05			

Table S3: Open circuit potential (V vs. Ag/AgCl_(sat.)) at which electrochemical impedance spectra (Table S2) were measured. In the table, average values deduced from several repetitions at different samples are given (SD - standard deviation). Average values are presented in Fig. 5b.

<i>OCP</i> vs Ag/AgCl (sat.) / V									
<i>Sample</i>	1 h	1 d	2 d	3 d	4 d	5 d	6 d	7 d	10 d
<i>MP</i>	-0.70	-0.72	-0.73	-0.74	-0.76	-0.76			
<i>SD</i>	0.00	0.00	0.00	0.00	0.04	0.01			
<i>CP</i>	-0.76	-0.77	-0.77	-0.79	-0.81	-0.79			
<i>SD</i>	0.03	0.07	0.06	0.05	0.06	0.04			
<i>100 ppm</i>	-1.06	-0.68	-0.75	-0.77	-0.76	-0.80			
<i>SD</i>	0.00	0.01	0.03	0.05	0.07	0.06			
<i>150 ppm</i>	-1.07	-0.68	-0.71	-0.70	-0.72	-0.73			
<i>SD</i>	0.00	0.00	0.02	0.01	0.01	0.00			
<i>175 ppm</i>	-1.06	-0.67	-0.67	-0.67	-0.68	-0.68			
<i>SD</i>	0.01	0.01	0.00	0.00	0.02	0.00			
<i>200 ppm</i>	-1.11	-0.77	-0.71	-0.65	-0.63	-0.66	-0.68	-0.68	-0.67
<i>SD</i>	0.02	0.04	0.03	0.02	0.02	0.05	0.04	0.01	0.03
<i>300 ppm</i>	-1.07	-0.68	-0.67	-0.68	-0.69	-0.69			
<i>SD</i>	0.02	0.02	0.01	0.01	0.01	0.01			
<i>500 ppm</i>	-1.05	-0.69	-0.69	-0.67	-0.68	-0.70			
<i>SD</i>	0.01	0.01	0.03	0.01	0.01	0.02			

Table S4: Electrochemical data deduced from potentiodynamic polarization measurements recorded in 0.5 M NaCl (Fig. 8a) for mechanically pre-treated (MP), chemically pre-treated (CP) and zirconium conversion coated AlSi7Mg0.3. Samples were rested at OCP for 1 hour prior to electrochemical measurements. * $\Delta E = |E_{pit} - E_{corr}|$. Representative curves taken for figures in the article are shaded with yellow. (SD - standard deviation).

Sample	J_{corr} A cm ⁻²	E_{ocp} V	E_{corr} V	E_{pit} V	ΔE^* V	Ba mV/dec	$-\beta c$ mV/dec	$R_{p,LPR}$ Ω cm ²	$R_{p,tafel}$ Ω cm ²
MP	1.2E-07	—	—	—	0.07	107	205	1.7E+05	2.5E+05
SD	2.9E-08	0.69	0.72	0.65	0.02	42	1	9.3E+04	5.3E+04
CP	6.1E-08	—	—	—	0.05	116	180	4.6E+05	5.2E+05
SD	1.4E-08	0.70	0.71	0.66	0.04	19	43	8.7E+04	7.8E+04
100ppm	8.8E-08	—	—	—	0.49	302	185	4.5E+05	5.5E+05
SD	5.0E-09	1.00	0.98	0.50	0.03	49	44	7.3E+04	2.3E+04
150ppm	8.7E-08	—	—	—	0.53	279	202	4.3E+05	5.1E+05
SD	6.5E-09	1.07	1.04	0.51	0.04	16	25	6.9E+04	3.0E+04
175ppm	8.3E-08	—	—	—	0.41	289	190	4.7E+05	6.0E+05
SD	1.0E-08	0.97	0.99	0.58	0.11	27	27	1.4E+04	4.4E+04
200ppm	7.3E-08	—	—	—	0.45	264	206	5.9E+05	6.6E+05
SD	8.8E-09	0.98	0.99	0.54	0.11	24	13	1.7E+05	9.7E+04
300ppm	1.1E-07	—	—	—	0.53	281	179	3.9E+05	4.4E+05
SD	2.4E-08	1.08	1.09	0.56	0.02	9	11	6.8E+04	8.8E+04
500ppm	1.6E-07	—	—	—	0.47	262	219	2.8E+05	3.4E+05
SD	3.0E-08	1.04	1.01	0.54	0.08	14	40	9.0E+04	6.9E+04

Table S5: EDS analysis of the cross-section for zirconium conversion coatings prepared in a 200 ppm H_2ZrF_6 conversion bath for 10 minutes on AlSi7Mg0.3 after 5 days of immersion in 0.5 M NaCl (Fig. 13a). Map is the concentration within the white rectangle and spots 1 to 3 are point concentrations. The electron beam voltage of analysed spots 1-3 was 3 kV (ca. 100 nm).

Spot	at. % Al	at. % O	at. % Zr	at. % F	at. % Mg	at. % Si	at. % Zn	at. % Cu
1	13.4	58.9	/	0.5	/	2.6	24.7	/
2	44.8	43.8	6.1	1.0	0.3	3.0	0.9	/
3	15.8	44.5	7.9	0.9	0.3	28.6	2.0	/
Map	24.1	49.2	7.6	0.9	0.3	12.9	4.4	0.6

Table S6: EDS analysis of zirconium conversion coating on AlSi7Mg0.3 prepared in a 200 ppm H_2ZrF_6 conversion bath for 10 minutes and immersed in 0.5 M NaCl solution for 5 days. The analysis was performed at enumerated spots denoted in SEM images in Fig. 14. The electron beam voltage of analysed spots was 3 kV, corresponding to an analysis depth of ca. 100 nm and 20 kV corresponding to an analysis depth of ca. 3 μm .

spot	at. % Al	at. % O	at. % Zr	at. % F	at. % Mg	at. % Fe	at. % Si	at. % Zn	at. % Cu	at. % Ti
3kV										
1	31.4	61.9	2.0	0.5	0.1	/	3.0	0.6	0.4	/
2	22.2	49.6	/	0.6	1.0	/	24.7	1.9	/	/
3	30.6	62.9	2.1	0.6	/	/	1.8	0.8	1.1	/
4	22.2	66.3	/	0.5	/	/	/	/	/	/
5	33.4	61.6	3.3	0.6	/	/	1.1	/	/	/
6	30.5	69.5	/	/	/	/	/	/	/	/
20 kV										
1	71.1	20.2	0.3	/	0.3	0.1	7.8	0.1	trace	0.1
2	49.6	24.1	0.2	/	0.6	0.2	24.7	0.3	0.2	0.1
3	68.6	17.4	0.3	/	1.0	0.3	12.4	/	/	/
4	76.2	20.4	0.3	/	/	/	3.0	/	/	0.1
5	74.0	19.1	0.3	0.1	0.3	trace	6.1	/	/	0.1
6	47.0	44.2	0.2	/	0.5	/	7.8	/	0.2	/

Chapter 5

Comparison of Electrochemical Behaviour and Self-Sealing Effect of Zirconium Conversion Coatings Applied to Aluminium Alloy 2024, 3005, A356.0, 380.0, 5754 and 7075 in 0.5 M NaCl Solution

Abstract

Zirconium conversion coatings prepared in 200 ppm H_2ZrF_6 bath for optimal conversion time were applied on different aluminium alloys starting from 1xxx up to 7xxx series. Electrochemical behaviour and self-sealing ability of coatings were investigated by electrochemical impedance spectroscopy during immersion in 0.5 M NaCl for five days. Microstructural and surface characterization was carried out using SEM-EDS, XPS and ToF-SIMS techniques. All zirconium conversion coatings had a bi-layer structure, and average thickness in a range of 30–60 nm, except the coating applied on AA2024 which exhibited a single-layer structure and thickness of 12 nm. Coatings provided excellent corrosion protection and self-sealing behaviour when applied on AA3005, AAA356.0 and very good corrosion protection for AA380.0, AA5754 and AA1050A. On the other hand, these coatings did not provide adequate corrosion protection for AA2024 and AA7075.

Keywords: aluminium alloys, zirconium conversion coating, self-sealing

5.1 Introduction

Aluminium alloys (AAs) are one of the most important structural materials. They possess excellent strength to weight ratio, electrical and thermal conductivity and corrosion resistance [1]. Depending on their composition and type of fabrication (cast or wrought), these alloys differ in corrosion resistance and mechanical properties. AA2024 and AA7075 are mainly used in the aerospace industry due to their excellent strength-to-weight ratio;

however, they are most susceptible to corrosion. AA1050A and AA3005 have excellent corrosion resistance and medium strength and are used in packaging, appliance, architectural and chemical industry. AA5754 has excellent corrosion resistance and high strength; thanks to that, it is used in shipbuilding, marine industries and for crafting mechanical parts. It gains a metallic blue colour when anodized and is a preferable choice for use in the architectural industry. Due to its high strength-to-weight ratio and excellent corrosion resistance cast, AAA356.0 is used in shipbuilding, marine industries, automotive industries, and for crafting aircraft engine parts. Cast AA380.0 has excellent mechanical properties but lower corrosion resistance in comparison to AAA356.0; it is used in automotive industries and crafting mechanical parts.

In the presence of Cl^- ions or harsh environments, aluminium alloys are prone to localized corrosion and require additional protection [2, 23]. The best possible protection for aluminium alloys is an application of coats. The coating system is complex and consists of conversion coatings/anodization, primers and topcoat [52]. The first step in the application of coat is conversion coating or anodization. The anodized layer is thicker and provides better corrosion protection than conversion coatings. It is mainly used when excellent corrosion protection is required like in aircraft industries. When a simple and economical process is required, the conversion coating is a preferable choice, for example, in the automotive and appliance industries.

The primary role of conversion coating is to promote adhesion of topcoats and reduce the rate of cathodic delamination and filiform corrosion. For the last 90 years, chromate conversion coatings have been the best conversion coatings for the protection of aluminium alloys. However, chromate conversion coatings are forbidden due to health and environmental hazards. [16] Currently, the only viable chromium-free conversion coating on the market are zirconium conversion coatings (ZrCCs) [53]. ZrCCs are applied mainly by immersion of a metal sample in H_2ZrF_6 conversion baths. In addition to H_2ZrF_6 , conversion bath can contain different inorganic and organic components [53, 89]. Organic components promote adhesion and improve corrosion resistance while inorganic components mainly accelerate the conversion process. Zirconium conversion coating is nano-coating with a thickness of 30 nm to 100 nm. It typically has a bi-layer structure, where the outer layer is composed of zirconium oxide/hydroxide, and the inner layer is composed of aluminium oxyfluoride, zirconium oxide and aluminium oxide.

Since the discovery of ZrCCs in the late 1980s and pioneering research in early 1990, zirconium conversion technology has been developing quickly [83-86]. There have been more than 100 hundred scientific papers about zirconium conversion coatings applied on aluminium alloys, [64, 66, 83-86, 90-93, 96, 99-101, 103, 104, 106, 107, 112-130] magnesium alloys, [131, 132] zinc [133, 134] and steel [89, 97, 102, 135-143] in the last 30 years. The process of ZrCC formation has three stages: initiation, growth and overgrowth [53, 93]. It can be monitored by measuring the open circuit potential of a substrate during the formation of conversion coating which is driven by the difference in Volta potentials between cathodic (more noble) areas at the surface, like intermetallic particles and grain boundaries, and anodic (less noble) aluminium alloy matrix. The process is initiated by a chemical attack of free fluoride ions that removes natural aluminium oxide and activates aluminium alloy [94, 95]. At the same time, the surface is activated by hydrogen evolution, and oxygen reduction reactions at noble areas leading to local alkalization up to $\text{pH}=8.5$ [96]. In such an alkaline environment zirconium oxide/hydroxide is precipitated, and conversion coating is formed firstly at noble areas and then

continues to grow in lateral direction covering the whole aluminium alloy surface [93, 99, 100]. The final zirconium conversion coating will be much thicker at initiation sites compared to the aluminium alloy matrix.

Several studies showed that zirconium conversion coatings increase the adhesiveness of substrate and the interfacial bond strength between substrate/topcoats [105, 113, 140, 144-148]. They also reduce the rate of cathodic delamination/filiform corrosion [64, 65, 105, 142, 143]. Surface cleaning/pre-treatment before application of ZrCC has an essential effect on the rate of the conversion process and final properties of coatings, i.e., pre-treatments that produce more cathodic sites (e.g. conversion baths containing copper or other noble metal ions) will increase the rate of the conversion, while pre-treatments that produce a more hydroxylated surface were reported to be more prone to interactions with F^- ions and thus stimulate the chemical dissolution of the metal surface in the first stage of the process allowing faster deposition rate and thicker final coating [66, 103]. It was reported that the rate of conversion increases by increasing the concentration of free fluoride ions in the conversion bath. Introduction of inorganic corrosion inhibitors (such as cerium-based compounds) in conversion bath formulas was beneficial for final coatings, providing a certain level of active corrosion protection [129, 149]. Studies showed that the addition of phosphate compounds increased the thickness and corrosion resistance of ZrCCs, whereas sealing of anodized AA7075 showed promising results and outperformed hot water sealing [130, 150]. ZrCCs improve dry/wet adhesion and interfacial bond strength of organic coats [105]. It is commonly accepted that ZrCCs provide only barrier protection to aluminium alloys. However, in our last studies, we reported that the impedance magnitude of ZrCCs applied on wrought alloys AA3003, AA3005 and cast alloy AAA356.0 was improving during immersion in 0.5 M NaCl [91, 92, 107]. This effect was more pronounced on ZrCC applied on AA3005 compared to that applied on AAA356.0 [92]. We ascribed the improvement of corrosion resistance of ZrCCs to a self-sealing effect and possible active corrosion protection. It appears that this effect depends on the aluminium alloy composition. The aim of this work was therefore to evaluate the corrosion resistance, and extent of the self-sealing effect of ZrCC applied on seven aluminium alloys of different series and fabrication processes (wrought and cast): AA1050A (Al, 1xxx), AA2024 (Al-Cu-Mn-Mg, 2xxx), AA3005 (Al-Mn-Mg, 3xxx), AAA356.0 (Al-Si-Mg, 3xx.x), AA380.0 (Al-Si-Cu, 3xx.x), AA5754 (Al-Mg-Mn, 5xxx) and AA7075 (Al-Zn-Mg-Cu, 7xxx). This investigation should provide more insight into the influence of a specific alloying element on the performance of ZrCC. The composition of the ZrCC was selected based on our previous studies to give the optimal results: 200 ppm H_2ZrF_6 bath, pH 4.5, stirring rate 450 rpm and room temperature; optimal conversion time was then determined for each alloy individually [91, 92]. Microstructure and surface composition of ZrCCs were investigated with scanning electron spectroscopy with energy-dispersive X-ray spectroscopy (SEM-EDS), X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) methods. Electrochemical behaviour of ZrCCs was investigated by measuring the open circuit potential (OCP) vs. time curves, potentiodynamic polarization curves and electrochemical impedance spectra (EIS) in 0.5 M NaCl solution.

5.2 Experimental

5.2.1 Materials, sample preparation and chemicals

Aluminium alloy substrates

The following aluminium alloys were used as substrates:

(1) 1050A-O / EN AW⁵-1050A / EN AW-Al99.5 / UNS⁶-A91050 with nominal composition (Al 99.50 wt.%, Fe 0-0.4 wt.%, Si 0-0.25 wt.%, Zn 0-0.07 wt.%, Mn 0-0.05 wt.%, Ti 0-0.05 wt.%, Cu 0-0.05 wt.%, Mg 0-0.05 wt.%) produced by Impol 2000 d.d. (Slovenska Bistrica, Slovenia) in the form of a 1.5 mm thick sheet. Samples used in experiments were cut in a rectangular shape with dimensions 3 cm × 3 cm.

(2) 2024-T3 / EN AW-2024 / EN AW-AlCu4Mg1 / UNS-A92024 with a nominal composition (Cu 4.35 wt.%, Mg 1.33 wt.%, Fe 0.25 wt.%, Mn 0.53 wt.%, Zn 0.1 wt.%, other 0.07 wt.%, Al remaining) produced by Kaiser Aluminum in the form of 1 mm thick sheet. Samples used in experiments were cut in a rectangular shape with dimensions 3 cm × 3 cm.

(3) 3005-O / EN AW-3005 / EN AW-AlMn1Mg0.5 / UNS-A93005 with nominal composition (Mn 1-1.5 wt.%, Mg 0.2- 0.6 wt.%, Fe 0-0.7 wt.%, Si 0-0.6 wt.%, Cu 0-0.3, Zn 0-0.25 wt.%, Cr 0-0.1 wt.%, Ti 0-0.1 wt.%, residuals 0.15 wt.%) in the form of a foil (thickness 70 microns) produced by Impol 2000 d.d. (Slovenska Bistrica, Slovenia) was used as a substrate. The composition given is provided by the supplier. Samples used in experiments were cut in a rectangular shape with dimensions 3 cm × 3 cm.

(4) A356.0-T6 / EN AC⁷ 42100 / EN AC-AlSi7Mg0.3 / UNS-A13560 with nominal composition (Si 6.5-7.5 wt.%, Fe 0.15 wt.%, Cu 0.03 wt.%, Mn 0.10 wt.%, Mg 0.30-0.45 wt.%, Zn 0.07 wt.%, Ti 0.18 wt.%) produced by TALUM d.d. (Kidričevo, Slovenia) was used as a substrate. This is the alloy used for castings and corresponds to the following standards: International ISO-A356.0, Germany-3.2371, UNS-A13560, A356.0 and USA-A356.0. Samples used in experiments were cut in a rectangular shape with dimensions 2.5 cm × 4 cm × 0.3 cm.

(5) 380.0-T6 / EN AC 46000 / EN AC-AlSi9Cu3(Fe) / UNS-A03800 with nominal composition (Si 8.0-11.0 wt.%, Cu 2.0-4.0 wt.%, Fe 0.6-1.1 wt.%, Zn 1.2 wt.%, Mn 0.55 wt.%, Mg 0.15-0.55 wt.%, Cr 0.15 wt.%, Ni 0.55 wt.%, Pb 0.35 wt.%, Sn 0.25 wt.%, Ti 0.20 wt.%) produced by TALUM d.d. (Kidričevo, Slovenia) was used as a substrate. Samples used in experiments were cut in a rectangular shape with dimensions 2.5 cm × 4 cm × 0.3 cm.

(6) 5754-H18 / EN AW-5754 / EN AW-AlMg3 / UNS-A95754 with nominal composition (Mg 2.6-3.6 wt.%, Mn 0-0.5 wt.%, Si 0-0.4 wt.%, Fe 0-0.4 wt.%, Cr 0-0.3 wt.%, Zn 0-0.2 wt.%, Ti 0-0.15 wt.%, Cu 0-0.1 wt.%) produced by Impol 2000 d.d. (Slovenska Bistrica, Slovenia) in the form of a 1.5 mm thick sheet. Samples used in experiments were cut in a rectangular shape with dimensions 3 cm × 3 cm.

(7) 7075-T6 / EN AW-7075 / EN AW-AlZn5,5MgCu / UNS-A97075 with a nominal composition (Zn 5.81 wt%, Mg 2.55 wt%, Fe 0.21 wt%, Si 0.08 wt%, Cu 1.67 wt%, Al remaining) produced by Kaiser Aluminum in the form of a 1 mm thick sheet. Samples used in experiments were cut in a rectangular shape with dimensions 3 cm × 3 cm.

⁵ EN AW = European standard (Euronorm) Aluminium Wrought

⁶ UNS = Unified numbering system

⁷ EN AC = European standard (Euronorm) Aluminium Cast

The following chemicals were used for experiments: NaCl (for analysis, Fischer Scientific, Leicestershire), H_2ZrF_6 (50 wt.% in water, Sigma-Aldrich, Saint Louis, USA), NH_4HCO_3 (reagent grade, Sigma-Aldrich, Steinheim, Germany) and Metaclean® (alkaline cleaner, Amity international, Barnsley, United Kingdom). Milli-Q Direct water with a resistivity of $18.2 \text{ M}\Omega\cdot\text{cm}$ at 25°C (Merck, Darmstadt, Germany) was used for rinsing and for solution preparation.

pH was measured using a pH meter 827 pH-lab equipped with Unitrode/Pt1000 (Metrohm AG, Herisau, Switzerland). Teflon beakers ($V=1 \text{ L}$) were used for conversion baths, while glass beakers ($V=600 \text{ mL}$) were used for alkaline cleaner and rinsing baths. Sample holders were made of Teflon and conversion coating solutions were stored in polyethylene bottles.

5.2.2 Preparation of conversion coatings

Before immersion in a conversion coating bath, samples were ground on SiC papers ranging from 320- to 4000-grit using a grinding/polishing machine LaboPol-20 (Struers, Ballerup, Denmark). Immediately after grinding, samples were ultrasonicated in absolute ethanol for 5 minutes using an ultrasonic bath Elmasonic P (Elma, Germany) at 37 kHz and 100% power. After cleaning, samples were dried with N_2 and conserved in a desiccator until the chemical cleaning step. Samples were chemically cleaned by immersion in 5 wt.% Metaclean solution ($T=57^\circ\text{C}$, stirring rate 150 rpm) for 3 minutes. Immediately afterwards, samples were firstly washed off with Milli-Q Direct water and then dipped in Milli-Q Direct water bath for 45 seconds. The sample was then immediately dipped in a conversion coating bath ($T=25^\circ\text{C}$, stirring rate 450 rpm). The concentration of conversion bath was 200 ppm of H_2ZrF_6 . pH was set to 4.8 with 15 wt. % NH_4HCO_3 . Following the conversion bath step, the sample was immediately rinsed with Milli-Q Direct water and then dipped in Milli-Q Direct water bath for 1 minute. Samples were then dried with an N_2 stream and left to dry in air for 24 hours. Mechanically ground/polished samples are denoted MP, mechanically ground/polished and chemically pre-treated samples are denoted CP, and zirconium conversion coated CP samples are denoted ZrCC-xxxx or ZrCC-xxx, where xxxx and xxx.x stand for four digits used to designate wrought and cast aluminium alloys, respectively; note that for AA A356.0 the designation ZrCC-A356.0 is used.

5.2.3 Electrochemical characterization

Electrochemical experiments were carried out with a Multi Autolab/M204 (Metrohm Autolab, Utrecht, Netherlands) potentiostat/galvanostat controlled by Nova 2.1 software. Measurements were conducted in a standard three-electrode flat cell with a volume of 250 mL. The sample was the working electrode, carbon rod was the counter electrode, and a saturated $\text{Ag}/\text{AgCl}_{(\text{sat})}$ electrode as the reference electrode ($E_{\text{SHE}} = 0.198 \text{ V}$). All potentials in the text refer to the $\text{Ag}/\text{AgCl}_{(\text{sat})}$ scale. The electrolyte was freshly prepared 0.5 M NaCl. The area of the working electrode was 1 cm^2 and the temperature of the electrolyte was 25°C .

Prior to electrochemical measurements, the sample was allowed to rest at open circuit potential (OCP) for 1 hour. Electrochemical measurements were conducted in the following sequence from least destructive to more destructive: (i) measurement of the OCP as a function of resting time, (ii) recording of linear polarization resistance curves, and (iii) recording of potentiodynamic polarization curves. The system was allowed to rest for 10 seconds before switching to the next electrochemical technique.

Linear polarization resistance curves (LPR) were run in the range - 10 to 10 mV vs. OCP using a 0.1 mV/s scan rate. Polarization resistance ($R_{p, LPR}$) was determined as the slope of the fitted potential (E) vs. current density (j) curve using Nova 2.1 software. Potentiodynamic polarization curves were recorded in the potential range starting -250 mV vs. OCP in an anodic direction until current density reached 0.1 mA/cm². The scan rate was 1 mV/s.

Corrosion current density and corrosion potential were determined using Nova 2.1 software based on the Tafel extrapolation method [151]. Polarization resistance was calculated from parameters obtained with the Tafel extrapolation ($R_{p, Tafel}$) method using Nova 2.1 software based on equation (11) in accordance with standard ASTM G59-97 [152].

$$R_{p, Tafel} = B / J_{corr} \quad (11)$$

where B is the Stern-Geary constant.

Electrochemical impedance spectroscopy (EIS) spectra were recorded from 100 kHz to 3 mHz frequency using an AC potential amplitude of 10 mV (rms). Spectra were recorded at the OCP, periodically every day up to 5 days of immersion.

Electrochemical measurements were repeated for each condition for at least three different samples. Representative measurements are presented in plots, and average values with standard deviation are given. When indicated, average values are also given in plots (i.e. for $|Z|_{3mHz}$ and OCP).

5.2.4 Microstructural characterization

SEM images were taken in secondary electron (SE) and back-scattered (BSE) modes using an FEI Helios Nanolab 650 microscope, and EDS spectra were taken using an Oxford Instruments AZtec system with X-max SDD (50 mm²) detector. The analysed area was 100 nm² with an analysis depth of 100 nm (near-surface condition) at 3 kV beam energy. EDS mapping was recorded with 3 kV beam energy and resolution of 1024 lines. Prior to analysis, samples were coated with a thin carbon layer to reduce the charging effect.

ToF-SIMS ion depth profiles were made using the ToF-SIMS V spectrometer (ION TOF GmbH - Munster, Germany). The analysis chamber was operated at a pressure below $\sim 10^{-9}$ mbar. Depth profiles for negative ions were recorded by interlacing a pulsed 30 keV Bi⁺ primary ion source delivering 1.2 pA of target current over a $100 \times 100 \mu\text{m}^2$ area with sputtering using a 2 keV Cs⁺ source beam delivering 523 nA of target current over a $400 \times 400 \mu\text{m}^2$ area. The sputtering rate for ToF-SIMS depth profiling was determined by depth profiling of a thin film of Al₂O₃ of known thickness (50 nm) on Si substrate under the same condition as applied for other samples. The sputtering rate was 0.30 nm/s (± 0.02 nm/s).

XPS was carried out using a PHI-TFA XPS spectrometer (Physical Electronics Inc.). The vacuum during the XPS analysis was in the range of 10^{-9} mbar. The analysed area was 0.4 mm in diameter, and the depth about 3-5 nm and X-rays were provided from a monochromatic Al K α source at a photon energy of 1486.6 eV. XPS spectrometer was nominally operated at an energy resolution of 0.6 eV measured on the Ag 3d_{5/2} peak. XPS spectra were analysed by Multipack software, version 8.0 (Physical Electronics Inc.). Spectra to normalized relative to the position of C 1s peak at 284.8 eV.

5.3 Results and Discussion

5.3.1 OCP measurements during the formation of conversion coating

The conversion coating process was followed by measuring the open circuit potential of aluminium alloys immersed in conversion bath of 200 ppm H_2ZrF_6 (Fig. 5.1). Declining parts of OCP vs. time curves represent the phase of surface activation and initiation of coating formation (Fig. 5.1). During this phase, natural aluminium oxide is removed by an attack of free F^- ions and surface is activated for coating formation [94, 95]. Immediately after the removal of natural aluminium oxide, hydrogen evolution and oxygen reduction reactions start at intermetallic particles (IMPs). These reactions increase local pH up to 8.5, causing precipitation of ZrCC [96]. The minimum in OCP curve represents the point at which the rate of surface activation and the rate of conversion coating formation are equal. Afterwards, the rate of conversion coating formation prevails, leading to coating growth in a lateral direction (Fig. 5.1). Maximum or plateau in OCP diagram (Fig. 5.1, asterisk marks) represents an optimal conversion time at which the coating is fully formed. At longer times, the coating tends to grow further, but due to internal stress and formation of hydrogen microbubbles, it will crack and lose barrier properties (Fig. 5.1) [91, 98, 102].

Rate of activation, coating formation and optimal conversion time depends on aluminium alloy microstructure and conversion bath composition. The presence of more noble areas (IMPs, grain boundaries or phases) compared to aluminium alloy matrix will increase the rate of conversion coating growth, giving a shorter optimal conversion time. At the same time, the less stable natural aluminium oxide film will be easier to remove by the action of free F^- ions giving a faster rate of surface activation, and, consequently, a shorter optimal conversion time. Optimal conversion times for ZrCC formation in 200 ppm H_2ZrF_6 conversion bath as a function of aluminium alloy substrates are given in Table 5.1.

AA2024 required the shortest conversion time due to the presence of a high amount of Cu containing IMPs. In contrast, AA1050A required the longest optimal conversion time due to a small number of IMPs. Optimal conversion times listed in Table 5.1 were used in the following experiments.

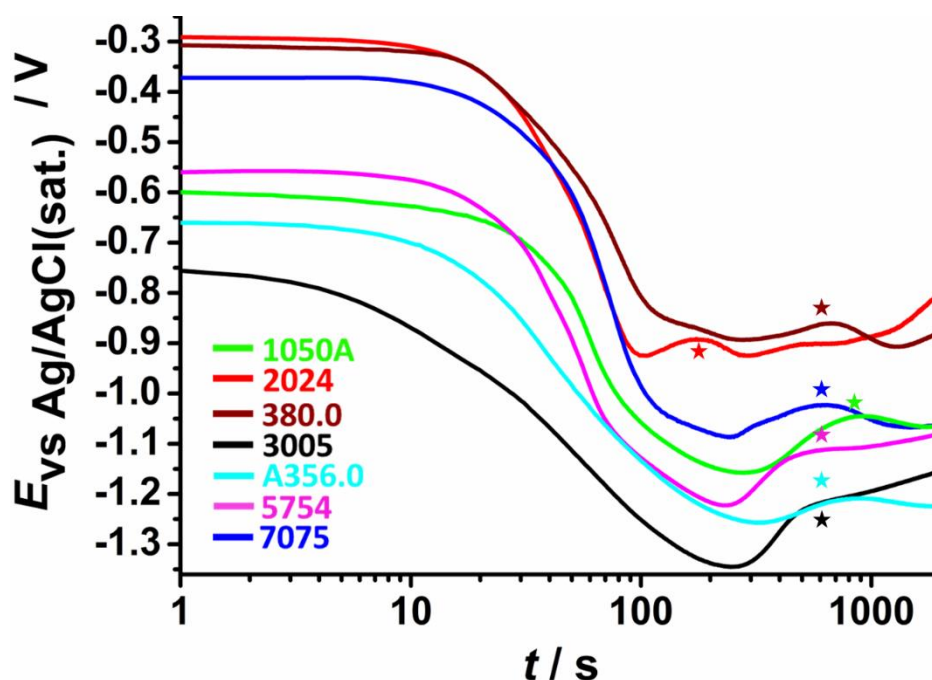


Figure 5.1: Open circuit potential during the formation of zirconium conversion coatings on aluminium alloys. Presented curves are mean values of three measurements.

Table 5.1: Optimal conversion times for the formation of ZrCC on different aluminium alloys in 200 ppm H_2ZrF_6 conversion bath.

Aluminium alloy	Optimal conversion time, minutes
1050A	15
2024	3
3005	10
A356.0	10
380.0	10
5754	10
7075	10

5.3.2 Electrochemical potentiodynamic curves

Potentiodynamic polarization curves of MP, CP and ZrCC aluminium alloys immersed in 0.5 M NaCl are presented in Fig. 5.2. Before measurements, samples were rested for 1 h. Electrochemical data deduced from potentiodynamic polarization curves are presented in Tables 5.2-5.4. The corrosion resistance of mechanically pre-treated aluminium alloys based on electrochemical data (small j_{corr} , large R_p) was in the following order: $380.0 \leq 2024 \leq 7075 \leq 1050 \leq 5754 \leq \text{A356.0} \leq 3005$ (Fig. 5.2a, Table 5.2). AAs 380.0, 2024 and 7075 had corrosion current densities in range $5 \cdot 10^{-7} \text{ A} \cdot \text{cm}^{-2}$ to $7 \cdot 10^{-7} \text{ A} \cdot \text{cm}^{-2}$ and did not show any passivity ($\Delta E \approx 0 \text{ V}$). This result indicates their low corrosion resistance and high susceptibility to pitting due to the presence of a high amount of noble Cu containing IMPs in AA380.0 and AA2024 and less noble Zn containing IMPs in AA7075. The AA1050A showed high resistance to pitting

corrosion due to the absence of noble IMPs resulting in a passivity window ($\Delta E = |E_{\text{pit}} - E_{\text{corr}}|$) of ≈ 0.13 V and current density of $7 \cdot 10^{-7} \text{ A} \cdot \text{cm}^{-2}$. Thanks to the presence of Si and Mg, AAs A356.0 and 5754 exhibit better corrosion resistance with ΔE of 0.07 V and 0.05 V and j_{corr} of $1.7 \cdot 10^{-7} \text{ A} \cdot \text{cm}^{-2}$ and $1.2 \cdot 10^{-7} \text{ A} \cdot \text{cm}^{-2}$, respectively. The AA3005, that contains Mn, showed the highest corrosion resistance with $\Delta E = 0.15$ V and j_{corr} of $3.9 \cdot 10^{-7} \text{ A} \cdot \text{cm}^{-2}$. These results were expected and were in good agreement with the literature [4].

Chemical pre-treatment induced the reduction of the passivity window and j_{corr} values for most of the alloys (Fig. 5.2b, Table 5.2). In other words, chemical pre-treatment cleaned and activated the surface of aluminium alloys by removing the aluminium oxide layer from IMPs. The only exception was AAA356.0 which was passivated after chemical pre-treatment exhibiting j_{corr} of $6.1 \cdot 10^{-8} \text{ A} \cdot \text{cm}^{-2}$ and ΔE of 0.05 V (Fig. 5.2b, Table 5.2). This was probably due to the production of a more uniform aluminium oxide passive layer and passivation of Mg-rich IMPs in the alkaline environment.

Zirconium conversion coating process improved the corrosion resistance of aluminium alloys; it provided barrier protection by increasing ΔE and reducing j_{corr} (Fig. 5.2C, Table 5.4). The corrosion potential of ZrCC-coated alloys was shifted towards more negative values in comparison with MP and CP, indicating cathodic inhibition. Barrier protection of ZrCCs based on the ΔE values was in the following order: A356.0 $\geq$ 1050A $\geq$ 5754 $\geq$ 3005 $\geq$ 2024 $\geq$ 7075 $\geq$ 380.0, while in the following order based on the j_{corr} values (from the lowest to the highest): 380.0 $\leq$ A356.0 $\leq$ 2024 $\leq$ 7075 $\leq$ 3005 $\leq$ 5754 $\leq$ 1050A.

To summarize, zirconium conversion coating acted as a cathodic inhibitor regardless of the aluminium substrate and provided barrier protection after 1 hour of immersion in 0.5 M NaCl. Evaluation of corrosion protection level requires examination of the electrochemical behaviour of ZrCC during prolonged immersion in chloride solution, which was achieved by EIS measurements.

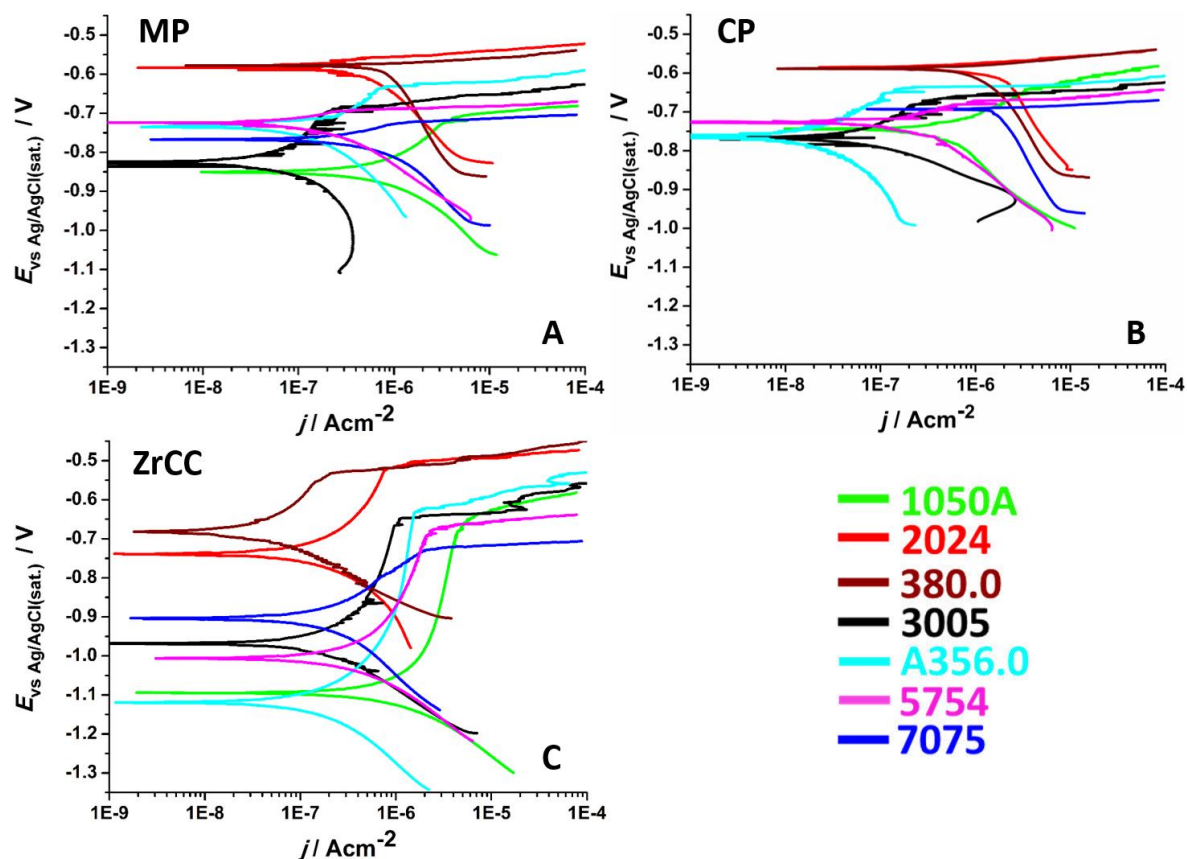


Figure 5.2: Potentiodynamic polarization curves recorded in 0.5 M NaCl for mechanically pre-treated (MP), chemically pre-treated (CP) and ZrCC-coated aluminium alloys. Zirconium conversion coatings were prepared in 200 ppm conversion bath for optimal conversion time (Table 5.1). Samples were rested at the OCP for 1 h before electrochemical measurement. Electrochemical data deduced from polarization curves are given in Tables 5.2-5.4.

Table 5.2: Electrochemical data deduced from measurements of potentiodynamic polarization (Fig. 5.2a) recorded in 0.5 M NaCl for

<i>Sample</i>	J_{corr} A cm ⁻²	E_{ocp} V	E_{corr} V	E_{pit} V	ΔE^* V	βa mV/dec	$-\beta c$ mV/dec	$R_{P,LPR}$ Ω cm ²	$R_{P,Tafe}$ Ω cm ²
1050A	6.8E-07	—	—	—	0.13	167	175	3.2E+04	5.6E+04
SD	1.4E-07	0.03	0.03	0.00	0.03	32	18	2.3E+03	4.2E+03
2024	3.9E-07	—	—	—	0.03	32	217	1.8E+04	3.2E+04
SD	7.9E-08	0.02	0.02	0.01	0.01	17	18	1.2E+04	1.8E+04
3005	3.9E-08	—	—	—	0.15	226	120	8.6E+05	9.3E+05
SD	1.1E-08	0.02	0.03	0.03	0.04	24	19	1.5E+05	3.2E+05
A356.0	1.5E-07	—	—	—	0.07	140	205	2.1E+05	2.5E+05
SD	5.0E-08	0.02	0.02	0.01	0.02	33	1	4.5E+04	5.1E+04
380.0	7.0E-07	—	—	—	0.00	17	350	2.9E+04	1.1E+04
SD	1.5E-07	0.00	0.00	0.00	0.00	4	51	1.3E+04	5.4E+03
5754	1.2E-07	—	—	—	0.04	44	135	7.8E+04	1.2E+05
SD	1.9E-08	0.00	0.01	0.00	0.01	12	13	1.9E+04	3.4E+04
7075	4.8E-07	—	—	—	0.05	60	187	1.3E+04	4.6E+04
SD	1.6E-07	0.00	0.01	0.00	0.01	8	51	2.8E+03	1.9E+04

mechanically pre-treated (MP) aluminium alloys. Samples were allowed to rest at OCP for 1h before electrochemical measurements. In the table, average values deduced from several repetitions at different samples are given (SD - standard deviation).

Table 5.3: Electrochemical data deduced from measurements of potentiodynamic polarization (Fig. 5.2b) recorded in 0.5 M NaCl for chemically pre-treated (CP) aluminium alloys. Samples were allowed

Sample	J_{corr} A cm ⁻²	E_{ocp} V	E_{corr} V	E_{pit} V	ΔE^* V	β_a mV/dec	$-\beta_c$ mV/dec	$R_{P,LPR}$ Ω cm ²	$R_{P,Tafe}$ Ω cm ²
1050A	5.1E-07	—	—	—	0.11	106	218	3.6E+04	6.2E+04
SD	2.7E-08	0.01	0.02	0.01	0.02	4	11	6.2E+03	5.6E+03
2024	1.3E-06	—	—	—	0.00	10	426	1.2E+04	4.7E+03
SD	6.5E-07	0.02	0.02	0.02	0.00	5	114	4.2E+03	2.8E+03
3005	7.5E-08	—	—	—	0.10	176	102	4.6E+05	3.8E+05
SD	1.2E-08	0.01	0.01	0.02	0.02	44	4	2.0E+05	4.6E+04
A356.0	6.1E-08	—	—	—	0.05	116	180	4.6E+05	5.2E+05
SD	1.4E-08	0.03	0.02	0.62	0.03	19	43	8.7E+04	7.8E+04
380.0	1.1E-06	—	—	—	0.00	24	366	1.5E+04	1.0E+04
SD	3.2E-07	0.01	0.00	0.00	0.00	1	23	6.9E+03	3.8E+03
5754	2.3E-07	—	—	—	0.06	65	191	6.9E+04	9.0E+04
SD	4.1E-08	0.02	0.01	0.00	0.01	11	5	7.4E+03	6.9E+03
7075	1.7E-06	—	—	—	0.00	11	444	1.2E+03	2.7E+03
SD	8.5E-08	0.00	0.01	0.01	0.00	2	9	4.6E+02	4.6E+02

to rest at OCP for 1h before electrochemical measurement. In the table, average values deduced from several repetitions at different samples are given (SD* - standard deviation).

Table 5.4: Electrochemical data deduced from measurements of potentiodynamic polarization (Fig. 5.2c) recorded in 0.5 M NaCl for zirconium conversion coatings applied on aluminium alloys. Zirconium conversion coatings were prepared in 200 ppm conversion

Sample	J_{corr} A cm ⁻²	E_{ocp} V	E_{corr} V	E_{pit} V	ΔE^* V	βa mV/dec	$-\beta c$ mV/dec	$R_{p,LPR}$ Ω cm ²	$R_{p,Tafe}$ Ω cm ²
1050A	9.1E-07	—	—	—	0.42	402	159	5.0E+04	5.8E+04
SD	1.9E-07	0.04	0.04	0.01	0.04	4	3	1.1E+04	1.2E+04
2024	1.6E-07	—	—	—	0.21	239	186	3.2E+05	2.9E+05
SD	2.1E-08	0.02	0.00	0.01	0.01	12	49	2.2E+04	2.7E+04
3005	2.3E-07	—	—	—	0.31	416	177	2.6E+05	2.4E+05
SD	4.4E-08	0.01	0.03	0.02	0.02	56	30	3.3E+04	3.8E+04
A356.0	7.3E-08	—	—	—	0.44	264	206	5.9E+05	6.6E+05
SD	8.8E-09	0.11	0.10	0.08	0.12	24	13	1.7E+05	9.7E+04
380.0	4.9E-08	—	—	—	0.13	221	147	6.7E+05	8.1E+05
SD	7.6E-09	0.01	0.01	0.00	0.01	13	9	3.8E+04	1.3E+05
5754	5.4E-07	—	—	—	0.35	400	168	1.2E+05	1.0E+05
SD	3.7E-08	0.02	0.01	0.01	0.01	11	10	1.4E+04	1.5E+04
7075	1.8E-07	—	—	—	0.17	188	179	2.8E+05	2.9E+05
SD	1.2E-07	0.09	0.08	0.07	0.08	29	57	1.4E+05	1.8E+05

bath for optimal conversion time (Table 5.1). Samples were allowed to rest at OCP for 1h before electrochemical measurement. In the table, average values deduced from several repetitions at different samples are given (SD - standard deviation).

5.3.3 Electrochemical impedance spectroscopy

Electrochemical behaviour of ZrCCs applied on aluminium alloys was studied using EIS during five days of immersion in 0.5 M NaCl (Figs. 5.3-5.9 and Tables 5.5-5.7). Corrosion resistance, self-sealing effect and active corrosion protection of zirconium conversion coatings can be estimated with impedance modulus at low frequencies (3 mHz) which is approximately equal to total polarization resistance ($|Z|_{3\text{mHz}} \approx R_p$) [109, 110]. Values of $|Z|_{3\text{mHz}}$ for ZrCC applied on aluminium alloys during prolonged immersion in 0.5 M NaCl solution are presented in Fig. 5.3g-i and Tables 5.5. ZrCC-3005 showed the best corrosion resistance with values of $|Z|_{3\text{mHz}}$ continually increasing during five days of immersion, from $2.9 \cdot 10^5 \Omega \cdot \text{cm}^2$ to $7 \cdot 10^6 \Omega \cdot \text{cm}^2$ (Fig. 5.3g). ZrCC-A356.0 showed excellent corrosion resistance as well with the value of $|Z|_{3\text{mHz}}$ increasing up to 3 days of immersion reaching $2.6 \cdot 10^6 \Omega \cdot \text{cm}^2$; at longer times it decreased slowly reaching values of $1.4 \cdot 10^6 \Omega \cdot \text{cm}^2$ indicating that pitting occurred. However, a slight decrease of $|Z|_{3\text{mHz}}$ and relatively high final values suggest that active corrosion protection occurred. Values of $|Z|_{3\text{mHz}}$ for ZrCC-380.0 and ZrCC-5754 increased after one day of immersion but then slowly decreased reaching steady values of $7.6 \cdot 10^5 \Omega \cdot \text{cm}^2$ and $1.1 \cdot 10^5 \Omega \cdot \text{cm}^2$, respectively, indicating similar behaviour as ZrCC-A356.0 but with smaller $|Z|_{3\text{mHz}}$ values. ZrCC-1050A exhibited a similar trend with values increasing up to three days, and afterwards decreased reaching $2 \cdot 10^5 \Omega \cdot \text{cm}^2$ on the fifth day of immersion (Fig. 5.3h). In contrast, $|Z|_{3\text{mHz}}$ for ZrCC-2024 and ZrCC-7075 sharply decreased from the starting values of $5.2 \cdot 10^5 \Omega \cdot \text{cm}^2$ and $5.6 \cdot 10^5 \Omega \cdot \text{cm}^2$ down to $2.6 \cdot 10^5 \Omega \cdot \text{cm}^2$ and $1.6 \cdot 10^5 \Omega \cdot \text{cm}^2$ after one day of immersion, indicating the initiation of localized pitting corrosion. Afterwards, the values of $|Z|$ continued to decrease until the end of the test (Fig. 5.3h).

Increasing values of $|Z|_{3\text{mHz}}$ for ZrCC during immersion in 0.5 M NaCl were related to self-sealing effect / active corrosion protection. The presented results show that this effect of ZrCC is closely related to chemical composition and microstructure of aluminium alloy substrates and occurred in the following order: $3005 \geq \text{A356.0} \geq 5754 \approx 380.0 \geq 1050\text{A}$. Self-sealing and active corrosion did not occur for ZrCC-2024 and ZrCC-7075, probably due to the presence of a high amount of Cu- and Zn-rich IMPs, respectively. Mechanically and chemically pre-treated aluminium alloys had much lower values of $|Z|_{3\text{mHz}}$ during immersion (Figs. 5.3a-f). The only exception was mechanically and chemically pre-treated AA3005 that showed improvement of corrosion resistance during immersion up to 1-2 days (Figs. 5.3a, 5.3d). This trend was probably caused by the presence of Mn that improved the barrier properties and stability of the natural aluminium oxide film during immersion. The trend in increasing $|Z|_{3\text{mHz}}$ values is accompanied by the progressive shift in OCP to more positive values for all ZrCCs-coated alloys except AA2024 and AA7075 which do not show the self-sealing effect (Fig. 5.3i). For the best performing ZrC-3005, this shift was about 400 mV.

To summarize, EIS results show that ZrCCs provide excellent corrosion protection of AAs 3005 and A356.0, good corrosion protection of AAs 380.0, 5754 and 1050A, and inadequate corrosion protection of 2024 and 7075 aluminium alloys.

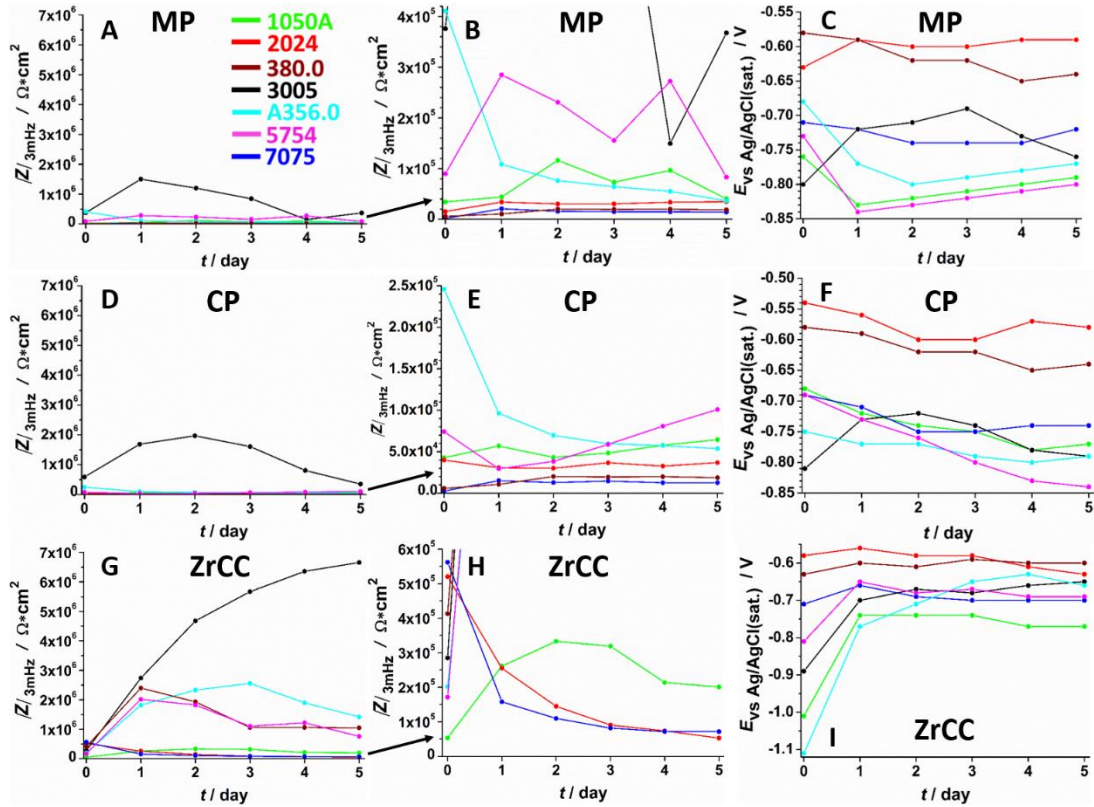


Figure 5.3: (a,b) Average impedance modulus at 3 mHz ($|Z|_{3\text{mHz}}$) and (c) average open circuit potential (OCP) as a function of immersion time in 0.5 M NaCl solution for: mechanically pre-treated (MP), chemically pre-treated (CP) and zirconium conversion coated aluminium alloys. ZrCCs were prepared in 200 ppm H_2ZrF_6 conversion bath for optimal conversion time (Table 5.1). Please note that the y-scale is broader in (b) than in (a). Lines were drawn to guide the eye. Original EIS spectra (three repetitions) are given in figures for MP (Figs. 5.4, 5.5), CP (Figs. 5.6, 5.7) and ZrCC-coated alloys (Figs. 5.8, 5.9). Average data of $|Z|_{3\text{mHz}}$ and OCP, together with standard deviations, are given in Tables 5.5–5.7.

Table 5.5: The impedance modulus at 3 mHz ($|Z|_{3\text{mHz}}$) and average open circuit potential (OCP) as a function of immersion time in 0.5 M NaCl solution for ZrCC applied on aluminium alloys. ZrCCs were prepared in 200ppm H_2ZrF_6 conversion bath for optimal conversion time (Table 5.1). In the table, average values deduced from several repetitions at different samples are given (SD - standard deviation).

	$ Z _{3\text{mHz}} / \Omega \cdot \text{cm}^2$					
Sample	1 h	1 d	2 d	3 d	4 d	5 d
1050A	5.3E+04	2.6E+05	3.3E+05	3.2E+05	2.1E+05	2.0E+05
SD	1.7E+04	6.4E+04	1.1E+05	1.1E+05	6.5E+04	3.5E+04
2024	5.2E+05	2.6E+05	1.5E+05	9.1E+04	7.4E+04	5.3E+04
SD	2.1E+05	1.1E+05	5.90E+04	2.7E+04	2.5E+04	1.3E+04
3005	2.9E+05	2.7E+06	4.7E+06	5.7E+06	6.4E+06	6.7E+06
SD	1.4E+03	4.2E+05	6.9E+05	9.5E+05	8.5E+05	9.5E+05
A356.0	2.0E+05	1.8E+06	2.3E+06	2.6E+06	1.9E+06	1.4E+06
SD	1.6E+04	7.5E+04	1.5E+05	1.9E+05	1.3E+06	1.1E+06
380.0	4.1E+05	2.4E+06	1.9E+06	1.1E+06	1.1E+06	1.1E+06
SD	2.1E+05	5.2E+05	4.5E+05	2.3E+05	5.3E+05	5.2E+05
5754	1.7E+05	2.0E+06	1.8E+06	1.1E+06	1.1E+06	7.6E+05
SD	1.0E+04	7.4E+04	1.4E+05	2.9E+05	2.5E+05	3.3E+05
7075	5.6E+05	1.6E+05	1.1E+05	8.2E+04	7.2E+04	7.2E+04
SD	1.5E+05	3.0E+04	1.7E+04	5.4E+03	1.4E+04	1.4E+04
OCP vs Ag/AgCl (sat.) / V						
1050A	-1.01	-0.74	-0.74	-0.74	-0.77	-0.77
SD	0.01	0.02	0.03	0.04	0.01	0.01
2024	-0.58	-0.56	-0.58	-0.58	-0.61	-0.63
SD	0.02	0.03	0.04	0.03	0.02	0.03
3005	-0.89	-0.70	-0.67	-0.68	-0.66	-0.65
SD	0.02	0.01	0.02	0.01	0.00	0.01
A356.0	-1.11	-0.77	-0.71	-0.65	-0.63	-0.66
SD	0.02	0.04	0.03	0.02	0.02	0.05
380.0	-0.63	-0.60	-0.61	-0.59	-0.60	-0.60
SD	0.06	0.03	0.04	0.04	0.04	0.04
5754	-0.81	-0.65	-0.68	-0.67	-0.69	-0.69
SD	0.03	0.01	0.01	0.01	0.02	0.01
7075	-0.71	-0.66	-0.69	-0.70	-0.70	-0.70
SD	0.08	0.02	0.02	0.02	0.02	0.01

Table 5.6: The impedance modulus at 3 mHz ($|Z|_{3\text{mHz}}$) and average open circuit potential (OCP) as a function of immersion time in 0.5 M NaCl solution for mechanically pre-treated (MP), aluminium alloys. In the table, average values deduced from several repetitions at different samples are given (SD - standard deviation).

Sample	$ Z _{3\text{mHz}} / \Omega \cdot \text{cm}^2$					
	1 h	1 d	2 d	3 d	4 d	5 d
1050A	4.3E+04	5.7E+04	4.3E+04	4.8E+04	5.8E+04	6.5E+04
SD	1.4E+04	4.1E+04	1.0E+04	1.4E+04	1.6E+04	2.6E+04
2024	4.0E+04	3.1E+04	3.0E+04	3.7E+04	3.3E+04	3.7E+04
SD	2.1E+04	3.9E+03	2.2E+03	5.9E+03	2.2E+03	5.4E+03
3005	5.9E+05	1.7E+06	2.0E+06	1.6E+06	8.1E+05	3.5E+05
SD	1.1E+05	5.3E+05	8.7E+05	3.7E+05	1.3E+05	9.1E+04
A356.0	2.5E+05	9.6E+04	7.0E+04	6.0E+04	5.7E+04	5.4E+04
SD	4.9E+03	1.4E+03	3.0E+03	1.4E+03	2.0E+03	6.0E+03
380.0	5.9E+03	1.1E+04	2.0E+04	2.0E+04	2.0E+04	1.9E+04
SD	3.8E+03	3.3E+03	7.3E+03	7.0E+03	5.2E+03	4.6E+03
5754	7.4E+04	2.9E+04	3.8E+04	5.9E+04	8.1E+04	1.0E+05
SD	1.7E+04	5.9E+03	4.4E+03	1.3E+04	1.5E+04	1.5E+04
7075	2.6E+03	1.5E+04	1.3E+04	1.5E+04	1.3E+04	1.3E+04
SD	1.9E+03	2.8E+03	5.0E+03	4.3E+03	2.1E+03	2.8E+03
OCP vs Ag/AgCl (sat.) / V						
1050A	-0.76	-0.83	-0.82	-0.81	-0.80	-0.79
SD	0.09	0.06	0.03	0.03	0.03	0.03
2024	-0.63	-0.59	-0.60	-0.60	-0.59	-0.59
SD	0.09	0.03	0.03	0.01	0.01	0.01
3005	-0.80	-0.72	-0.71	-0.69	-0.73	-0.76
SD	0.02	0.01	0.03	0.03	0.01	0.01
A356.0	-0.68	-0.77	-0.80	-0.79	-0.78	-0.77
SD	0.01	0.01	0.02	0.01	0.00	0.00
380.0	-0.58	-0.59	-0.62	-0.62	-0.65	-0.64
SD	0.02	0.02	0.04	0.05	0.04	0.05
5754	-0.73	-0.84	-0.83	-0.82	-0.81	-0.80
SD	0.04	0.02	0.02	0.03	0.02	0.02
7075	-0.71	-0.72	-0.74	-0.74	-0.74	-0.72
SD	0.03	0.04	0.03	0.03	0.03	0.02

Table 5.7: The impedance modulus at 3 mHz ($|Z|_{3\text{mHz}}$) and average open circuit potential (OCP) as a function of immersion time in 0.5 M NaCl solution for chemically pre-treated (CP), aluminium alloys. In the table, average values deduced from several repetitions at different samples are given (SD - standard deviation).

$ Z _{3\text{mHz}} / \Omega \cdot \text{cm}^2$						
Sample	1 h	1 d	2 d	3 d	4 d	5 d
1050A	3.4E+04	4.4E+04	1.2E+05	7.3E+04	9.6E+04	4.0E+04
SD	6.0E+03	2.6E+04	8.5E+04	4.7E+04	3.6E+03	2.4E+04
2024	1.5E+04	3.4E+04	3.0E+04	3.0E+04	3.4E+04	3.5E+04
SD	1.7E+03	9.4E+02	2.5E+03	8.8E+02	2.3E+03	1.1E+03
3005	3.8E+05	1.5E+06	1.2E+06	8.5E+05	1.5E+05	3.7E+05
SD	8.2E+03	5.4E+04	8.6E+05	9.8E+05	4.7E+03	9.0E+03
A356.0	4.1E+05	1.1E+05	7.6E+04	6.4E+04	5.5E+04	3.6E+04
SD	7.8E+04	4.3E+04	1.9E+04	9.9E+03	4.6E+03	1.3E+04
380.0	5.9E+03	1.1E+04	2.0E+04	2.0E+04	2.0E+04	1.9E+04
SD	3.8E+03	3.3E+03	7.3E+03	7.0E+03	5.2E+03	4.6E+03
5754	9.0E+04	2.9E+05	2.3E+05	1.6E+05	2.7E+05	8.3E+04
SD	6.3E+04	9.2E+04	7.5E+04	8.4E+04	2.8E+05	1.6E+04
7075	1.6E+03	2.1E+04	1.6E+04	1.5E+04	1.5E+04	1.4E+04
SD	8.9E+02	3.3E+03	5.0E+03	4.0E+03	6.9E+03	3.9E+03
OCP vs Ag/AgCl (sat.) / V						
1050A	-0.68	-0.72	-0.74	-0.75	-0.78	-0.77
SD	0.01	0.03	0.03	0.02	0.00	0.01
2024	-0.54	-0.56	-0.60	-0.60	-0.57	-0.58
SD	0.00	0.01	0.02	0.01	0.00	0.01
3005	-0.81	-0.73	-0.72	-0.74	-0.78	-0.79
SD	0.02	0.00	0.02	0.04	0.05	0.03
A356.0	-0.75	-0.77	-0.77	-0.79	-0.80	-0.79
SD	0.02	0.06	0.04	0.04	0.04	0.03
380.0	-0.58	-0.59	-0.62	-0.62	-0.65	-0.64
SD	0.02	0.02	0.04	0.05	0.04	0.05
5754	-0.69	-0.73	-0.76	-0.80	-0.83	-0.84
SD	0.00	0.02	0.02	0.01	0.02	0.01
7075	-0.69	-0.71	-0.75	-0.75	-0.74	-0.74
SD	0.04	0.04	0.03	0.02	0.02	0.02

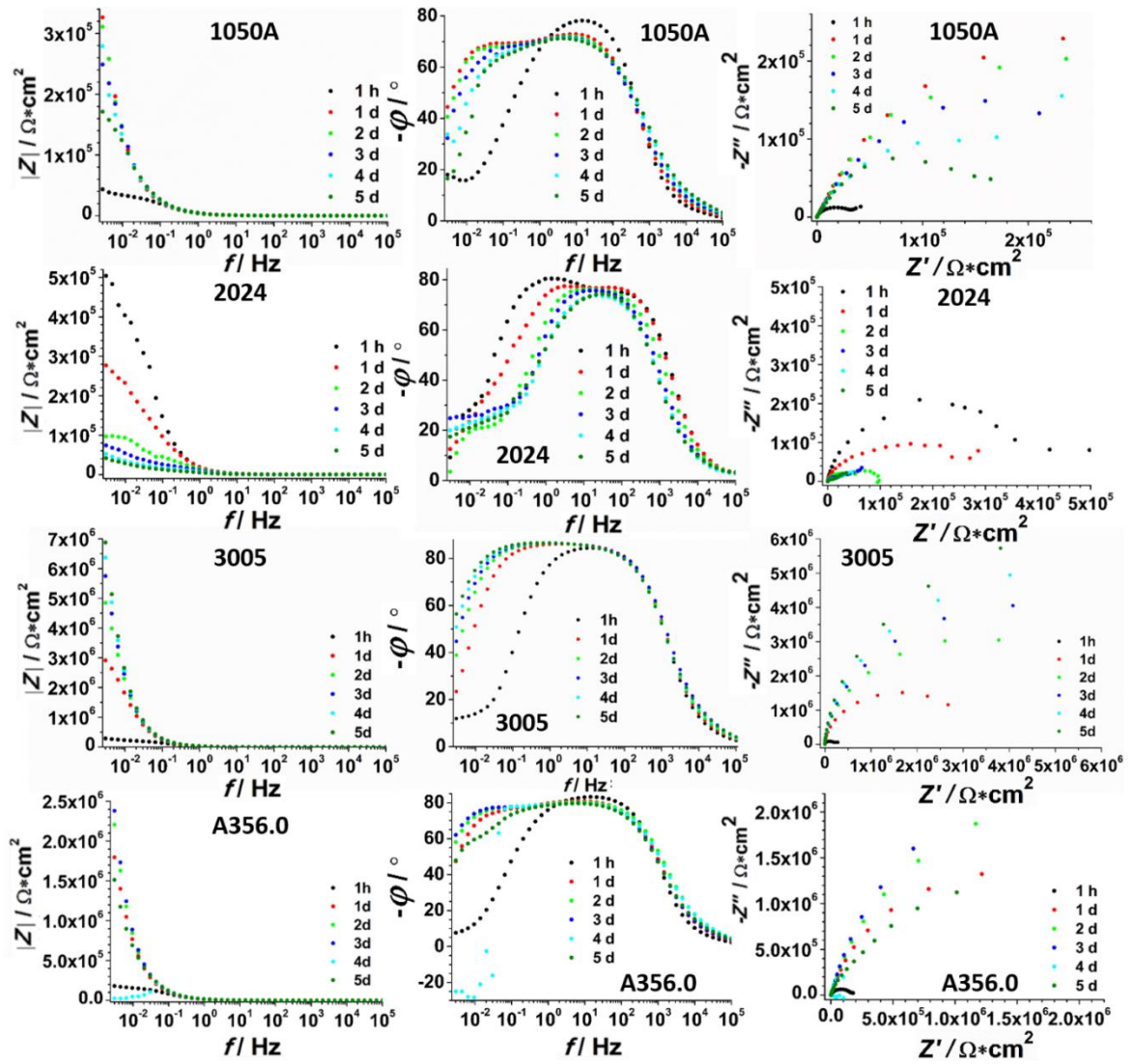


Figure 5.4: Bode and Nyquist diagrams for zirconium conversion coated aluminium alloys 1050A, 2024, 3005, A356.0 immersed in 0.5 M NaCl solution for up to 5 days. Representative measurements from 3 repetitions are presented.

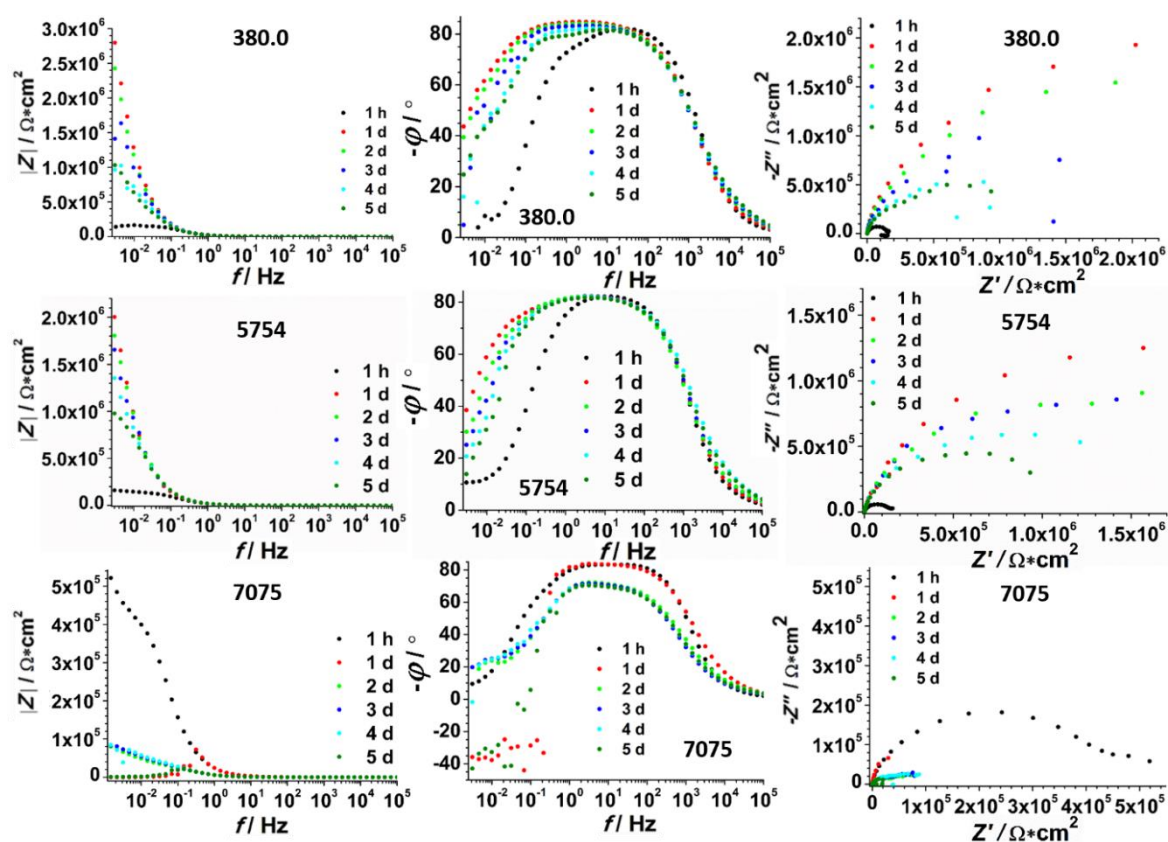


Figure 5.5: Bode and Nyquist diagrams for zirconium conversion coated aluminium alloys 380.0, 5754, 7075 immersed in 0.5 M NaCl solution for up to 5 days. Representative measurements from 3 repetitions are presented.

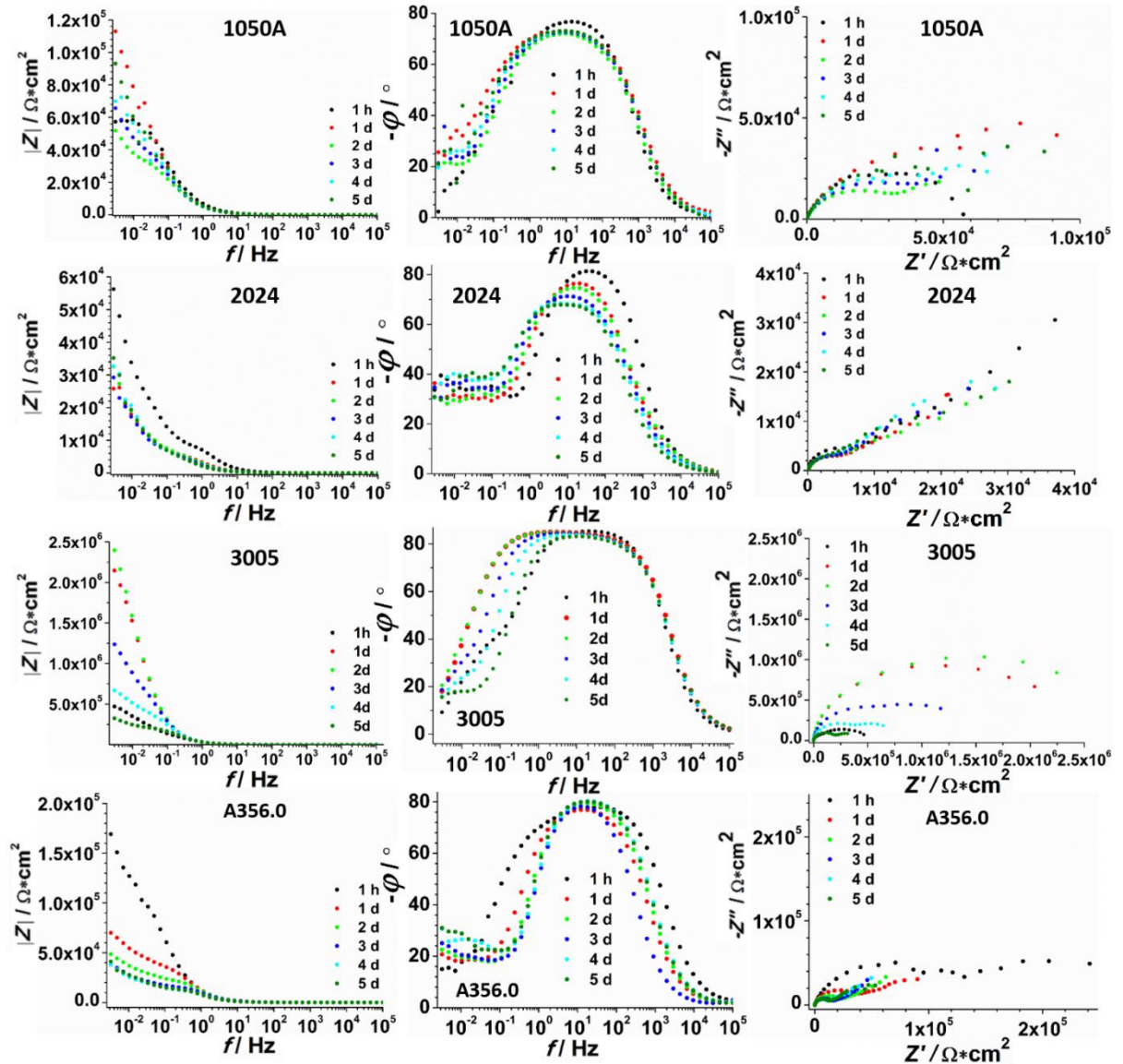


Figure 5.6: Bode and Nyquist diagrams for mechanically pre-treated aluminium alloys 1050A, 2024, 3005, A356.0 immersed in 0.5 M NaCl solution for up to 5 days. Representative measurements from 3 repetitions are presented.

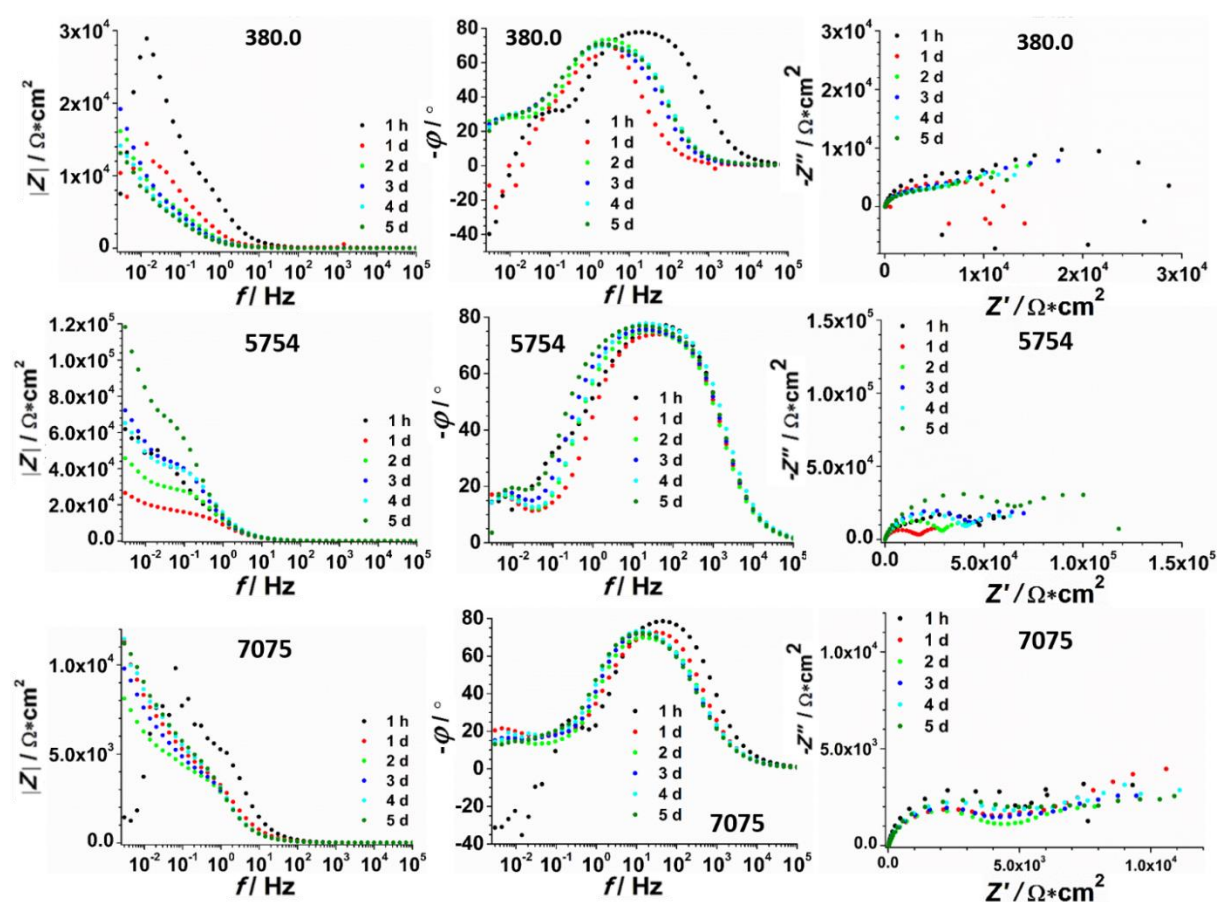


Figure 5.7: Bode and Nyquist diagrams for mechanically pre-treated aluminium alloys 380.0, 5754, 7075 immersed in 0.5 M NaCl solution for up to 5 days. Representative measurements from 3 repetitions are presented.

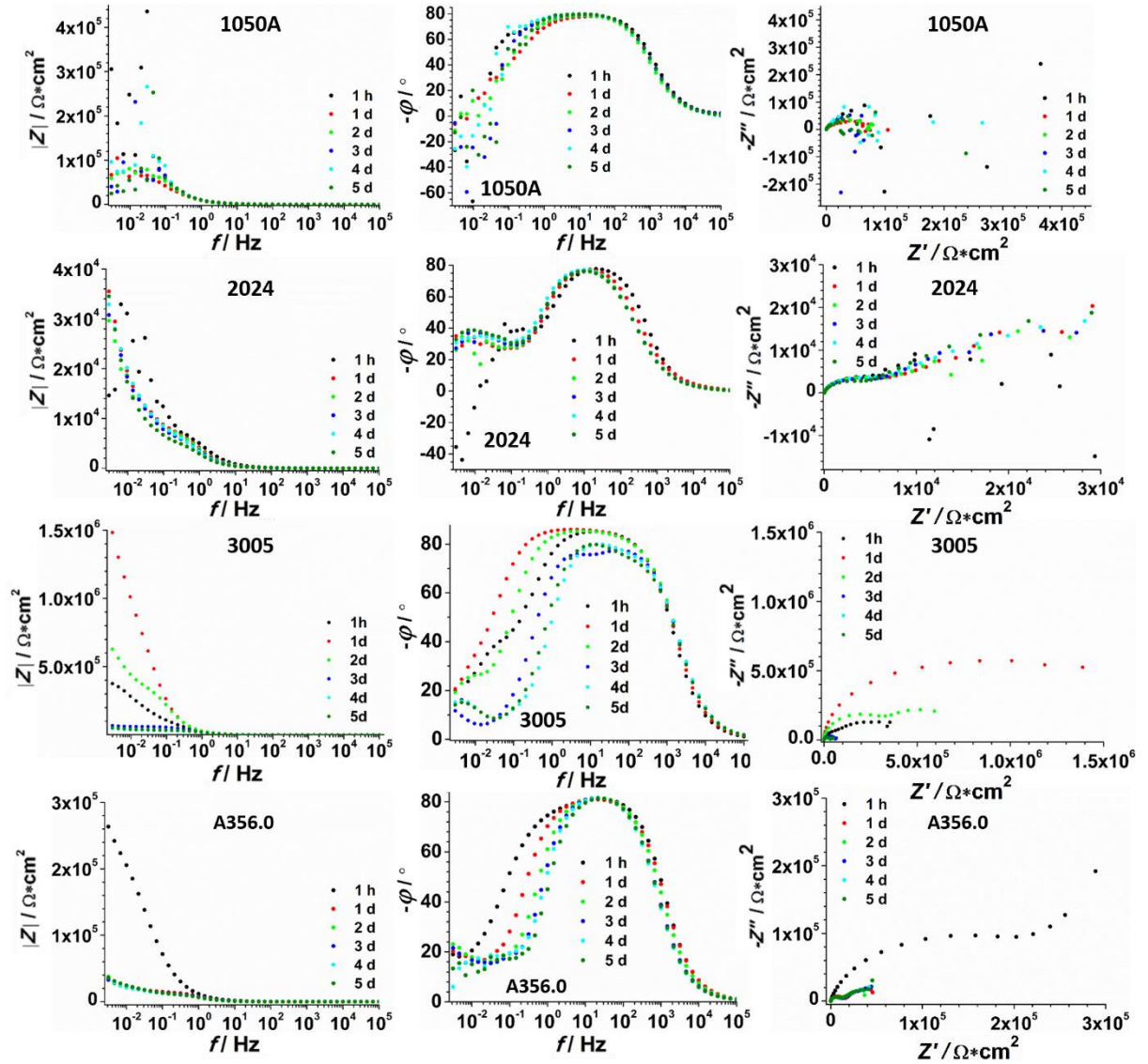


Figure 5.8: Bode and Nyquist diagrams for chemically pre-treated aluminium alloys 1050A, 2024, 3005, A356.0 immersed in 0.5 M NaCl solution for up to 5 days. Representative measurements from 3 repetitions are presented.

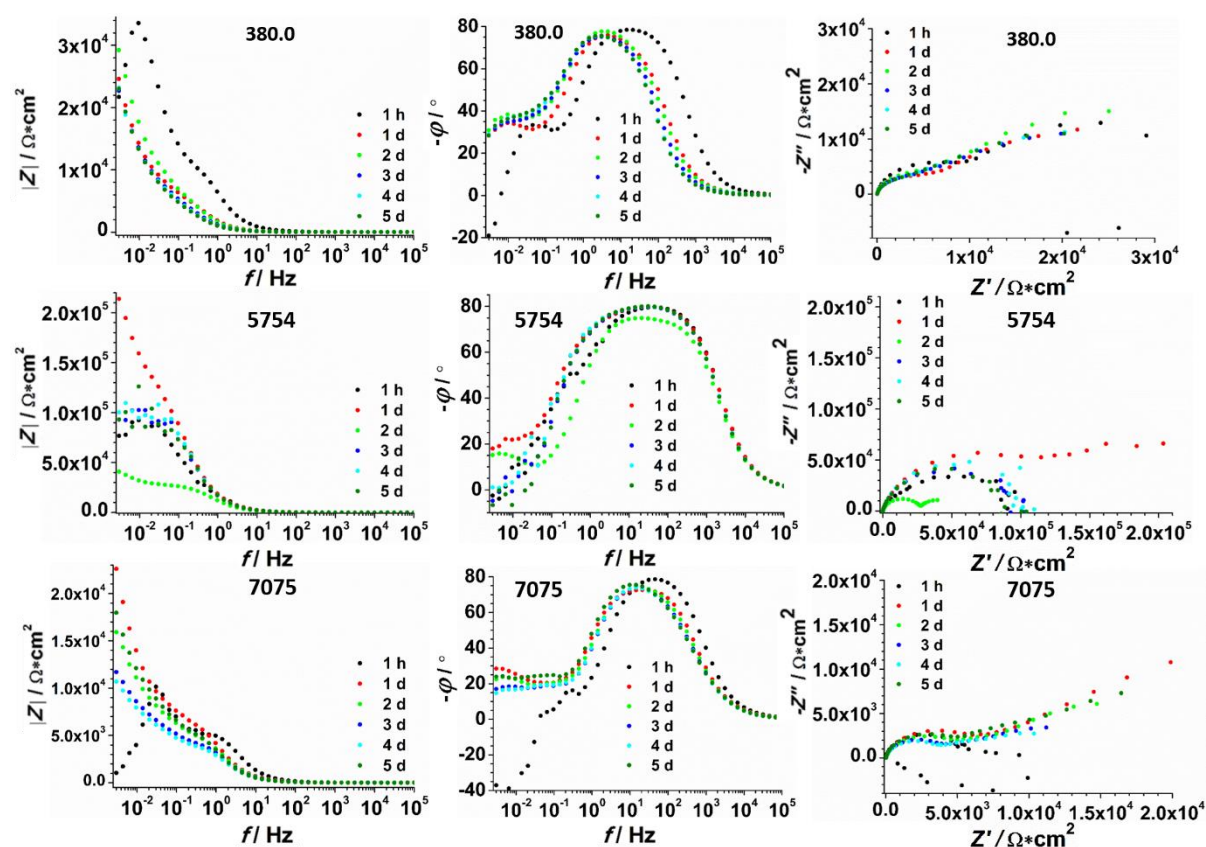


Figure 5.9: Bode and Nyquist diagrams for chemically pre-treated aluminium alloys 380.0, 5754, and 7075 immersed in 0.5 M NaCl solution for up to 5 days. Representative measurements from 3 repetitions are presented.

5.3.4 Microstructural and surface characterization SEM-EDS characterization of aluminium alloys

SEM secondary electron (SE) and backscattered (BSE) images of chemically pre-treated aluminium alloys are presented in Fig. 5.10, and corresponding EDS analysis of numerated spots are given in Tables 5.8–5.14. EDS analysis was performed with 3 keV beam energy corresponding to 100 nm analysis depth (near-surface condition).

EDS analysis was carried out to obtain the basic composition of the surface; therefore, it was not so detailed because the microstructure of these alloys is already well known in the scientific literature (*vide infra*).

The surfaces of chemically pre-treated alloys predominantly consisted of spontaneously formed aluminium oxide (Tables 5.8-5.14). Depending on the substrate, other elements were detected as well, ranging from 0.6 at % up to 10.8 at % at spot 1 (larger area). When IMPs were analysed, the concentration of individual elements was larger (Tables 5.8-5.14), in accordance with the predominant type of IMP in alloys. Due to the presence of a relatively high amount of Fe and Si, IMPs in AA1050 are AlFe_3 and $\alpha\text{-AlFeSi}$. Both of these IMPs are noble compared to the alloy matrix [154]. Please note that the microstructures for AA3005 and AAA356.0 were reported in more detail in our previous studies [9].

AA2024 has two main groups of IMPs based on chemical composition. The first group represents round-shaped S-phase (Al-Cu-Mg) IMPs that are more electrochemically active and susceptible to anodic dissolution but due to dealloying become local cathodes. Larger, irregularly shaped Al-Cu-Mn-Fe ($\text{Al}_7\text{Cu}_2\text{Fe}$, $\text{Al}_{20}\text{Cu}_2\text{Mn}_3$, and Al_2Cu) IMPs belong to the second group [9, 10, 13, 155, 156]. These IMPs are nobler compared to AA2024-matrix and represent local cathodes in the corrosion process [9].

AA3005 and AA5754 contain the same IMPs: $(\text{MnFe})\text{Al}_6$ or $\alpha\text{-(MnFe)}_3\text{SiAl}_{12}$. [157] However, AA3005 contains larger IMPs, and a higher number of IMPs compared to AA5754. Also, AA3005 contains a significant amount of $\alpha\text{-(MnFe)}_3\text{SiAl}_{12}$, while AA5754 contains mainly $(\text{MnFe})\text{Al}_6$ with a much higher ratio of $\text{Fe/Mn} = 7.8$ compared to AA3005 that has the Fe/Mn ratio of 0.8. [157] Also, AA3005 contains more small IMPs (dispersoids) compared to AA5754. Dispersoids are $(\text{MnFe})\text{Al}_6$ and $\alpha\text{-Al(Fe,Mn)Si}$ IMPs. AA5754 also contain AlFe_3 , Mg_2Si and sporadically Al_6CuMg_4 . [158]. Both of these IMPs are noble relative to the alloy's matrix and act as a local cathode.

The microstructure of AAA356.0 consists of an $\alpha\text{-Al}$ matrix (grains), eutectic Si grain boundaries, and IMPs [9, 51, 91, 159-165]. Typical IMPs in AAA356.0 are Al-Si-Fe , Mg-Si and Al-Si-Fe-Mg IMPs ($\beta\text{-Al}_5\text{FeSi}$ -needles, $\pi\text{-Al}_8\text{FeMg}_3\text{Si}_6$, Mg_2Si); if there is a higher amount of Mn in an alloy composition, $\alpha\text{-Al-Si-Fe-Mn}$ IMPs and $\alpha\text{-Al}_{15}(\text{FeMn})_3\text{Si}_2$ - Chinese script or skeleton formations will be found. Sporadically, it is possible to find $\text{Al}_5\text{Cu}_2\text{Mg}_8\text{Si}_6$. All these IMPs and eutectic-Si are noble to the $\alpha\text{-Al}$ matrix except Mg_2Si that is less noble (anodic).

Main AA380.0 microstructural components are $\alpha\text{-Al}$ matrix (grains), eutectic Si grain boundaries, and IMPs ($\beta\text{-Al}_5\text{FeSi}$ -needles, Al_2Cu , Al(FeCuCr) and $\alpha\text{-Al-Si-Fe-Mn}$, which are formed at grain boundaries [159, 164, 166-168]. It is possible to find $\text{Al}_{15}(\text{FeMn})_3\text{Si}_2$ - Chinese script as well if the content of Mn in the alloy is high enough. All these IMPs and eutectic-Si are noble relative to the $\alpha\text{-Al}$ matrix.

IMPs in AA7075 are MgZn_2 and Mg_2Si which are susceptible to anodic dissolution, and Al_2Cu , Al_3Fe and $\text{Al}_7\text{Cu}_2\text{Fe}$ that can sustain high cathodic currents and S-phase (Al_2CuMg) [9, 11, 67, 155, 156, 169, 170]. S-phase is susceptible to anodic dissolution. Once when Mg is removed from the S-phase, it reverses the corrosion potential (behaviour) and starts acting as a local cathode.

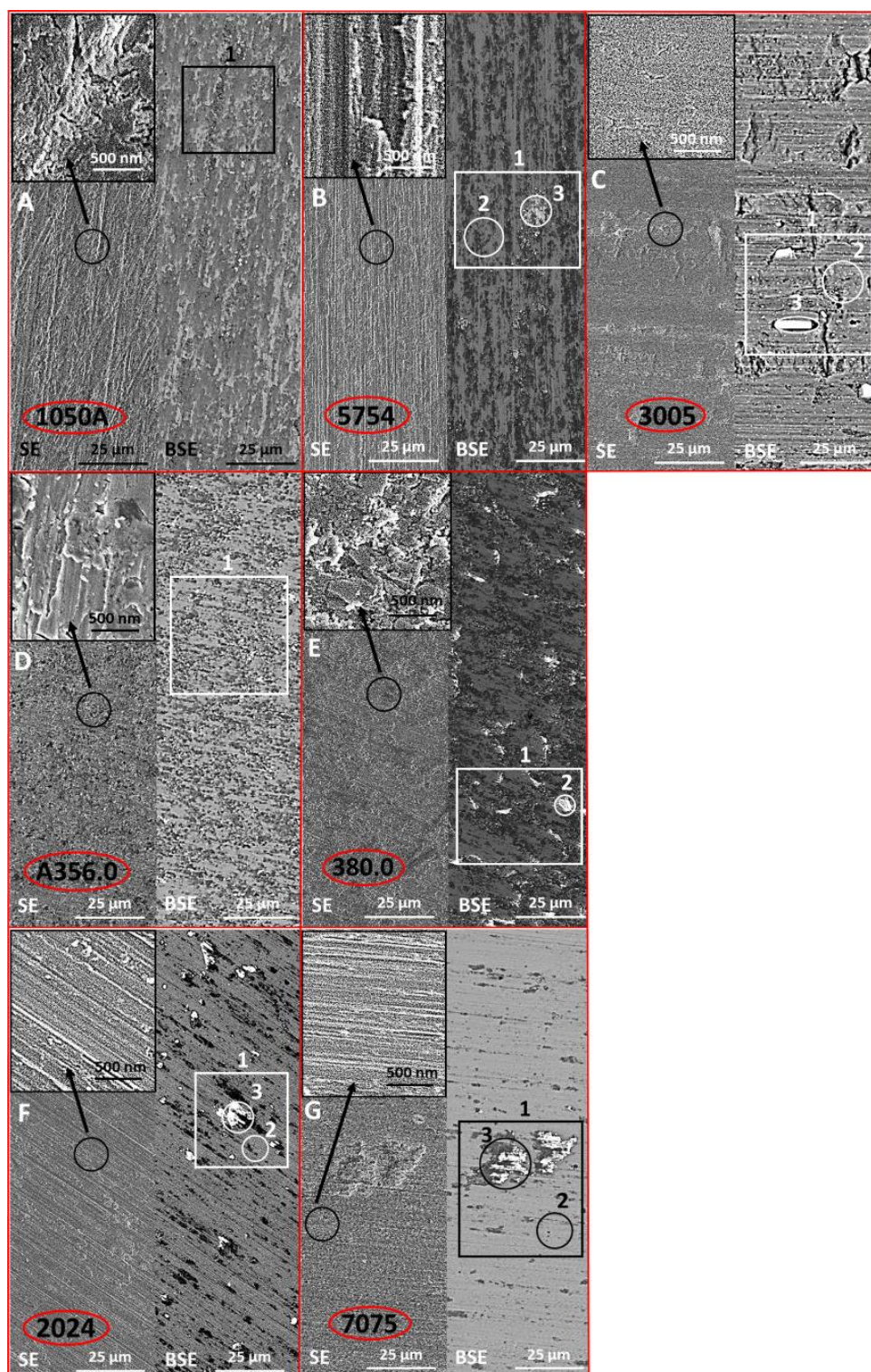


Figure 5.10: SEM SE and BSE images and EDS mapping of chemically pre-treated (CP) aluminium alloys. (a) 1050A, (b) 5754, (c) 3005, (d) A356.0, (e) 380.0, (f) 2024 and (g) 7075. For each alloy, three SEM images are given: SE and BSE image at a lower magnification and SE image at the spot denoted by a black circle recorded at a higher magnification (inset). EDS analysis was carried out at the larger area (1, rectangle) and the smaller area (2, 3, circles). The EDS results are presented in Tables 5.8-5.14.

5.3.5 SEM-EDS characterization of zirconium conversion coatings applied on aluminium alloys

SEM secondary electron (SE) and backscattered (BSE) images of zirconium conversion coatings are presented in Figs. 5.11–5.12, and corresponding EDS analyses of numerated spots are given in Tables 5.8–5.14. Images are given for as-prepared coatings (Figs. 5.11–5.12a–a3), and after a 1-day (Figs. 5.11–5.12b–b3) and a 3-day (Figs. 5.11–5.12c–c3) immersion in 0.5 M NaCl. In SEM SE mode, the nodular structure of conversion coatings is visible only at higher magnification. On the other hand, the formation and lateral distribution of ZrCC throughout the surface was much better visible in SEM BSE mode and was indicated by the bright areas [91]. These denote the spots where the formation of ZrCC was initiated and resulted in a much thicker final ZrCC. Noble IMPs and eutectic Si grain boundaries of AA356.0 and AA380.0 aluminium cast alloys were present beneath ZrCC (Figs. 5.11–5.12). EDS analysis shows that as-prepared ZrCC contained ca. 13–18 at. % Zr, 7–12 at. % F, 27–44 at. % O and a minor amount of elements originating from the substrate and/or IMPs (Tables 5.8–5.14). The only exception was ZrCC-2024 that contained a much lesser amount of Zr (5.3 at. %), F (2.0 at. %), O (16.9 at. %) and a much higher amount of Al (72.2 at. %) compared to other as-prepared ZrCCs. On the other hand, it had a higher concentration of Zr (24.6 at. %), F (6.2 at. %) and O (54.6 at. %) at bright spots (Fig. 5.11a1). Based on these results it can be stated that ZrCC-2024 prepared after a 3-min conversion time was non-uniformly formed across the AA2024 surface and was much thicker at bright spots (IMPs) and much thinner at the matrix. These bright spots were noble, Cu containing IMPs that caused this unequal formation of ZrCC-2024. The overall result was that the mean thickness of ZrCC-2024 was much smaller compared to other ZrCCs and did not provide adequate corrosion protection, according to EIS measurements (Fig. 5.3).

The general trend during immersion of ZrCC in 0.5 M NaCl solution was a decrease of F concentration, indicating leaching of F from the conversion coating (Tables 5.8–5.14). After three days of immersion, the concentration of Zr remained at the approximately same level, while that of O increased for 10–15 at. % for ZrCC-1050A, ZrCC-5754, ZrCC-3005, ZrCC-A356.0 and ZrCC-380.0. The surfaces of ZrCC-1050A, ZrCC-5754 and ZrCC-3005 did not show any signs of corrosion (Figs. 5.12c–c2), in good correlation with EIS measurements (Fig. 5.3) and indicated that this ZrCCs was self-sealed. For ZrCC-A356.0 and ZrCC-380.0 there was no corrosion damage after one day of immersion (Figs. 5.11b3, 5.12b); however, after three days the corrosion damage appeared in the form of crack/pits in both alloys (Figs. 5.11c3, 5.12c). At these areas, increased concentration of Zn was detected and indicated that the presence of Zn caused pitting (Tables 5.11–5.12). The extent of corrosion damage in both alloys was low. However, corrosion damage was lesser for ZrCC-A356.0 compared to ZrCC-380.0, probably due to a higher concentration of Zn and Cu in the latter.

ZrCC-2024 and ZrCC-7075 exhibited different behaviour during immersion in 0.5 M NaCl. Already after one day of immersion, the corrosion products appeared at ZrCC-2024, especially around IMPs (Fig. 5.12b1). The concentration of O was increased for ca. 30 at.%, and that of Zr and F decreased compared to as-prepared coatings (Tables 5.13). After three days, severe corrosion damage was visible in the form of cracks (Fig. 5.12c1). An even higher concentration of O (61.0 at. %) and a lower concentration of Zr (3.0 at. %) and F (0.9 at. %) were detected. These results reflect the extensive coverage of the surface with $\text{Al}(\text{OH})_3$ corrosion products and dissolution of ZrCC during the immersion, indicating that ZrCC was not able to provide proper corrosion protection for AA2024.

The corrosion of ZrCC-7075 was also initiated after one day of immersion in 0.5 M NaCl (Fig. 5.12b2, dark spots). At these spots, the concentration of Zn and Cu was larger, indicating the presence of CuZn-rich IMPs under the corrosion products in the form of aluminium oxide/hydroxide (Table 5.14). After three days of immersion, corrosion damage was more severe in the form of a big crack/pit. At these spots, the concentration of Cu, Zn, Fe was increased, correlating with the presence of CuZnFe IMPs (Fig. 5.12c2, Table 5.14). At the same time, the formation of corrosion products in the form of $\text{Al}(\text{OH})_3$ is indicated. The concentration of Zr was significantly decreased at this spot due to the dissolution of ZrCC and coverage with corrosion products. The general trend during the immersion of ZrCC-7075 in 0.5 M NaCl was that the concentration of F decreased 5-fold, indicating leaching of fluorine, and the concentration of O increased. However, the most interesting feature is that the concentration of Zr decreased by 30% after three days of immersion, proving severe dissolution of the coating and its coverage with corrosion products. These results are in good correlation with EIS measurements (Fig. 5.3) and show that ZrCC was not able to provide proper corrosion protection to AA7075.

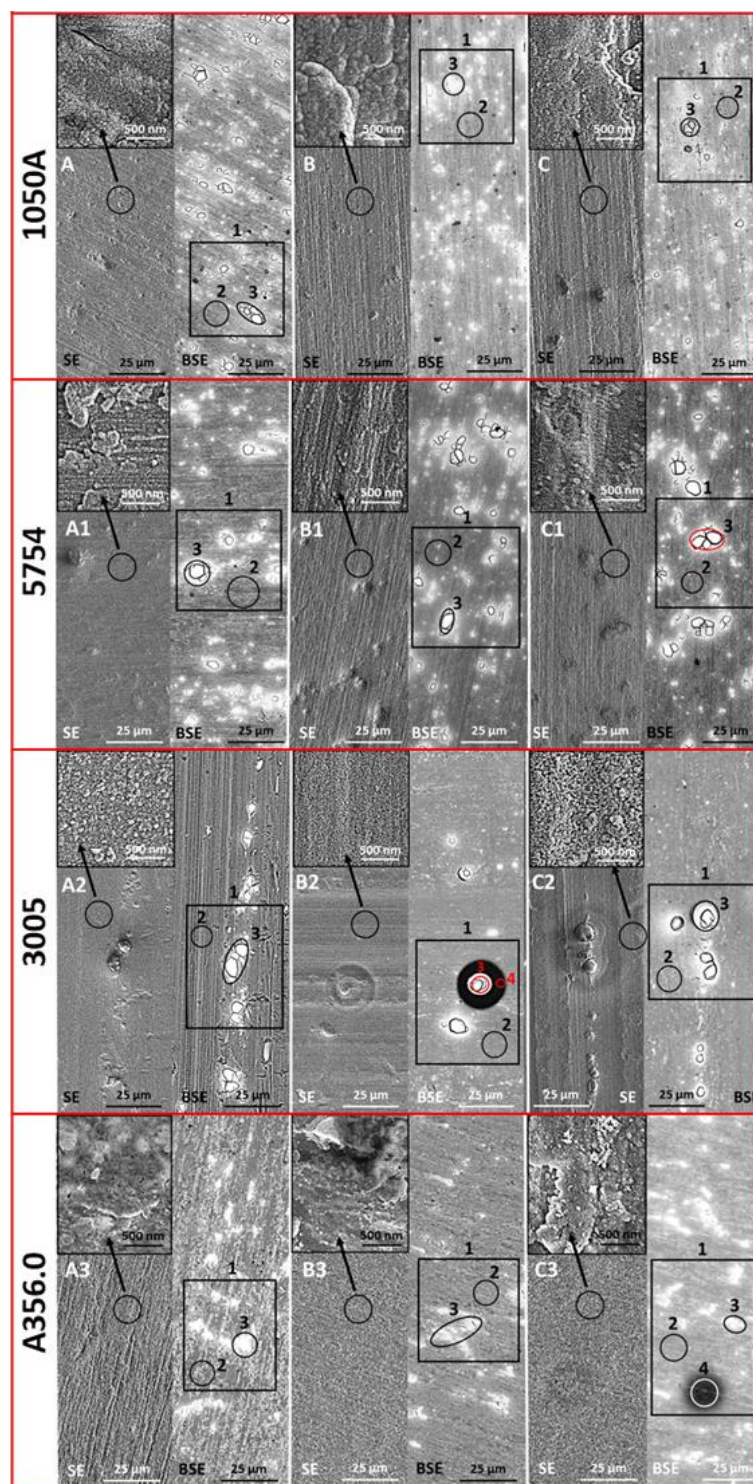


Figure 5.11: SEM SE and BSE images of ZrCC applied on aluminium alloys 1050A, 5754, 3005 and A356.0. (a) As-prepared ZrCC, (b) ZrCC immersed in 0.5 M NaCl for 1 day and (c) ZrCC immersed in 0.5 M NaCl for 3 days. ZrCC were prepared in 200 ppm H_2ZrF_6 baths for optimal conversion times (Table 5.1). For each alloy, three SEM images are given: SE and BSE image at lower magnification and SE image at the spot denoted by a black circle recorded at higher magnification (inset). EDS analysis was carried out at the larger area (1, rectangle) and a smaller area (2-4, circles) as shown in Tables 5.8–5.14.

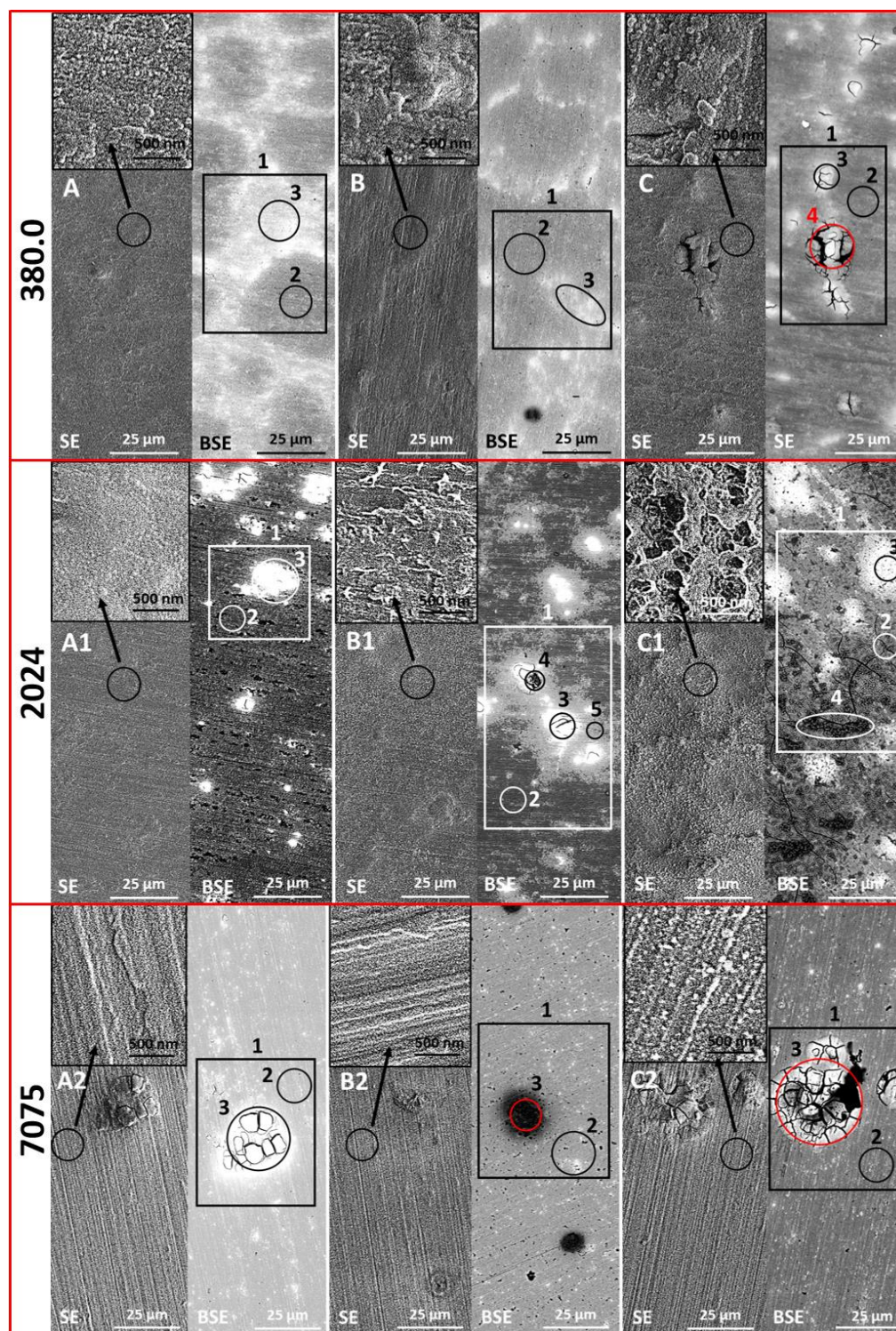


Figure 5.12: SEM SE and BSE images of ZrCC applied on aluminium alloys 380.0, 2024 and 7075. (a) As-prepared ZrCC, (b) ZrCC immersed in 0.5 M NaCl for 1 day and (c) ZrCC immersed in 0.5 M NaCl for 3 days. ZrCC were prepared in 200 ppm H_2ZrF_6 baths for optimal conversion times (Table 5.1). For each alloy, three SEM images are given: SE and BSE image at lower magnification and SE image at the spot denoted by a black circle recorded at higher magnification (inset). EDS analysis was carried out at the larger area (1, rectangle) and a smaller area (2-4, circles) as shown in Tables 5.8-5.14.

Table 5.8: EDS analysis of chemically pre-treated and zirconium-coated aluminium alloy 1050A. ZrCC were prepared from a 200 ppm H_2ZrF_6 conversion bath for 15 min. The analysis was performed at enumerated spots in SEM BSE images in Fig. 5.10a, Fig. 5.11. The electron beam voltage of the analysed spots was 3 kV, corresponding to an analysis depth of ca. 100 nm.

spot	at. % Al	at. % O	at. % Zr	at. % F	at. % Fe	at. % Si
<i>Chemically pre-treated</i>						
1	71.7	27.8	/	/	/	0.5
<i>ZrCC- as prepared</i>						
1	25.7	43.3	18.2	12.0	/	0.8
2	30.1	42.5	15.3	12.0	/	/
3	11.3	53.0	21.6	14.1	/	/
<i>ZrCC-1d</i>						
1	23.6	57.4	16.1	2.3	/	0.5
2	26.5	56.7	14.4	2.4	/	/
3	10.9	64.9	22.9	1.3	/	/
<i>ZrCC-3d</i>						
1	22.0	59.4	16.2	1.9	/	0.5
2	28.0	54.5	15.5	2.0	/	/
3	12.6	66.6	19.3	1.5	/	/

Table 5.9: EDS analysis of chemically pre-treated and zirconium-coated aluminium alloy 5754. ZrCC were prepared from a 200 ppm H_2ZrF_6 conversion bath for 10 min. The analysis was performed at enumerated spots in SEM BSE images in Fig. 5.10b, Fig. 5.11. The electron beam voltage of the analysed spots was 3 kV, corresponding to an analysis depth of ca. 100 nm.

spot	at. % Al	at. % O	at. % Zr	at. % F	at. % Mg	at. % Fe
<i>CP</i>						
1	71.4	25.1	/	/	2.1	1.0
2	71.6	25.3	/	/	2.1	1.0
3	53.3	32.1	/	/	/	14.6
<i>ZrCC-as prepared</i>						
1	39.4	34.8	14.8	9.7	1.4	/
2	44.4	31.2	13.2	9.6	1.6	/
3	12.4	50.2	24.8	12.7	/	/
<i>ZrCC-1d</i>						
1	30.9	49.7	16.6	1.7	1.0	/
2	38.5	45.7	13.1	1.4	1.3	/
3	13.6	61.1	24.1	1.1	0.1	/
<i>ZrCC-3d</i>						
1	35.9	46.3	15.0	1.7	1.1	/
2	46.0	38.9	12.1	1.7	1.3	/
3	12.1	63.3	23.8	0.8	/	/

Table 5.10: EDS analysis of chemically pre-treated and zirconium-coated aluminium alloy 3005. ZrCC were prepared from a 200 ppm H_2ZrF_6 conversion bath for 10 min. The analysis was performed at enumerated spots in SEM BSE images in Fig. 5.10c, Fig. 5.11. The electron beam voltage of the analysed spots was 3 kV, corresponding to an analysis depth of ca. 100 nm.

spot	at. % Al	at. % O	at. % Zr	at. % F	at. % Mg
<i>Chemically pre-treated</i>					
1	88.8	10.6	/	/	0.6
2	88.8	10.6	/	/	0.6
3	82.3	17.7	/	/	/
<i>ZrCC-as prepared</i>					
1	54.7	25.5	13.2	6.6	/
2	54.4	27.0	11.8	6.8	/
3	/	57.1	32.8	10.1	/
<i>ZrCC-1d</i>					
1	53.1	33.5	11.9	1.6	/
2	58.0	29.2	11.4	1.4	/
3	/	72.9	27.1	/	/
4	32.7	63.5	0.9	2.9	/
<i>ZrCC-3d</i>					
1	54.2	33.4	11.2	1.2	/
2	54.5	33.4	10.9	1.2	/
3	/	74.8	25.2	/	/

Table 5.11: EDS analysis of chemically pre-treated and zirconium-coated aluminium alloy A356.0. ZrCC were prepared from a 200 ppm H_2ZrF_6 conversion bath for 10 min. The analysis was performed at enumerated spots in SEM BSE images in Fig. 5.10d, Fig. 5.11. The electron beam voltage of the analysed spots was 3 kV, corresponding to an analysis depth of ca. 100 nm.

spot	at. % Al	at. % O	at. % Zr	at. % F	at. % Mg	at. % Zn	at. % Si
<i>CP</i>							
1	67.8	20.9	/	/	0.5	/	10.8
2	60.2	39.0	/	/	/	/	0.8
3	27.6	62.1	/	/	/	/	10.4
<i>ZrCC-as prepared</i>							
1	37.1	35.7	14.3	7.7	/	/	5.2
2	41.2	33.8	13.5	7.5	/	/	4.0
3	10.5	59.1	18.3	8.6	/	/	3.5
<i>ZrCC-1d</i>							
1	25.6	55.1	13.3	1.5	/	/	4.5
2	26.0	54.2	13.0	1.4	/	/	5.4
3	14.2	65.2	19.1	/	/	/	1.5
<i>ZrCC-3d</i>							
1	32.5	48.4	13.1	1.1	/	/	4.9
2	35.0	46.8	12.1	1.0	/	/	5.1
3	19.4	58.1	18.7	/	/	/	3.8
4	15.8	63.7	9.6	0.1	/	0.5	10.3

Table 5.12: EDS analysis of chemically pre-treated and zirconium-coated aluminium alloy 380.0. ZrCC were prepared from a 200 ppm H_2ZrF_6 conversion bath for 10 min. The analysis was performed at enumerated spots in SEM BSE images in Fig. 5.10e, Fig. 5.12. The electron beam voltage of the analysed spots was 3 kV, corresponding to an analysis depth of ca. 100 nm.

<i>spot</i>	at. % Al	at. % O	at. % Zr	at. % F	at. % Cu	at. % Si	at. % Zn
<i>CP</i>							
1	62.4	27.0	/	/	1.9	8.9	/
2	73.8	19.4	/	/	0.5	6.2	/
3	58.4	30.9	/	/	1.3	9.5	/
4	55.8	17.4	/	/	17.9	9.0	/
<i>ZrCC-as-prepared</i>							
1	32.1	38.1	16.0	9.7	0.7	3.4	/
2	49.1	29.5	12.4	8.6	0.4	/	/
3	14.5	45.7	21.5	11.5	1.1	5.9	/
<i>ZrCC-1d</i>							
1	27.6	49.6	15.0	1.7	0.7	5.4	/
2	37.0	44.2	14.1	1.9	0.4	2.4	/
3	18.3	54.9	15.7	1.4	1.2	8.4	/
<i>ZrCC-3d</i>							
1	27.4	51.1	15.0	1.0	0.7	4.3	0.6
2	34.5	45.3	14.2	1.0	0.8	3.5	0.7
3	16.5	59.2	21.7	0.8	1.9	/	/
4	13.3	61.3	17.2	0.7	2.7	3.5	1.3

Table 5.13: EDS analysis of chemically pre-treated and zirconium-coated aluminium alloy 2024. ZrCC were prepared from a 200 ppm H_2ZrF_6 conversion bath for 3 min. The analysis was performed at enumerated spots in SEM BSE images in Fig. Fig. 5.10f, Fig. 5.12. The electron beam voltage of the analysed spots was 3 kV, corresponding to an analysis depth of ca. 100 nm.

spot	at. % Al	at. % O	at. % Zr	at. % F	at. % Cu	at. % Mg	at. % Fe
<i>Chemically pre-treated</i>							
1	84.0	11.8	/	/	2.4	1.2	0.5
2	87.4	9.4	/	/	2.1	1.2	/
3	63.1	17.8	/	/	10.6	/	10.6
<i>ZrCC- as-prepared</i>							
1	72.2	16.9	5.3	2.0	2.6	1.0	/
2	77.9	13.4	4.5	1.2	1.9	1.1	/
3	13.5	54.6	24.6	6.2	1.2	/	/
<i>ZrCC-1d</i>							
1	37.2	53.9	4.9	0.9	3.1	0.9	/
2	26.2	68.6	2.8	/	2.4	/	/
3	10.2	67.6	20.0	/	2.1	/	/
4	13.5	78.8	/	/	7.7	/	/
5	29.8	68.2	/	/	2.0	/	/
<i>ZrCC-3d</i>							
1	31.6	61.0	3.3	0.6	3.0	0.6	/
2	27.1	66.1	2.7	0.9	3.2	/	/
3	30.9	53.1	11.6	0.8	3.1	0.4	/
4	29.9	64.3	1.8	0.8	2.9	0.3	/

Table 5.14: EDS analysis of chemically pre-treated and zirconium-coated aluminium alloy 7075. ZrCC were prepared from a 200 ppm H_2ZrF_6 conversion bath for 10 min. The analysis was performed at enumerated spots in SEM BSE images in Fig. 5.10g, Fig. 5.12. The electron beam voltage of the analysed spots was 3 kV, corresponding to an analysis depth of ca. 100 nm.

spot	at. % Al	at. % O	at. % Zr	at. % F	at. % Mg	at. % Zn	at. % Cu	at. % Fe
<i>CP</i>								
1	83.1	10.4	/	/	2.1	2.6	1.1	0.6
2	86.8	8.8	/	/	2.2	2.2	/	/
3	41.5	39.7	/	/	1.6	/	10.2	7.0
<i>ZrCC-as-prepared</i>								
1	42.1	27.7	16.1	9.2	1.3	2.5	1.1	/
2	49.3	25.5	13.3	8.4	1.8	1.8	/	/
3	10.7	48.3	27.6	11.8	0.8	/	0.7	/
<i>ZrCC-1d</i>								
1	37.1	41.8	14.8	1.8	1.0	2.3	1.2	/
2	44.3	36.9	13.6	1.8	1.2	/	/	/
3	21.9	56.7	15.6	1.3	/	3.3	1.2	/
<i>ZrCC-3d</i>								
1	40.9	43.1	10.3	1.8	1.1	2.0	0.8	1.9
2	44.0	44.1	10.2	2.0	1.1	1.6	/	/
3	25.4	60.6	4.1	1.5	/	3.1	1.2	4.1

5.3.6 XPS characterization

Chemically pre-treated aluminium alloys, as-prepared ZrCCs and ZrCCs immersed in 0.5 M NaCl solution for three days were characterized with XPS. XPS method with an analysis depth of ca. 10 nm provides information from the top-most surface of the ZrCC. The composition of the surface obtained from the XPS survey spectra is presented in Table 5.15.

A general characteristic of aluminium alloys is that the surface was composed of Al, O and P. In addition, AA5754 and AA7075 contained Mg at the surface, cast AAA356.0 and AA380.0 contained Si and AA2024 contained a small amount of Cu. Phosphorous originates from the Metaclean alkaline cleaner used in chemical pre-treatment of aluminium alloy, while aluminium and oxygen originate from the aluminium oxide/hydroxide. The Metaclean alkaline cleaner contains NaSiO_3 and probably some P-based corrosion inhibitor/surfactant. After the conversion coating process, most of the ZrCC contained 20–23 at. % Zr, 8–10 at. % F and around 1 at. % Al. ZrCC-2024, and ZrCC-7075 contained a lesser amount of Zr and a higher amount of Al. The latter indicates that ZrCC-2024 and ZrCC-7075 were thinner compared to other alloys, as also shown by EDS (Figs. 5.11–5.12). After three days of immersion in NaCl solution the concentration of F was reduced for all ZrCCs. The concentration of Zr remained at high levels for most ZrCCs except for ZrCC-2024 and ZrCC-7075 where it decreased down to 3 at. %. At the same time, the concentrations of O and Al increased for all aluminium alloys, but the amount of Al was much higher for ZrCC-2024 and ZrCC-7075. The latter two also contained a significant amount of Cl. These results indicate that ZrCC-2024 and ZrCC-7075 dissolved and were covered by a large amount of corrosion products of aluminium hydroxide/oxide. In contrast, ZrCCs applied on other aluminium alloys were very stable and did not corrode.

High energy resolution XPS spectra for elements of interest are presented in Figs. 5.13–5.19. For the most alloys, two peaks appeared in the Al 2p spectrum for CP substrates at binding energy (E_b) 72.5 eV and 74.5 eV (Figs. 5.13–5.19) corresponding to Al metal and $\text{Al}(\text{OH})_3$, respectively [171, 172]. For CP-1050A and CP-380.0, only one peak appeared at 74.5 eV corresponding to $\text{Al}(\text{OH})_3$. This indicates that the surface of CP-1050A and CP-380.0 was covered with a thicker layer of $\text{Al}(\text{OH})_3$, while the hydroxide layer was thinner on other aluminium alloys, thus allowing the detection of Al metal underneath.

In accordance with Table 5.15, Al peaks were not detected for most of the as-prepared ZrCC-coated substrates proving a complete coverage with the coating. Only for ZrCC-2024, Al peak was detected at a binding energy of 75.5 eV suggesting that ZrCC was very thin, and could be related to aluminium fluoride compounds.

After three days of immersion, for the most of ZrCCs the peak at 74.4–74.8 eV re-appeared, indicating the formation of $\text{Al}(\text{OH})_3$ in the top layer of coating, or the formation of corrosion products. However, in the case of 2024-ZrCC a broad peak appeared at 72.8 eV related to pure Al.

For all chemically pre-treated aluminium alloys, the O 1s peaks were centred at 531.7–531.9 eVs indicating the prevalence of hydroxide over oxide (Figs. 5.13–5.19). Qualitatively, one could identify three peaks for bound H_2O , $\text{Al}(\text{OH})_3$ and $\text{ZrO}_2 \cdot x\text{H}_2\text{O}$ at binding energies at 533 eV, 532 (531.9) eV and 530.5 eV, respectively [172, 173]. After the conversion coating process, the centre of O 1s peak shifted to the E_b 530.8–531.7 eV depending on the aluminium alloy showing a shoulder at 530.5 eV that corresponds to hydrated Zr oxide and oxyfluoride ($\text{ZrO}_2 \cdot x\text{H}_2\text{O}$ / ZrF_xO_y).

In general, after immersion ZrCC in NaCl solution, the centre of O 1s peak shifted back to a slightly higher binding energy 531.5–531.7 eV corresponding to $\text{ZrO}_2 \cdot x\text{H}_2\text{O}$ and $\text{Al}(\text{OH})_3$, the only exception was

ZrCC-2024. In the latter case, the centre shifted from 531.7 eV to 530.5 eV, corresponding to aluminium oxide.

The F 1s peak was centred at E_b 684.6–685.2 eV and was present only for the as-prepared ZrCC suggesting the presence of ZrF_4/ZrF_xO_y in the top layer (Figs. 5.13–5.19). After a three-day immersion, the F 1s peak disappeared, indicating leaching of fluorine from the conversion coating and transformation of ZrF_4/ZrF_xO_y to $ZrO_2 \cdot xH_2O$, in accordance with O 1s peak (Figs. 5.13–5.19).

After the conversion coating process, high energy resolution Zr 3d spectra were detected for all aluminium alloys (Figs. 5.13–5.19). The Zr 3d_{5/2} and 3d_{3/2} peaks for the as-prepared conversion coatings were centred at 185.0–185.6 eV and 182.7–183.3 eV depending on aluminium alloy. This spectrum was related to a mixture of ZrF_4/ZrF_xO_y and $ZrO_2 \cdot xH_2O$, considering a relatively high fluorine and oxygen concentration [174].

After immersion in NaCl solution, the peaks were shifted to lower E_b of 184.5–185.0 eV and 182.1–182.6 eV, respectively, indicating the transformation of Zr-fluoride/oxyfluoride to $ZrO_2 \cdot xH_2O$. These results are in correlation with the disappearance of the fluorine peak in the F 1s spectrum. The changes were especially pronounced for ZrCC-2024 and ZrCC-7075 with significantly reduced intensity of Zr 3d peaks related to the dissolution of ZrCC.

Table 5.15: The concentration of elements obtained by XPS analysis of chemically pre-treated (CP) and zirconium conversion coated aluminium alloys: as-prepared and immersed in 0.5 M NaCl solution for 3 days.

AAA	at. % Al	at. % O	at. % Zr	at. % F	at. % Si	at. % Mg	at. % Cu	at. % Zn	at. % P	at. % Na	at. % Cl
<i>CP</i>											
1050A	22.1	73.4	/	/	/	/	/	/	3.9	0.4	/
2024	22.1	73.2	/	/	/	/	/	/	4.6	/	/
3005	12.8	75.1	/	/	/	/	/	/	7.2	4.9	/
A356.0	24.6	67.8	/	/	1.8	/	/	/	5.8	/	/
380.0	23.0	72.8	/	/	1.8	/	0.3	/	2.1	/	/
5754	16.4	71.3	/	/	/	6.9	/	/	5.4	/	/
7075	20.5	67.7	/	/	/	7.5	/	/	4.3	/	/
<i>ZrCC-as-prepared</i>											
1050A	1.5	65.8	22.5	10.1	/	/	/	/	/	/	/
2024	7.1	68.7	18.3	5.9	/	/	/	/	/	/	/
3005	1.0	67.2	23.4	8.4	/	/	/	/	/	/	/
A356.0	/	64.4	24.4	11.3	/	/	/	/	/	/	/
380.0	1.1	66.3	23.3	9.3	/	/	/	/	/	/	/
5754	2.4	64.4	22.8	10.4	/	/	/	/	/	/	/
7075	7.0	67.7	18.0	5.8	/	1.5	/	/	/	/	/
<i>ZrCC-3d</i>											
1050A	5.0	74.4	19.7	0.8	/	/	/	/	/	/	/
2024	23.8	69.3	2.7	/	/	/	1.4	/	1.3	/	1.5
3005	4.9	73.6	17.2	1.5	2.9	/	/	/	/	/	/
A356.0	7.2	75.3	15.5	1.6	1.9	/	/	/	/	/	/
380.0	4.3	75.9	19.2	0.6	/	/	/	/	/	/	/
5754	6.8	72.9	15.9	1.3	/	/	/	/	/	/	/
7075	16.4	69.5	7.7	/	/	2.9	0.4	0.7	1.6	/	8.3

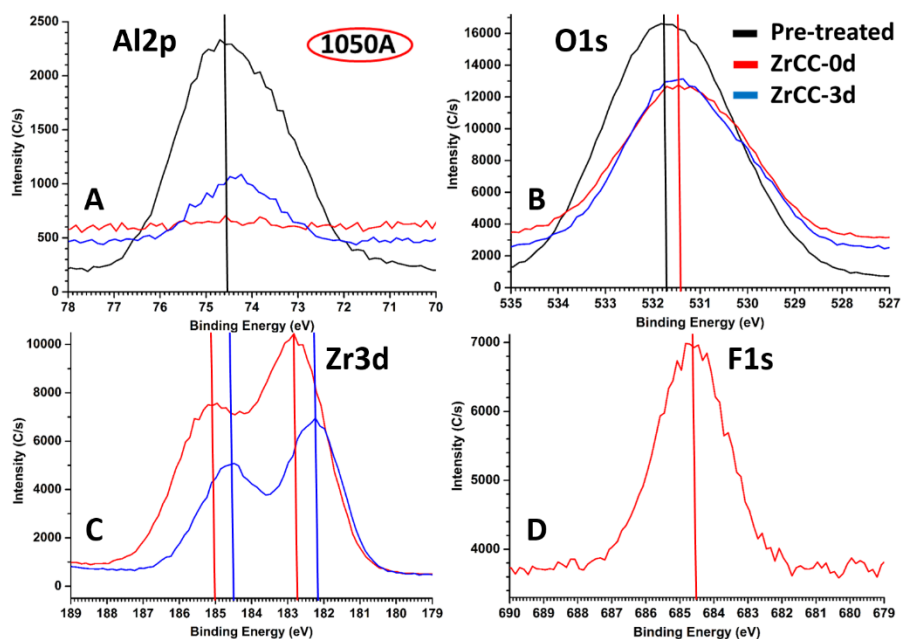


Figure 5.13: High energy resolution XPS spectra (a) Al 2p, (b) O 1s, (c) Zr 3d and (d) F 1s for chemically pre-treated AA1050A and zirconium conversion coated AA1050A, as-prepared, and then immersed in 0.5 M NaCl solution for 3 days. ZrCC were prepared in a 200 ppm H_2ZrF_6 conversion bath for 15 min. Spectra were not normalized on the intensity scale.

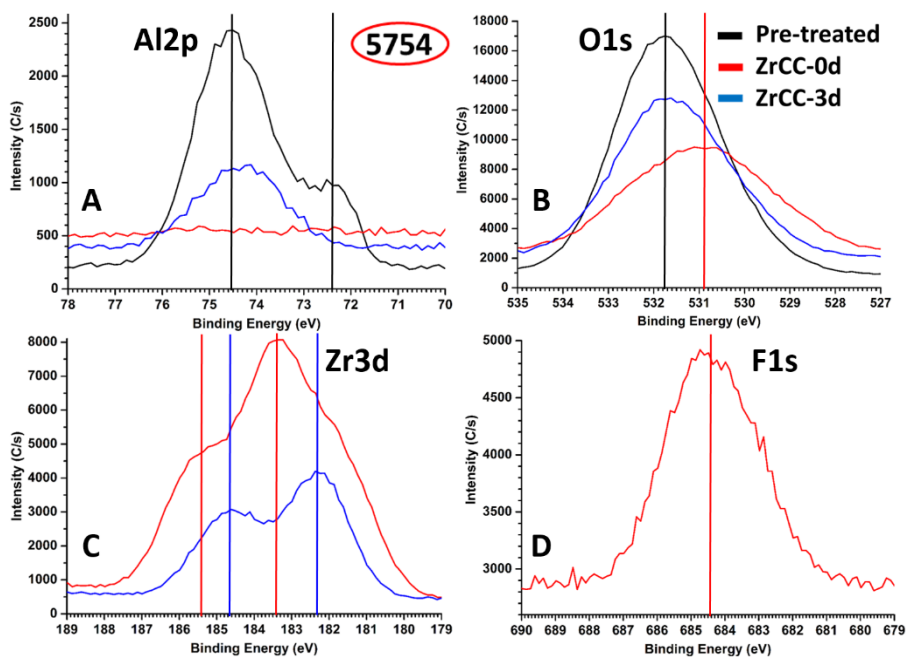


Figure 5.14: High energy resolution XPS spectra (a) Al 2p, (b) O 1s, (c) Zr 3d and (d) F 1s for chemically pre-treated AA5754 and zirconium conversion coated AA5754, as-prepared, then immersed in 0.5 M NaCl solution for 3 days. ZrCC were prepared in a 200 ppm H_2ZrF_6 conversion bath for 10 min. Spectra were not normalized on the intensity scale.

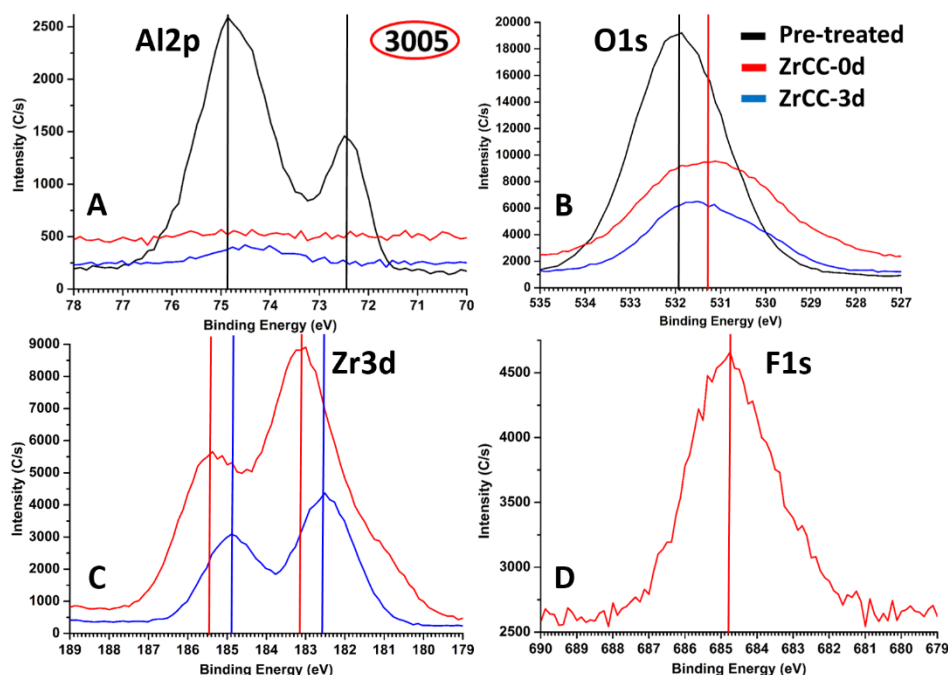


Figure 5.15: High energy resolution XPS spectra (a) Al 2p, (b) O 1s, (c) Zr 3d and (d) F 1s for chemically pre-treated AA3005 and zirconium conversion coated AA3005, as-prepared, then immersed in 0.5 M NaCl solution for 3 days. ZrCC were prepared in a 200 ppm H_2ZrF_6 conversion bath for 10 min. Spectra were not normalized on the intensity scale.

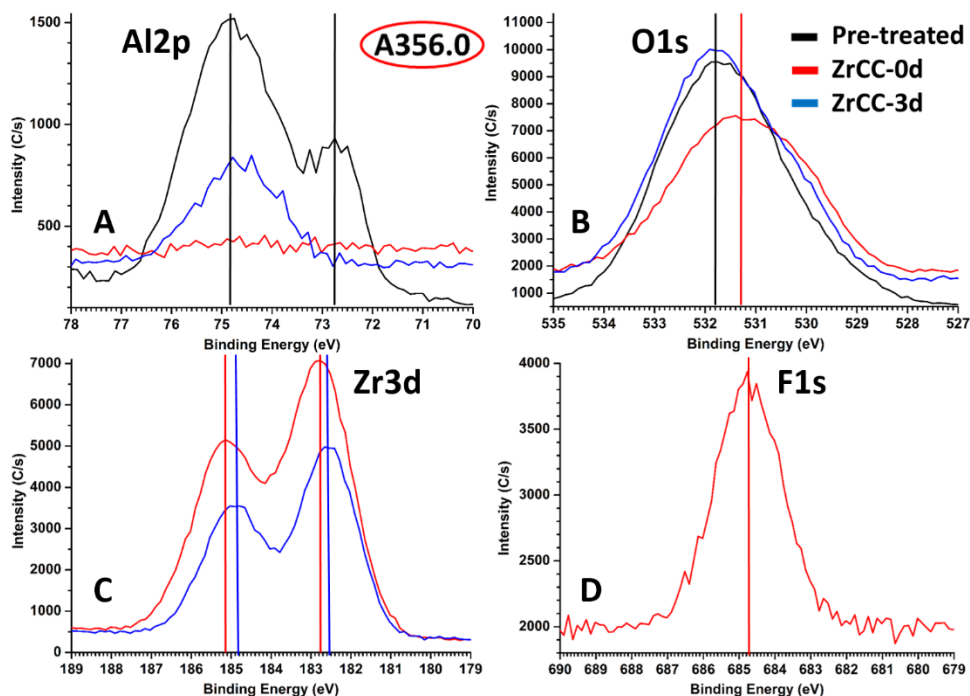


Figure 5.16: High energy resolution XPS spectra (a) Al 2p, (b) O 1s, (c) Zr 3d and (d) F 1s for chemically pre-treated AAA356.0 and zirconium conversion coated AAA356.0, as-prepared, then immersed in 0.5 M NaCl solution for 3 days. ZrCC were prepared in a 200 ppm H_2ZrF_6 conversion bath for 10 min. Spectra were not normalized on the intensity scale.

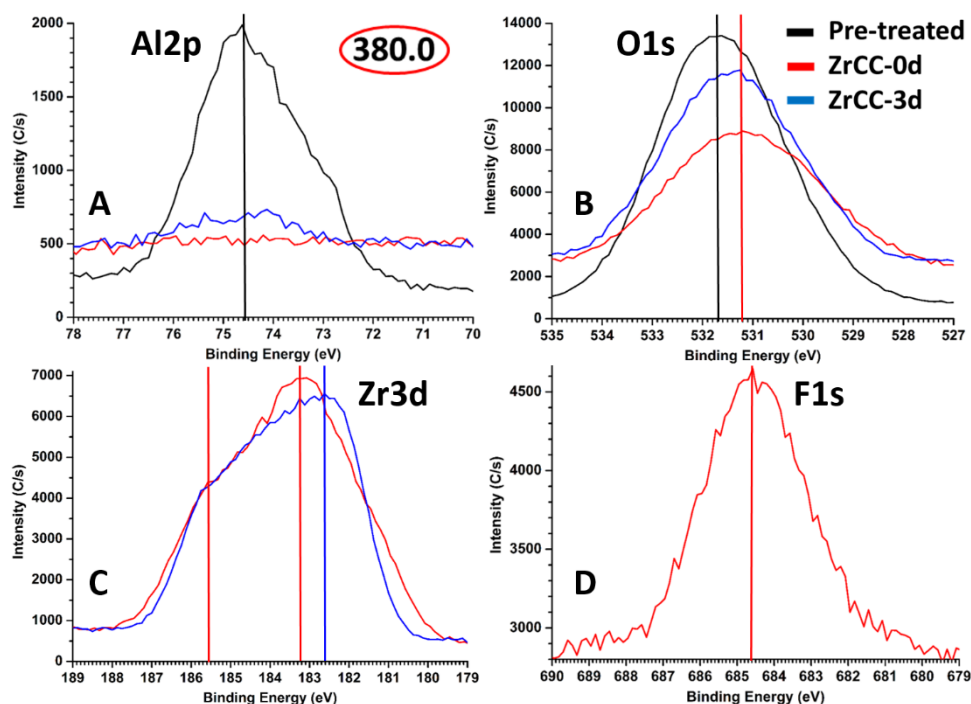


Figure 5.17: High energy resolution XPS spectra (a) Al 2p, (b) O 1s, (c) Zr 3d and (d) F 1s for chemically pre-treated AA380.0 and zirconium conversion coated AA380.0, as-prepared, then immersed in 0.5 M NaCl solution for 3 days. ZrCC were prepared in a 200 ppm H_2ZrF_6 conversion bath for 10 min. Spectra were not normalized on the intensity scale.

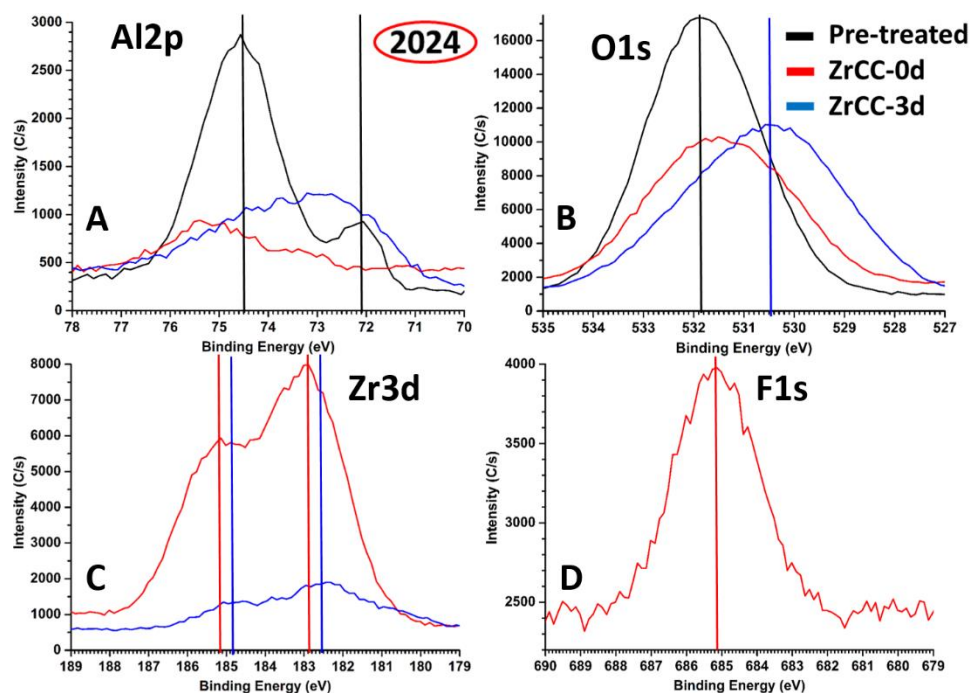


Figure 5.18: High energy resolution XPS spectra (a) Al 2p, (b) O 1s, (c) Zr 3d and (d) F 1s for chemically pre-treated AA2024 and zirconium conversion coated AA2024, as-prepared, then immersed in 0.5 M NaCl solution for 3 days. ZrCC were prepared from a 200 ppm H_2ZrF_6 conversion bath for 3 min. Spectra were not normalized on the intensity scale.

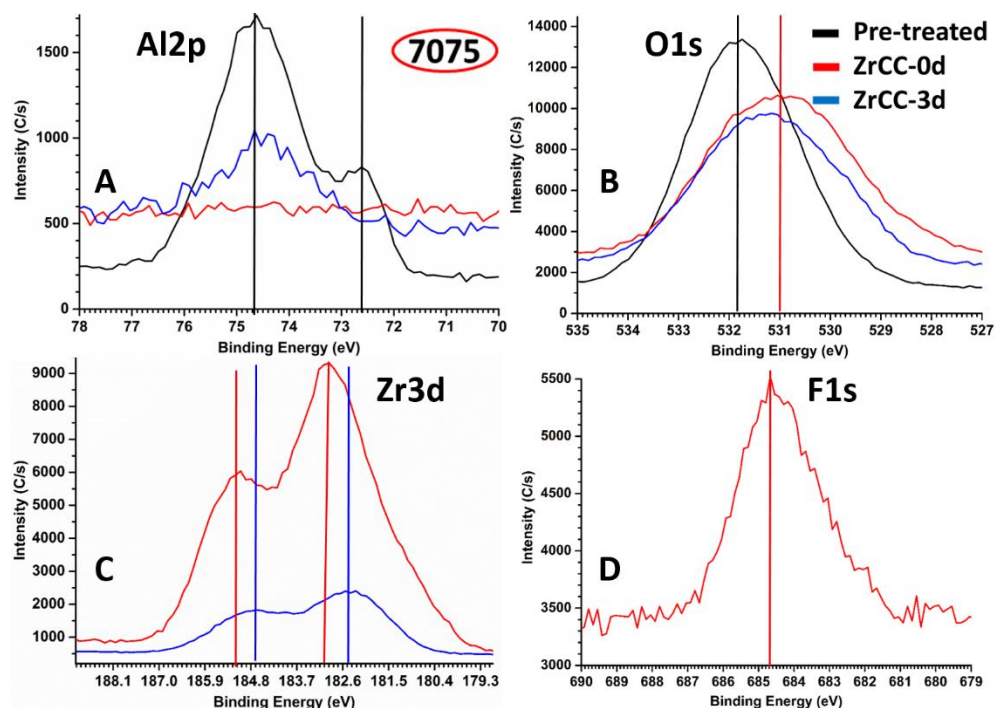


Figure 5.19: High energy resolution XPS spectra (a) Al 2p, (b) O 1s, (c) Zr 3d and (d) F 1s for chemically pre-treated AA7075 and zirconium conversion coated AA7075, as-prepared, then immersed in 0.5 M NaCl solution for 3 days. ZrCC were prepared from a 200 ppm H_2ZrF_6 conversion bath for 10 min. Spectra were not normalized on the intensity scale.

5.3.7 ToF-SIMS characterization

To check the thickness of ZrCCs and their structure, we recorded ToF-SIMS negative ion profiles for as-prepared conditions and after immersion in 0.5 M NaCl solution for three days (Figs. 5.20-5.21). The sputtering rate was 0.30 nm/s (± 0.02 nm/s). ToF-SIMS ion depth profiles recorded on areas of 500 μm^2 provide a mean conversion coating thickness (Table 5.16). The boundary between the outer layer and the inner layer was determined as the depth at which the intensity of ZrO^- dropped to a half compared to its value at the layer surface. The depth at which the AlOF^- intensity dropped to half its maximum intensity was taken as the boundary between the inner layer and the substrate.

Table 5.16: The average thickness of zirconium conversion coatings applied on aluminium alloys. ZrCCs were prepared in a 200 ppm H_2ZrF_6 conversion bath for optimal conversion time (Table 5.1). Coating thickness was determined by the ToF-SIMS method (Fig. 5.21).

Aluminium Alloy Thickness, nm

1050A	60
2024	12
3005	30
A356.0	60
380.0	60
5754	60
7075	36

The general feature of ZrCCs applied on aluminium alloys was a bi-layer structure with an outer layer having a higher concentration of ZrO^- (it could be $\text{ZrO}_2 \cdot x\text{H}_2\text{O}$ / ZrO_xF_y species) and a lower concentration of AlOF^- . The inner layer had a higher concentration of AlOF^- ions and a lower concentration of ZrO^- ions compared to the outer layer. The ToF-SIMS profiles of AlOF^- ions were accompanied with profiles for AlO^- , MgO^- and SiO^- ions. The only exception to this behaviour was ZrCC-2024 that was much thinner than other conversion coatings and had a single-layer structure. An interesting detail to note is that for all ZrCCs the intensity of ZrO^- ions profile was higher or same as the intensity of the AlOF^- ions profile. However, in the case ZrCC-3005, the intensity of the AlOF^- ions profile was higher than the intensity of the ZrO^- ions profile.

After three days of immersion in 0.5 M NaCl, general features of ZrCC-1050A, ZrCC-3005, ZrCC-A356.0, ZrCC-380.0 and ZrCC-5754 that showed adequate corrosion protection were as follows. The profile of ZrO^- ions was similar having a maximum in the outer layer (Fig. 5.21). The intensity of F^- and AlOF^- ions profiles significantly decreased, while that of Cl^- ions increased. The latter followed the same shape as that of F^- ions. This suggests that Cl^- ions were exchanged with F^- ions and incorporated within the ZrCC structure. Compared to as-prepared coatings, the intensity of the AlO^- profile was larger in the outer layer, reached a maximum (most pronounced for ZrCC-3005) and then formed a plateau in the inner part of ZrCC. This trend indicates that with immersion in NaCl solution the coatings, especially the outer layers, become enriched in

$\text{Al}_2\text{O}_3/\text{Al}(\text{OH})_3$. For the ZrCC-3005, the enrichment in AlO^- was pronounced also at the inner layer/substrate interface which could be the reason for excellent performance of this particular coating. Upon immersion in NaCl, the AlOF^- profile is following the opposite trend to AlO^- and becomes strongly diminished in the outer layers suggesting that it is gradually transformed to AlO^- . These transformations could be one of the reasons for the improved corrosion resistance of ZrCCs. The MgO^- profile decreased and shifted deeper toward the substrate. The intensity of SiO^- profiles was the same and shifted towards the surface indicating incorporation of Si into the coating structure; an exception was ZrCC-5754.

ZrCC-2024 and ZrCC-7075 had different trends in negative ion profiles after immersion in NaCl. The intensity of ZrO^- , AlOF^- , AlO^- ions profiles decreased significantly for both alloys and was much lower compared to other aluminium alloys. The intensity of Cl^- ions profiles increased significantly for both alloys, however in the case of ZrCC-7075 it was much higher compared to other profiles. These results indicate that ZrCC-2024 and ZrCC-7075 dissolved and were covered with corrosion products. For ZrCC-2024, the intensity of CuO^- ions profiles increased, while for ZrCC-7075 that of FeO^- increased. Based on these results, it can be stated that ZrCC-2024 and ZrCC-7075 were not stable and did not provide proper corrosion protection during immersion in 0.5 M NaCl.

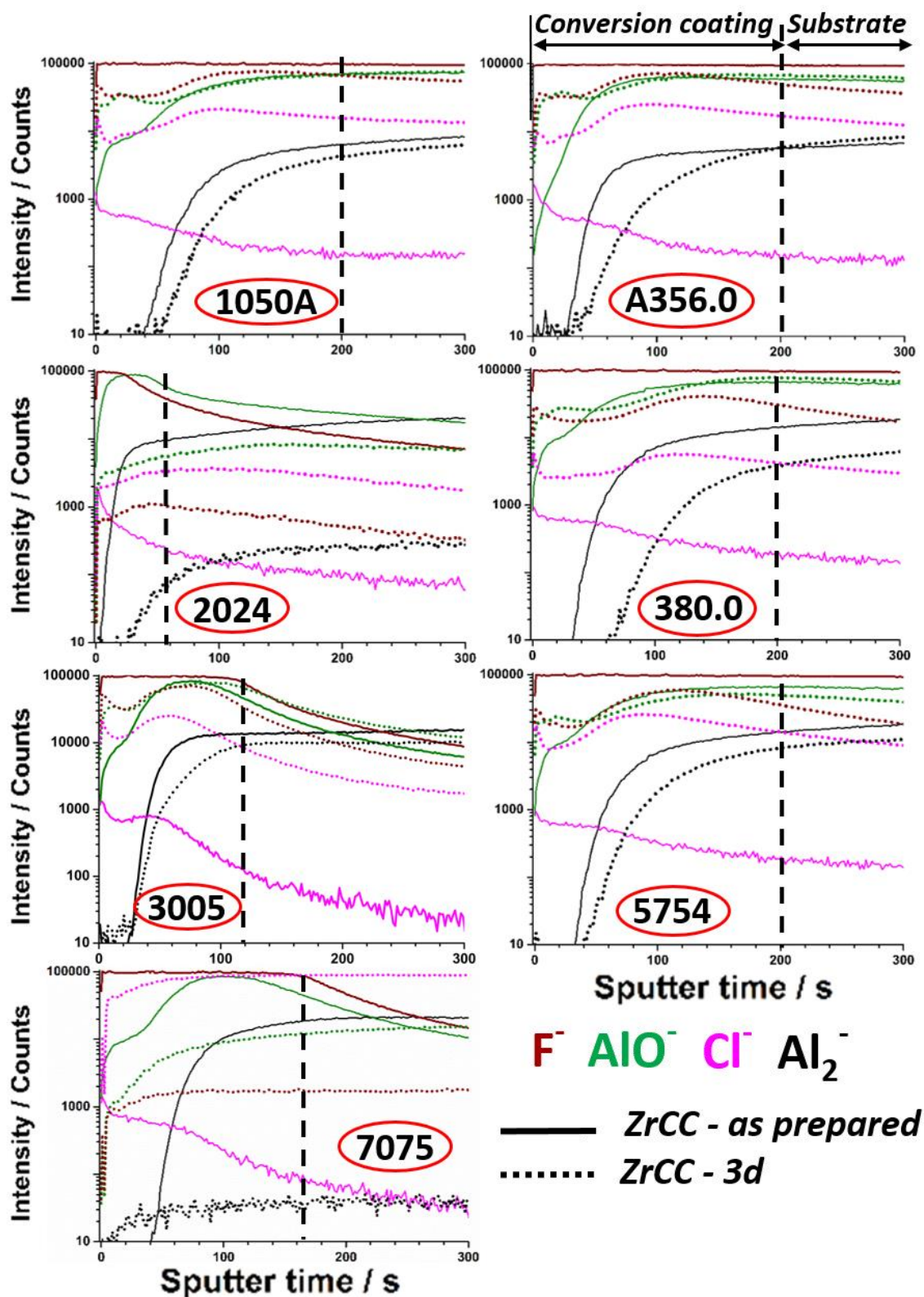


Figure 5.20: ToF-SIMS negative ions depth profiles of zirconium conversion coatings applied on aluminium alloys. The conversion time was 10 min. Full lines - as-prepared ZrCC; dotted lines - ZrCC after 3 days of immersion in 0.5 M NaCl solution. Black vertical dash line -border between the conversion coating and the substrate.

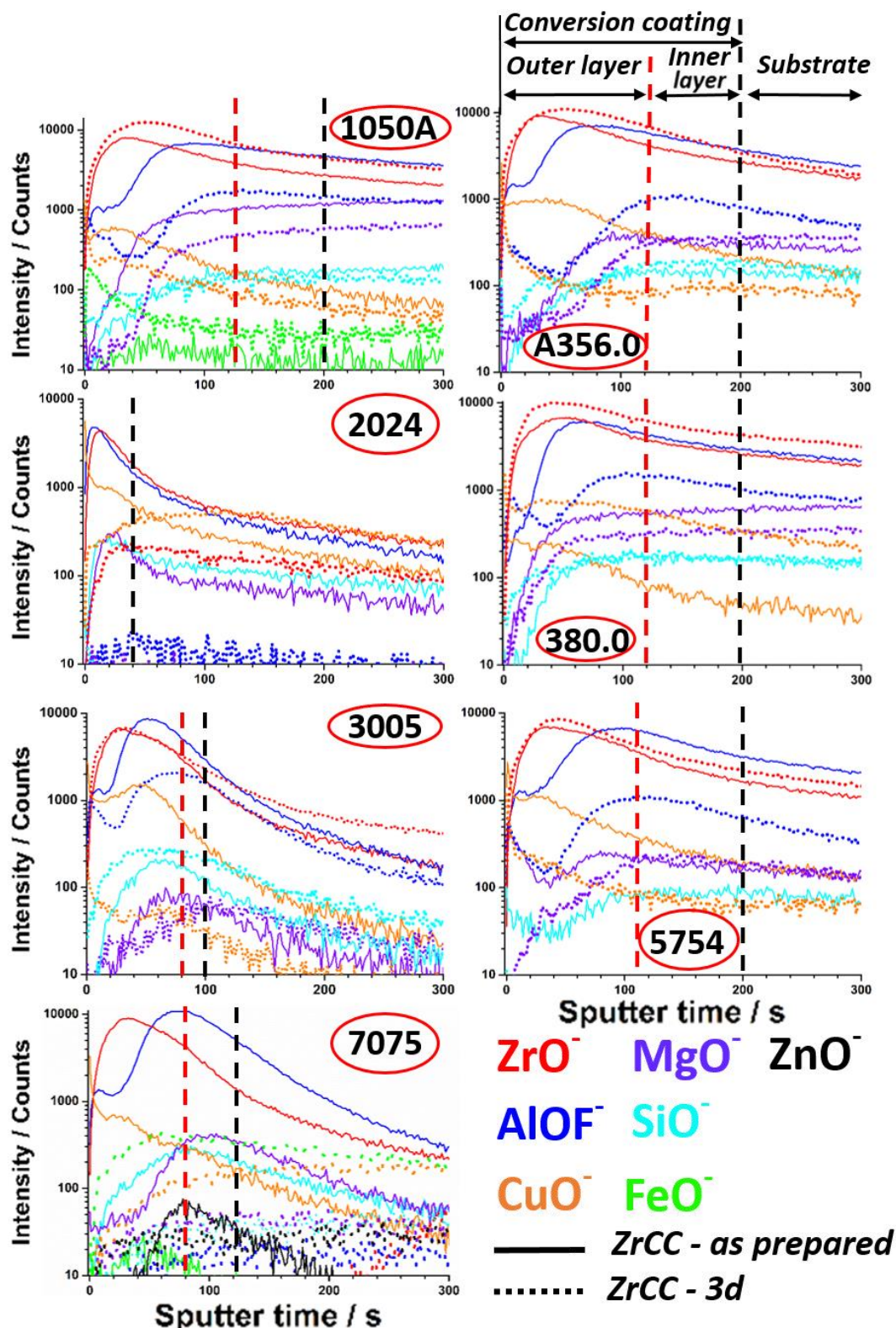


Figure 5.21: ToF-SIMS negative ions depth profiles of zirconium conversion coatings applied on aluminium alloys. The conversion time was 10 min. Full lines - as-prepared ZrCC; dotted lines - ZrCC after 3 days of immersion in 0.5M NaCl solution. Black vertical dash line - border between the conversion coating and the substrate; red vertical dash line - border between the outer layer and the inner layer.

5.4 Discussion

Electrochemical impedance spectroscopy measurements showed that corrosion resistance of ZrCC-3005 was continually increasing during five days of immersion in 0.5 M NaCl solution; corrosion resistance of ZrCC-1050A and ZrCC-A356.0 increased up to 3 days, but the fourth day of immersion average impedance modulus at low frequency decreased indicating that pitting occurred. However, for ZrCC-A356.0, the value recovered and remained at the steady value of ca. $1.4 \text{ M}\Omega\cdot\text{cm}^2$ indicating active corrosion protection. The same trend was noticed for ZrCC-5754 and ZrCC-380.0, but to a lesser extent; impedance modulus for these two alloys showed a similar trend at the beginning but then decreased slowly reaching values of ca. $1 \text{ M}\Omega\cdot\text{cm}^2$ on the fifth day of immersion. On the other hand, ZrCC-2024, and ZrCC-7075 showed the highest impedance modulus of all ZrCCs after 1 h immersion but then significantly decreased, indicating that pitting already occurred and that ZrCC-2024 and ZrCC-7075 did not provide proper corrosion protection.

SEM-EDS and XPS analyses showed that during immersion of ZrCC-1050A, ZrCC-3005, ZrCC-A356.0, ZrCC-380.0 and ZrCC-5754 in 0.5 M NaCl fluorine leached out, the concentration of oxygen increased and the concentration of Zr remained approximately at the same level. High-resolution XPS spectra showed that in the top part of the coatings $\text{ZrF}_4/\text{ZrO}_x\text{F}_y$ transformed into $\text{ZrO}_2\cdot x\text{H}_2\text{O}$ and was accompanied by the formation of $\text{Al}(\text{OH})_3$.

ToF-SIMS depth profiles of ZrCC-1050A, ZrCC-3005, ZrCC-A356.0, ZrCC-380.0 and ZrCC-5754 s had a similar shape and showed a similar trend during immersion in chloride solution. According to ToF-SIMS analysis, fluorine leached out from ZrCCs, but zirconium oxide was stable after three days of immersion. At the same time, the AlO^- profile increased, indicating the increased concentration of aluminium oxide/ hydroxide in the ZrCCs. Transformation of $\text{ZrF}_4/\text{ZrO}_x\text{F}_y$ into $\text{ZrO}_2\cdot x\text{H}_2\text{O}$ and incorporation of $\text{Al}(\text{OH})_3$ was responsible for the self-sealing of ZrCCs that provided increased corrosion resistance during immersion in 0.5 M NaCl solution. However, ZrCC-A356.0 and ZrCC-380.0 were pitted at Zn-rich IMPs/spots during immersion in 0.5 M NaCl.

For ZrCC-2024 and ZrCC-7075, SEM-EDS, XPS, and ToF-SIMS analyses showed that the coatings were not stable during immersion in chloride solution. Fluorine leached out but, at the same time, ZrO_2 dissolved and was covered with corrosion products of $\text{Al}(\text{OH})_3$, indicating that ZrCC did not provide proper corrosion protection for these two alloys. The ZrCC-2024 had a small average thickness of 12 nm, but SEM-EDS analysis showed that it was significantly thicker at Cu-rich IMPs compared to matrix. The small and unbalanced thickness of ZrCC-2024 was the main reason for inadequate corrosion protection. We assume that with an adequate surface pre-treatment that will dissolve large Cu-rich IMPs and redeposit Cu in the form of small cathodic sites, ZrCC-2024 would perform much better. In the case of ZrCC-7075 the average coating thickness (36 nm) was significantly higher compared to ZrCC-2024 (12 nm) and uniform across the substrate surface. Our opinion based on microstructural analysis and electrochemical data is that the main reason for poor corrosion protection of ZrCC-7075 was a too high content of Zn in the matrix (5.81 wt.%). Even for ZrCC-A356.0 and ZrCC-380.0, which contain substantially lower content of Zn in the matrix (0.07 and 1.2 wt.%, respectively), the pitting was initiated at Zn-rich areas. Proper surface pre-treatment for AA7075 before applying ZrCC could improve the ZrCC performance significantly. Optimal pre-treatment for AA7075 should remove or passivate Zn-rich IMPs at the alloy surface before the application of ZrCC.

5.5 Conclusions

- Zirconium conversion coatings provided excellent corrosion protection for aluminium alloys 3005 and A356.0 and very good corrosion protection for aluminium alloys 1050A, 380.0, 5754.
- Zirconium conversion coatings did not provide adequate corrosion protection for aluminium alloys 2024 and 7075.
- The coating had a bi-layer structure and thickness in the range of 30 nm to 60 nm. The exception was the ZrCC-2024 which had a single-layer structure and was on average only 12 nm thick with a very unbalanced thickness between IMPs and matrix.
- During immersion in 0.5 M NaCl, average impedance module $|Z|_{3\text{mHz}}$ of ZrCC-3005 increased continually up to 5 days, for ZrCC-1050A and ZrCC-A356.0 it increased up to 3 days and for ZrCC-380.0, and ZrCC-5754 it increased up to 1 day. The increase in $|Z|_{3\text{mHz}}$ indicates the self-sealing of the coating.
- ZrCC-2024 and ZrCC-7075 had the highest impedance modulus at the beginning of the immersion, but after only one day, the values dropped, indicating inadequate corrosion protection.
- During immersion in 0.5 M NaCl, flourine leached out of ZrCC, $\text{ZrF}_4/\text{ZrF}_x\text{O}_y$ was transformed into $\text{ZrO}_2 \cdot x\text{H}_2\text{O}$, and aluminium oxide/hydroxide was incorporated into a coating structure leading to self-sealing of ZrCC.
- Corrosion damage and pitting were initiated at Zn-rich areas in ZrCC-A356.0, ZrCC-380.0 and ZrCC-7075.

Chapter 6

Conclusions and Future Outlook

This chapter summarizes all the experimental results and thesis objectives. The effect of sodium sulphide on corrosion behaviour of AlSi7Mg0.3 aluminium alloy in artificial seawater was successfully studied and discussed. The formation of zirconium conversion coatings and their electrochemical behaviour was studied and discussed for aluminium alloys. For the first time, self-sealing effect and possible active corrosion protection were reported for zirconium conversion coatings applied to aluminium alloys.

The main conclusions are listed and discussed under each stated objective, as outlined in Chapter 1, Section 1.6.

1) To study the influence of Na₂S on the corrosion behaviour of AlSi7Mg0.3 aluminium alloy in artificial seawater.

According to the results obtained in Chapter 2, the addition of a small concentration of Na₂S up to 100 ppm has a beneficial effect on corrosion resistance of AlSi7Mg0.3 in artificial seawater. When the concentration of Na₂S was 20 ppm, sulfides improved barrier properties of natural aluminium oxide. Higher concentrations, from 50 to 100 ppm, caused the incorporation of Mg²⁺ ions from the solution into the outer layer of natural aluminium oxide providing additional corrosion protection to AlSi7Mg0.3 substrates.

The objective was achieved in Chapter 2.

2) To systematically study and obtain scientific data about the formation and electrochemical behaviour of zirconium conversion coatings applied on aluminium alloys: 1050, 2024, 380.0, 3005, A356.0, 5754, 7075.

According to the results obtained in Chapters 3-5, the performance of zirconium conversion coatings strongly depends on conversion time. At the same time, optimal conversion time depends on the conversion bath and conversion process parameters like stirring rate, pH, the concentration of H₂ZrF₆, etc. Optimally prepared ZrCC applied to AA 3005 (Chapter 3), and AlSi7Mg0.3 (Chapter 4) showed self-sealing and active corrosion protection behaviour. Microstructural characterization showed that during immersion in 0.5 M NaCl solution the concentration of fluorine in the ZrCC decreased, while that of Al and O increased. This indicated that during immersion in 0.5 M NaCl solution, zirconium fluoride was transformed into zirconium oxide. In contrast, aluminium oxide and elements from the substrate were incorporated into the bottom layer of ZrCC. This change in the microstructure of ZrCC leads to the closing of nano-pores and increased corrosion resistance of ZrCC – “self-sealing effect”, which was reported for the first time for this kind of coatings.

The results in Chapter 5 showed that the self-sealing effect strongly depends on the chemical composition of the substrate. The self-sealing effect was expressed in the following order from strongest to weakest: AA3005 $\geq$ AA A356.0 $\geq$ AA 5754 $\geq$ AA 380.0 $\geq$ 1050 $\geq$ 7075 $\approx$ 2024. Further, ZrCC applied to alloys: 3005, A356.0, 5754 and 380.0 showed recovery after pitting, indicating possible active corrosion protection behaviour. This result indicates that major alloying elements in certain alloys like Mn, Mg and Si could have incorporated into ZrCC during immersion in 0.5 M NaCl and improve the corrosion resistance of ZrCC by providing active corrosion protection.

The objective was achieved in Chapters 3, 4 and 5.

The hypotheses of this dissertation outlined in Chapter 1, Section 1.7 can be confirmed or refuted as follows:

- 1. Specific concentrations of sodium sulphide have a beneficial effect on corrosion behaviour of AlSi7Mg0.3 aluminium alloy in chloride-containing environments such as a solution of sodium chloride or artificial seawater.**

According to the results obtained in Chapter 2, this hypothesis was correct.

The addition of a small concentration of Na₂S up to 50 ppm was beneficial for corrosion resistance of AlSi7Mg0.3 aluminium alloy in artificial seawater.

- 2. Zirconium conversion coatings applied to aluminium alloys can achieve self-sealing characteristics.**

According to the results obtained in Chapters 3, 4 and 5, this hypothesis was correct.

The obtained results showed that, depending on aluminium alloy, some zirconium conversion coatings possess a self-healing ability/active corrosion protection when immersed in 0.5 M NaCl solution.

- 3. Novel, optimized zirconium conversion coatings can reach the performance to the level similar to chromate conversion coatings.**

According to the results obtained in Chapters 3, 4 and 5, this hypothesis was correct.

Based on the measured values of impedance modulus after 24 h in 0.5 M NaCl it can be projected with >80 % probability that the coatings will pass the 168 h neutral salt spray test which is required to be used in industrial applications.

Future Work

The work in this doctoral thesis highlighted some new fundamental insights about the formation and electrochemical behaviour of zirconium conversion coatings applied to aluminium alloys. For the first time, self-sealing effect and active corrosion protection of zirconium conversion coatings were reported in this work [91, 92, 108]. This result will help to develop novel zirconium coatings and a post-treatment/sealing process in future work. Results showed that some chemical elements are de-alloyed from substrates and incorporated into ZrCC when immersed in 0.5 M NaCl solution [91, 92, 108].

These results pointed the direction for the development of new zirconium-based conversion coatings that should contain elements like Mn, Mg and Si but in the first place Mn. Manganese and zirconium are crucial elements for the development of new green chromium-free conversion coatings with the same performance level as the chromate conversion coating or even better. Manganese has standard oxidation states +2, +3, +4, +6, and +7, although all oxidation states from -3 to +7 have been observed, and many soluble and insoluble oxides and compounds. These preconditions are required for the development of excellent conversion coating. However, its oxides are unstable in a wide range of pH and do not provide proper corrosion protection. Manganese, in combination with other elements such as Zr and Ti, could provide a green chromium-free conversion coating with excellent barrier properties and active corrosion protection.

This doctoral thesis reports the importance of leaching of fluorine from ZrCC when immersed in a NaCl solution. This could be one of the reasons why wet adhesion of organic coatings is much worse than dry adhesion and decreases during immersion in an aqueous solution. Proper post-treatment should provide sealing of ZrCC improving its barrier protection and possibly adding an active corrosion protection component. At the same time, good post-treatment should eliminate fluorine from the coating and improve the wet adhesion of the coating.

To summarize, the development of a novel zirconium-manganese conversion coating, development of effective post-treatments for zirconium conversion coating and studying the influence of fluorine leaching on wet adhesion of ZrCC will be the core of our future work.

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Publications Related to the Thesis

Journal Articles

G. Šekularac, J. Kovač and I. Milošev, "Comparison of Electrochemical Behaviour and Self-sealing of Zirconium Conversion Coatings Applied on Aluminium Alloys of Series 1xxx to 7xxx, " *Journal of The Electrochemical Society*, submitted, 2020

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Biography

Gavrilo Šekularac was born on April 21, 1984, in Belgrade, Serbia. He obtained a master's degree in Organic Chemical Technology and Polymer Engineering, at the Faculty of Technology and Metallurgy, University of Belgrade, in September 2011 under the mentorship of Dr. Jasmina Nikolić, associate professor.

In the period of 2012-2015, he worked as a researcher at the Department of Electrochemistry, Institute of Chemistry, Technology and Metallurgy, in Belgrade.

In October 2015, he enrolled his PhD studies at the Jožef Stefan International Postgraduate School in the field of Nanosciences and Nanotechnologies, and in December 2015, he was enrolled as a young researcher under the mentorship of Prof. Dr. Ingrid Milošev at the Jožef Stefan Institute. His PhD study was financed by the Slovenian Research Agency (ARRS).

Gavrilo Šekularac is the author of 16 original scientific papers (8 as first author and 8 as co-author) and one book chapter. His research interest is focused on electrochemistry, corrosion protection of aluminium alloys, surface pre-treatment of metals, chemical conversion coatings, electrochemical storage and conversion of energy.

His PhD study focused on the investigation of zirconium conversion coatings for corrosion protection of aluminium alloys.