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Tan, Juan; Crosio, Marco; Vinkel, Nadja Maria; Jensen, Peter; Abrahams, Shoshan Tamar; Gudla, Visweswara Chakravarthy; Ambat, Rajan

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Highlights

- Accelerated oxide growth on Al-Zr and Al-Ti coatings under hydrothermal conditions.
- Dual layered boehmite film with needle structure on top and compact oxide below.
- Zr and Ti enrichment in compact Al oxide film compared to needle like top layer.
- Reduced anodic activity for treated Al-Zr and Al-Ti compared to treated Aluminium.
- Dissolution starts at locations of non-uniform coverage of hydrothermal layer.

Hydrothermal Treatment
in Autoclave @ 1.3 bar

**On the Microstructural and Electrochemical Nature of Hydrothermally Treated Al-Zr and Al-Ti
Surfaces**

*Juan Tan¹, Marco Crosio¹, Nadja Vinkel¹, Peter Jensen¹, Shoshan Tamar Abrahimi², Visweswara
Chakravarthy Gudla^{1, 3*}, Rajan Ambat¹*

*¹Section of Materials and Surface Technology, Department of Mechanical Engineering, Technical
University of Denmark, Produktionstorvet, Kongens Lyngby, 2800 Denmark*

*²Department of Materials and Chemistry, Research Group Electrochemical and Surface
Engineering, Vrije Universiteit Brussel, Pleinlaan 2, 1050 Brussels, Belgium*

*³Henry Moseley X-ray Imaging Facility, Department of Materials, Alan Turing Building, Upper
Brook Street, The University of Manchester, Manchester, M13 9PL United Kingdom*

**Corresponding author – chakri_gvc@yahoo.co.in; vcgudla@manchester.ac.uk*

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Abstract

Hydrothermal treatment of sputtered Al-Zr and Al-Ti coatings was performed in an autoclave. Electron microscopy of generated conversion layers revealed dual layered boehmite films. Needle morphology at top, and thin compact oxide at interface with metal substrate was observed. X-ray Energy Dispersive, and photoelectron spectroscopy revealed enrichment of Zr or Ti in compact oxide, and oxidation of Zr, Ti and Al. Potentiodynamic polarisation showed decrease in passive current densities due to treatment. Treated Zr containing surfaces showed lower corrosion current density when compared to those containing Ti. The observed electrochemical properties are correlated with microstructure and composition of conversion layers.

Keywords – A. aluminium; A. sputtered films; B. polarization; B. TEM; C. passive films; C. interfaces.

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Author Contribution

JT, PJ, MC, and NV performed the electrochemical experiments and analysis of the results. SA performed the analysis of the XPS results. VCG performed the XPS and microscopy characterization. VCG and RA conceptualised the research work and execution. All the authors contributed to the writing and preparation of the manuscript. All the authors have approved the manuscript in its current format.

1. Introduction

Aluminium alloys are widely used as structural materials in various applications owing to their good strength to weight ratio, corrosion resistance, and ability to be surface modified to suit various functional needs. Alloying of aluminium to develop high strength materials increases the microstructural heterogeneity, and decreases the natural corrosion resistance provided by its tenacious native oxide layer [1–5]. Over the years, chromate based chemical and electrochemical conversion coatings have been applied successfully on aluminium to improve the corrosion resistance, and also as pre-treatments to improve adhesion to organic coatings and adhesives [6–9]. However, due to the well-established toxic and carcinogenic nature of the constituents in these coatings, the need for more environmentally friendly processes has led to the development of various chromate-free alternatives [10–14]. The majority of promising alternatives, particularly for aluminium alloys are based on the zirconium- and titanium- treatments [15–18]. Most of the studies reported for zirconium- and titanium- based coatings are applied as dip-treatment, typically using fluozirconate or fluotitanate acid based solutions [16,19]. Recently, investigations on the use of hydrothermal treatments based on high temperature steam have showed promise as alternatives for modification of aluminium surfaces for protection against corrosion as well as to serve as pre-treatments for further surface processing [20–25]. Jariyaboon et al. exposed AA1050 to pressurised steam to obtain a boehmite type oxide of approx. 600 nm thickness which resulted in a reduction of anodic and cathodic activities by a factor of 25 [20]. Din et al. further investigated the effect of hydrothermal treatment on the nature of the obtained conversion layers and found that a good coverage of the intermetallic phases in AA1090 was observed and TEM images showed a top dual layered conversion coating formation [23]. Further, it was observed that the presence of hydroxyl groups on the hydrothermal conversion layer improved the performance of applied powder coatings on these surfaces under acetic acid salt spray and filiform corrosion testing [21]. Recent developments in this area include use of different acidic chemistries in

the steam [26] as well as addition of species such as KMnO_4 [27], and TiO_2 nanoparticles [28]. The motivation for this is to obtain enhanced corrosion protection ability provided by the hydrothermally generated compact sub-micron thick boehmite layer on aluminium [29,30] under these treatment conditions, and further by incorporation of additional species to this layer and thus modifying its nature [31,32]. In this aspect, the incorporation of Zr and Ti species to the hydrothermally generated conversion layers on Aluminium is interesting to study due to the possibility of extending the corrosion protection by formation of mixed oxides/hydroxides of Al-Zr and Al-Ti on Al surfaces.

In this study, magnetron sputtering has been used to incorporate Zr and Ti into coatings on Al surfaces. The model binary alloy surfaces are used for investigating the structure and properties of the obtained conversion layers as a function of Zr or Ti content after hydrothermal treatment which in a more practical sense can then be extended towards better understanding the addition of Zr and Ti containing species into a hydrothermal bath that can be sprayed onto components for incorporation into the conversion layers at an industrial scale. Magnetron sputtered coatings have been extensively used for understanding the electrochemical behaviour of various binary and ternary systems and hence provide the advantage of model alloy preparation with tailored compositions [33–38]. Al-Zr and Al-Ti coatings of varying Zr and Ti concentrations prepared using magnetron sputtering were subjected to hydrothermal treatment in order to generate conversion layers. The microstructure, surface morphology, and composition of the oxide layer were investigated as a function of hydrothermal treatment using radio frequency glow discharge optical emission spectroscopy (RF-GDOES), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and energy dispersive X-ray spectroscopy (EDS). The electrochemical behaviour of the hydrothermally generated conversion coated surface is also investigated using potentiodynamic polarisation and open circuit potential measurements. Further, intermittent changes in the behaviour of the treated surface during potentiodynamic polarization is

characterized and observed using focused ion beam in-situ sectioning in a scanning electron microscope, specifically the passivation followed by breakdown resulting in onset of pitting corrosion. The obtained results are presented and compared with those obtained for treated pure Al surfaces and discussed.

2. Experimental

2.1. Materials and Pre-treatments

Aluminium substrates (Reinaluminium™, composition in accordance with AA1090 specifications) were obtained in dimensions of 100 mm × 25 mm × 5 mm from Alcan Rolled Products, Germany. The samples were mechanically polished using SiC polishing papers (120 grit size to 4000 grit size) and degreased using acetone between the individual polishing steps. Binary coatings containing Zr, or Ti in Al with concentrations aimed at four different values were deposited using DC magnetron sputtering process (described elsewhere in detail [39]). The thickness of the coatings was aimed at 5 µm. The composition of the coatings measured using SEM-EDS is presented in Table 1. The sputter coated surfaces were degreased in an ultrasonic bath for 10 min using acetone, followed by rinsing in the same solution and air dried at room temperature. Due to the presence of a heavily deformed surface layer (Beilby layer) [40–42], the polished uncoated Al samples (reference samples) were subjected to alkaline etching treatment by immersing in an aqueous solution of 10 wt.% NaOH at 60 °C for 10 min, rinsing in deionised water for 1 min followed by desmutting in 69 vol.% HNO₃ for 1 min. The specimens were then washed with deionised water, and dried in air at room temperature.

Table 1

2.2. Hydrothermal treatment

After pre-treatment, the surfaces of the specimens were exposed to 15 psi pressurised steam, generated from deionised water in an autoclave (All American Pressure Canners, USA). The treatment time measured from the point when 15 psi pressure is reached is kept at 10 min and the maximum temperature reached during the treatment was 118 °C. After the treatment, the steam pressure was gradually released and the samples were dried in warm air.

2.3. Characterization

2.3.1. Compositional Depth Profiling

Compositional depth profiling across the thickness of the surfaces was carried out using radio frequency glow discharge optical emission spectroscopy (RF-GDOES, GD-2 profiler, Horiba Jobin YVON). The instrument is equipped with a radio frequency generator, a standard discharge source with an anode of 4 mm internal diameter, a monochromator and a polychromator optical spectrometers, and coupled to a Quantum XP™ software. The optimised discharge conditions used in this work were 650 Pa pressure, and a RF power of 50 W. The average sputter rate of 45-50 nm/s for the hydrothermal conversion layer was measured by sputtering the conversion layers using RF-GDOES and measuring the depth of the obtained sputter crater using a surface profilometer.

2.3.2. Microstructure and Morphology

The morphology of the aluminium alloy surfaces before and after the hydrothermal treatment was observed using a field emission gun scanning electron microscope (Quanta 200™ ESEM FEG, FEI) with an Oxford Instrument X-max™ 80 mm² EDS analyser. In order to obtain higher resolution information from the treated surfaces, transmission electron microscopy was employed. Thin film

lamella of $\sim 1\ \mu\text{m}$ thickness were prepared using in-situ focused ion beam (Ga^+ liquid metal ion source) lift out (Helios Nanolab™ Dual Beam, FEI) and thinning using high energy ion milling [43,44]. The lamella from the region of interest were **lifted out** in-situ using an Omniprobe™ micromanipulator coupled to the dual beam FIB-SEM. Thinning down to approx. 120 nm thickness for electron transparency was performed using successively lower milling energies, and the final milling was performed using a 2 keV Ga ion beam for removing any high-energy ion beam milling induced damage and artefacts. Transmission electron microscopy on the prepared thin film lamella was carried out using a TEM (Model Tecnai T20 G², FEI) operating at 200 keV. The EDS compositional analysis was performed in Scanning TEM mode and the data was captured using an Oxford instruments X-max™ 80 mm² EDS analyser coupled to an Aztec™ TEM EDS software.

2.3.3. X-ray Photoelectron Spectroscopy (XPS)

The XPS analysis was performed using a Thermo Scientific K-Alpha X-ray photoelectron spectrometer equipped with an Al K α (1486.6 eV) X-ray source. **Hydrothermally treated specimens were pre-sputtered to different depths using RF-GDOES prior to the XPS measurement in order to obtain relevant data from different depths of the conversion layer, and the underlying sputtered coating. Spectra were recorded in vacuum of approximately 2×10^{-8} mbar. In addition to sputtering ex-situ using RF-GDOES, in-situ sputtering was also performed in the XPS on individual sputter craters to remove excess contamination from atmosphere during specimen transfer while still retaining some of it to obtain an adventitious C peak for charge correction.** Ar^+ ions sputtering of the surface was employed using an Ar ion gun operating at 2 keV accelerating voltage for 30 s in order to remove the adsorbed species from the atmosphere during specimen transfer. The high resolution spectra were acquired after Ar^+ sputtering treatment, and 10 scans were performed in each case with a dwell time of 50 ms. **The pass energy for the survey scans was 200 eV while that for the high resolution scans was 50 eV. Charge correction was performed using adventitious C 1s peak with a**

binding energy of 284.8 eV as a reference. Deconvolution and peak fitting of the recorded spectra were performed using Thermo Advantage™ software [45].

2.4. Electrochemical Analysis

Open circuit potential, and potentiodynamic polarisation measurements on the bare aluminium, sputter coated surfaces, and the hydrothermally treated surfaces were carried out using an ACM electrochemical Instrument (GillAC). A flat cell setup with an exposed area of 0.95 cm² was used for the measurements. The open circuit potential (OCP) was monitored for 30 min prior to performing the polarisation scans. The anodic and cathodic sweeps were conducted separately in naturally aerated 0.1 M NaCl solution at 22 °C. An Ag/AgCl reference electrode, and a Pt wire counter electrode were employed. All polarisation scans were conducted at a scan rate of 1 mV/s starting from a potential close to OCP. All experiments were repeated three times for repeatability on three different samples with fresh electrolyte for each measurement.

3. Results and Discussion

3.1. Compositional Depth Profiling

Figure 1

The RF-GDOES elemental depth profiles of the hydrothermal treated sputter coated surfaces are shown in Figure 1. The initial regions in the observed sputter profiles that are marked as ‘conversion layer’ correspond to the surface layer formed after hydrothermal treatment. These regions display high amount of O, and H along with Al. The transition region corresponds to the interface between the conversion layer and the underlying sputtered coating where the observed signal from O, and H gradually decreases, and that of Al, and Zr or Ti increases. The point of transition from

conversion layer to sputtered coating can be identified in the region where the H signal is at a maximum (marked with an arrow). This is due to the diffusion of H into the underlying Al-Zr or Ti sputtered coating during hydrothermal treatment [46]. The presence of Zr and Ti in the hydrothermal conversion layer is negligible, and their signal intensity increases in the transition region, reaching maximum concentration in the sputtered coating region. The thickness of the conversion layers generated by hydrothermal treatment on the pure Al and sputtered coatings as a function of the Zr or Ti content is presented in Table 2. It is evident that the thickness of the conversion layer decreases with increasing concentration of Zr, or Ti in the sputtered coating. In addition, the thickest conversion layers (approx. 1300 nm) are observed for pure Al surfaces after hydrothermal treatment, while the lowest thickness is measured for the highest concentration of Zr or Ti (approx. 500 nm).

Table 2

3.2. Microstructure and Morphology

Figure 2

The surface morphology of the sputtered Al-Zr coating in as-received condition and after hydrothermal treatment is shown in Figure 2. The Al-12Zr surface shows typical sputtered coating morphology with growth defects (Figure 2 (a)). The various growth defects displayed on the surface such as voids, pin-holes, cone-like defects etc. have been studied by Panjan et al. [47] and are characteristic of sputtered coatings. Though the observed defects have different morphology, the composition is similar to that of the bulk coating. Hydrothermal treatment of the sputter coated surfaces results in formation of needle like conversion coating (Figure 2 (b), (c)) over the surface of the sputter coated samples, including the growth defects arising from the sputter deposition process. However, the coverage of the surface by this conversion layer is not completely uniform as shown in Figure 2 (d). The morphology of the hydrothermally treated surfaces did not show any major

differences depending on the content of Zr, or Ti, and therefore not presented here. Similar conversion layers were also observed on the pure Al surfaces. The morphology of the obtained hydrothermal conversion layers appear similar to those reported by Rider et al. [48] and Gorman et al. [49] for boiling water treatment of different Al alloys, however the process times required to obtain similar density of the needle structure were longer for pure Al. Higher magnification images from the regions of non-uniform coverage of the conversion layer on the treated Al-Zr, and Al-Ti sputtered coatings are presented in Figure 3. The regions display absence of needle like conversion layer in some locations (mostly for Al-Zr coatings), and a thinner needle like conversion layer in other locations (mostly for Al-Ti coatings). These defects in the coverage by the conversion layer were not observed for the treated AA1090 surface.

Figure 3

Figure 4

Figure 4 and Figure 5 show the bright field transmission electron micrographs of the cross-section of the hydrothermally treated Al-12Zr and Al-12Ti surfaces. In general, the cross sections showed clearly distinguishable layers; namely, a layer displaying needle structure, a compact layer, and the underlying magnetron sputtered coating. The dual structure of the hydrothermally generated surface layer is similar to earlier reports of such treated surfaces [23,50,51].

Figure 5

The relative atomic concentration ratios in the three distinct regions of the conversion layers on Al-12Zr, and Al-12Ti measured using EDS in scanning TEM mode is presented in Table 3. The sputter coated region shows higher atomic ratios for Ti/Al when compared to Zr/Al for a similar sputtered coating wt. % due to the lower atomic weight of Ti. Comparing between the compact oxide and needle oxide, it can be observed that the Zr, or Ti to Al atomic ratios are higher in the compact

oxide region. This suggests that there is an enrichment of Zr, or Ti in the compact oxide region of the respective conversion layers when compared to that of the respective needle oxide regions. Further, the O/(Al+M) ratios are relatively higher for the compact oxide compared to the needle oxide. Higher O/Al ratios (>2) indicate a hydrated Aluminium oxy-hydroxide such as pseudo-boehmite with excess water, while lower O/Al ratios (1.5-2) would indicate partially dehydrated and/or crystallized pseudo-boehmite (assuming Zr or Ti in the compact oxide form MO_2 type oxides) [52].

Table 3

3.3. X-ray Photoelectron Spectroscopy

The high-resolution XPS spectra for Al 2*p* (oxide 74.8 eV, metal 72.8 eV), Zr 3*d* (oxide Zr 3*d*_{5/2} 183 eV, oxide Zr 3*d*_{3/2} 185.4 eV, metal Zr 3*d*_{5/2} 178.9 eV, metal Zr 3*d*_{3/2} 181.3 eV), and O 1*s* (O^{2-} 531.2 eV, OH^- 532.3 eV, water 533.6 eV) recorded from different regions of the hydrothermal conversion layer are presented in Figure 6 (a). The Al-12Zr sputtered coating region shows presence of Al, and Zr along with some O. The binding energies of the Al 2*p*, and Zr 3*d* XPS photopeaks reveal metallic state for these elements, which is as expected. The presence of O 1*s* signal in the sputtered coating is due to the contamination from atmosphere while specimen transfer from RF-GDOES to XPS [53]. This is the reason for the absence of relevant XPS photopeaks for Al and Zr oxides from the sputtered coating while a XPS photopeak of O 1*s* is present. The main difference observed within the XPS spectra recorded from the needle like conversion layer region, and the compact conversion layer is the presence of the signal from Zr 3*d*. The needle like conversion layer does not show presence of Zr, while the compact oxide presents XPS photopeaks that are fit to both metallic and oxide states of Zr [54–59]. This is in line with the EDS measurements presented in Table 3 that show an enrichment of Zr in the compact oxide layer. Quantification of the relative amounts of Al and Zr based oxides/hydroxides in the compact oxide region is however not feasible due to the roughness of

the GDOES sputter crater which is higher than the thickness of the compact oxide layer. This is also expected to be reason for presence of XPS photopeaks from metallic Zr in the compact oxide region, as it arises from the underlying sputtered coating exposed in the rough GDOES sputter crater.

Figure 6

The nature of the conversion layer in the needle like and the compact type can be derived from the O 1s spectra, where peak fitting allows designation of both oxide and hydroxide species, in addition to contribution from water [60–64]. However, due to lack of sufficient resolution due to the roughness of the RF-GDOES sputter carter, identification of the nature of oxide or hydroxides in the compact layer is not feasible. It is seen that the relative intensity of the hydroxide component is higher in the needle oxide when compared to that in the compact oxide. Further, the O 1s XPS photopeak in the compact oxide can be fit with the three components, while the O 1s XPS photopeak from the top needle oxide can be fit with just two components corresponding to oxide and hydroxide. This, when combined with the EDS analysis supports the suggestion that the top needle oxide is partially crystallised or dehydrated pseudo-boehmite. The higher O/(Al+M) ratio (>2) observed for compact oxide in the EDS and the contribution to the O 1s XPS photopeak from water also supports pseudo-boehmite with excess water in the compact oxide. The possibility of formation of mixed oxides cannot be ruled out and would need further analysis. Similar observations from the XPS spectra are made for the Ti containing surface after hydrothermal treatment (oxide Ti 2p_{3/2} 458.4 eV, oxide Ti 2p_{1/2} 464.1 eV, metal Ti 2p_{3/2} 454 eV, metal Ti 2p_{1/2} 460.1 eV).

3.4. Electrochemical Analysis

Table 4

The open circuit potential values for the pure Al, the different magnetron sputtered coatings, and the surfaces after they were subject to hydrothermal treatment are presented in Table 4. The OCP

values of the magnetron sputtered surfaces show a slight positive shift with increasing Zr, or Ti content. The reference pure Al surface (0 wt.%) has a slightly positive value compared to the sputtered coating with lower contents of Zr or Ti. Hydrothermal treatment of the pure Al surface shows a shift of approx. 600 mV towards the negative values. Surprisingly, for the magnetron sputtered surfaces, hydrothermal treatment shows a decrease in OCP value for the Zr containing surfaces and an increase in the OCP for Ti containing surfaces. There is no clear correlation between the OCP values for the hydrothermal treated magnetron sputtered coatings on the Zr, or Ti content in the coating. The reduction in the OCP value for the pure Al surface after hydrothermal treatment has been assigned to the coverage of the cathodic Fe, Mn, and Si based intermetallic phases by the conversion layer, thereby reducing the cathodic activity of the surface [65]. Due to the nature of the sputtering process, the magnetron sputtered coatings do not contain bulk intermetallic phases that could enhance the cathodic activity of the surface, and hence, do not show a major shift in the OCP values after hydrothermal treatment. In addition, the hydrothermal treated surfaces of the magnetron sputtered coatings, have defects in terms of the coverage by the conversion layer (as mentioned earlier). Thus, the OCP values obtained on the treated surface for the magnetron sputtered coating is a result of combination of needle like conversion layer, the exposed metallic sputtered coating (see Figure 3 (a)) and a thinner conversion layer in some of the defective regions, as seen in Figure 3 (b). The positive shift in the OCP for the Ti containing surfaces and the negative shift for the Zr containing surface after hydrothermal treatment is expected to be due to the nature of the passive oxide formed on the regions of the non-uniform conversion layer which dominate the electrochemical response of the surface.

Figure 7

The potentiodynamic anodic polarisation curves of AA1090, and the magnetron sputtered coatings containing Zr, and Ti, before and after hydrothermal treatment are presented in Figure 7, and

Figure 8 respectively. The anodic polarisation curves presented in Figure 7 (a) show that before treatment, there is a lower current density for the magnetron sputtered Al-Zr coatings compared to the AA1090 sample. In addition, the current density is independent of the Zr concentration in the coating. Hydrothermal treatment of these coatings showed a significant difference in the polarisation behaviour as seen in Figure 7 (b). Hydrothermal treated sputtered coatings exhibited a passive region and the breakdown potential shifted significantly towards the more noble direction when compared to that of treated AA1090. The passive current densities, though independent of the Zr concentration, were lower by at least two orders of magnitude when compared to that of treated AA1090.

Figure 8

Figure 8 compares the anodic potentiodynamic polarisation curves for AA1090 and the Al-Ti sputtered coatings before and after hydrothermal treatment. Similar to the observations in Figure 7, there is a trend towards a **more positive open circuit potential** for the hydrothermally treated Al-Ti coatings with increasing Ti concentration. This trend is present for the untreated surfaces but insignificant. Additionally, the hydrothermally treated Al-12Ti and Al-16Ti coatings in Figure 8 (b) have a higher pitting potential than the lower Ti containing surfaces. Comparing with the as received sputtered coatings in Figure 8 (a), the hydrothermal treated surfaces have notably higher difference in the **open circuit potential** with the respective AA190 surfaces. In addition, the passive region for the treated Al-Ti surfaces is very narrow when compared to the corresponding treated Al-Zr surfaces.

The potentiodynamic cathodic polarisation curves presented in Figure 9 and Figure 10 show that for the AA1090 surface, hydrothermal treatment reduces the cathodic activity by at least an order of magnitude. This is due to coverage of the cathodic intermetallic phases upon treatment thus reducing the cathodic active surface considerably. For the sputtered Al-Zr and Al-Ti coatings, the

cathodic activity shows little difference upon treatment due to the fact that the sputtered surfaces do not have cathodic intermetallic phase particles.

Figure 9

Figure 10

3.5. Post polarization morphology

The morphology of the Al-12Zr magnetron sputtered surface after it was subject to potentiodynamic polarisation is shown in Figure 11. Severe dissolution of the magnetron sputtered Al-12Zr coating and the underlying AA1090 substrate is observed in Figure 11 (a), and higher magnification image in Figure 11 (b) reveals crystallographic dissolution of the underlying AA1090 substrate. The Al-Zr and Al-Ti sputtered surfaces showed high number of large lateral dissolution regions for lower Zr or Ti containing surfaces, and deeper localised dissolution for higher concentrations of Zr or Ti. However, dissolution of the underlying AA1090 substrate was also observed in all instances of the un-treated sputter coated surfaces.

Figure 11

The morphology of hydrothermally treated Al-Zr coatings after potentiodynamic anodic polarisation is shown in Figure 12. Similar to the observations for the untreated surfaces, the hydrothermally treated surfaces showed a dependence of the dissolution morphology on the concentration of Zr or Ti in the coating. The lower Zr containing surface (Figure 12 (a)), Al-4Zr, displayed large lateral dissolution of the conversion layers and the magnetron sputtered coating in addition to corrosion of the underlying AA1090 substrate. In the case of higher Zr containing surfaces (Figure 12 (b)), Al-16Zr, localised dissolution of the underlying AA1090 substrate was observed. This localised dissolution preferentially occurred at the regions along the defects in the

hydrothermally generated conversion layer. Similar behaviour was also observed for the treated Al-Ti sputtered coatings after potentiodynamic anodic polarisation.

Figure 12

In order to obtain a more comprehensive understanding of the developments during potentiodynamic polarisation of the treated surfaces, the Al-12Zr treated sputtered coatings were subjected to anodic polarisation that corresponds to different regions in the observed polarisation scan. The polarisation tests were terminated at selected potentials of -600mV (Spot A); 0 mV (Spot B); and +550 mV (Spot C) with respect to saturated Ag/AgCl electrode as shown in Figure 13. Following polarization, the samples were immediately removed from the test solution, rinsed with distilled water, air dried, and subsequently investigated by SEM for the surface morphology, and further by site specific FIB milling of the region of interest for observing the cross-sections.

Figure 13

Figure 14 (a) shows SEM image of the sample removed after potentiodynamic polarisation up to -600 mV vs saturated Ag/AgCl (Spot A in Figure 13), corresponding to the start of the first anodic current peak on the polarisation curve. The needle like oxide morphology resulting from the hydrothermal treatment, as described in Figure 2 (c) can be observed, still intact. However, the cross section of this sample (Figure 14 (b)) prepared by FIB sectioning across the region of uneven conversion layer growth shows dissolution has already initiated below the needle like oxide layer and has caused some degree of delamination. The region of initiation of dissolution and delamination of the conversion layer by propagation at the interface of the oxide and the underlying Al-Zr sputtered metal substrate is found to be at the site of uneven oxide growth. At Spot B, corresponding to 0 mV vs. saturated Ag/AgCl on the polarisation curve, some areas without coverage of needle like oxide displayed a thin compact oxide layer which corresponds to the passive region in the anodic

polarisation curve (Figure 14 (d)). Corrosion products were observed on the surface of these regions shown in Figure 14 (c). Upon further polarising the sample to approx. 550 mV vs saturated Ag/AgCl, severe corrosion products were found on the surface of the treated Al-Zr sample (Figure 14 (e)). The FIB cross section prepared on the region with uneven oxide layer showed that at this potential, the thin oxide is absent and severe dissolution propagation is observed below the conversion layer into the sputtered Al-Zr coating (Figure 14 (f)).

Figure 14

3.6. General Discussion

In this study, an oxide/hydroxide layer formed on pure Al, sputtered Al-Zr and Al-Ti coatings after exposure to pressurised steam for 10 min in an autoclave with the thickness of few hundreds to thousands of nanometres is presented. Under hydrothermal treatment conditions, as the temperature and pressure in the autoclave increases, water droplets/film is expected to condense on the surface of the samples. As the temperature and steam pressure in the autoclave reach the required values for hydrothermal treatment, the formation of the conversion layer under this water film proceeds by formation of amorphous oxide, hydration of the oxide, followed by growth of the boehmite phase by dissolution and precipitation [23][66]. The thickness of the formed conversion layer is determined by the diffusion of species across the compact inner oxide, which is the rate limiting process. This process is however accelerated in the current hydrothermal treatment conditions in the autoclave resulting in thicker conversion layers in **shorter** treatment times when compared to boiling water treatment. It is evident from the growth mechanism of the conversion layer that the presence of a water film on the surface is crucial to obtain thick boehmite films. The uniformity of this water film is controlled by the wettability of the surfaces under hydrothermal conditions in non-immersion treatments. Lower wettability of the surface results in non-uniform

water film formation that leads to non-uniform formation of the conversion layer. This is the case for Al-Zr and Al-Ti, as supported by SEM micrographs in Figure 2 (d) and Figure 3 showing non-uniform regions on the hydrothermally treated sputter coated surfaces when compared to reference pure Al surface which showed a uniform conversion layer. This is because the pure Al surface has been pre-treated using caustic etching and desmutting which improves the surface wettability and also the anodic activity by removing the air formed natural oxide [28][67]. In the un-wetted regions on the sputter coated surfaces, the initial stage of dense compact oxide formation occurs thermally, or in presence of water vapour. The deficiency to form a complete water film due to improper wetting hindered the hydration of this compact oxide as well as the subsequent dissolution and precipitation process to form boehmite, resulting in the observed non-uniform regions in the hydrothermal conversion layer. This mechanism is outlined in the schematic in Figure 15.

Figure 15

On the sputter coated surfaces, the conversion layer in the wetted regions forms in a similar manner as described earlier for pure Al. However, Zr or Ti from the sputtered coatings are also incorporated in the initial amorphous oxide layer along with Al. This presence of Zr or Ti in the oxide subsequently reduces the diffusion of species across the compact layer resulting in reduced growth rate of boehmite by dissolution and precipitation. Further, as the activity of Al is higher compared to Zr and Ti, the top needle layer does not show significant Zr or Ti, as it is only Al that is dissolving and precipitating as boehmite, while the Zr and Ti in the sputtered coating are left behind at the metal-compact oxide interface, thus enriching within the compact oxide (Table 3) and further reducing the diffusion of species across this compact layer. This results in the increasingly lower conversion layer thicknesses with increasing Zr or Ti content, as seen in **Error! Reference source not found.**

The thickness of the needle like boehmite layer has been shown to reach a few hundred nanometres. However, it is permeable, and therefore has little effect on the electrochemical behaviour of the hydrothermally treated surfaces [20]. The compact oxide is thinner (around 100 nm thick), but the electrochemical studies showed that it plays a crucial role as a corrosion barrier during the potentiodynamic polarization, especially at the regions of the uneven coverage by the hydrothermal conversion layer. This is also supported by micrographs acquired from FIB cross sections of treated Al-Zr sputtered coating after being anodically polarized to selected potentials (Figure 14). It showed that the corrosion initiated under the compact oxide film, especially in the area with defects and later propagated along the metal/oxide interface. After the compact oxide film detached from the sputtered Al-Zr coating due to severe interfacial corrosion, corrosion current density increased dramatically.

The resistance of the hydrothermal conversion coated surface against corrosion under potentiodynamic polarization varied with the substrate material. In this study, the level of protection provided by the hydrothermal treatment on Al-Zr or Al-Ti sputtered coating was higher than for pure Al under the same hydrothermal treatment, as shown in Figure 7 and Figure 8. The improvement in electrochemical behaviour is attributed to the presence of Zr or Ti oxides in the compact oxide film, even in the regions of non-uniform coverage. Zr and Ti are regarded as sister elements with excellent resistance to many corrosives, including chloride solutions. As presented earlier, under the hydrothermal conditions, it is observed that both Zr and Ti are enriched and found in an oxidised state in the compact region. It is currently unclear though if the compact oxide comprises of Al-O species and Zr/Ti-O species, or Al-Zr/Ti-O species, or a mixture of both. Further investigations need to be performed in this aspect with the help of Electron Energy Loss Spectroscopy (EELS). However, since both Zr oxide and Ti oxide are stable, they improve the barrier layer properties of the compact oxide, and thus enhance the corrosion resistance by increasing the pitting potential and decreasing the corrosion current density. Al-Zr sputtered coating showed a relatively better performance

compared with Al-Ti coating after treatment, considering the corrosion current density for treated Al-Zr sputtered coating was two orders of magnitude lower than for pure Al after hydrothermal treatment, while the treated Al-Ti sputtered coating was only one order of magnitude lower than for pure Al. This agrees with early reports by Tomashov et al. [68], showing that in chloride solutions with free access of oxygen, Zr behaves more passive than Ti. Corrosion initiation on the hydrothermally treated sputtered coatings was mostly observed at the regions of non-uniform coverage by the conversion layer. Hence, the nature of the oxide in these regions plays a critical role and would lead to differences in the observed electrochemical behaviour depending on presence of Zr or Ti in the Al metal. Our knowledge concerning how to improve the homogeneity of the conversion layer on these sputtered coatings is quite limited. More systematic studies and characterization are needed to increase the fundamental knowledge about the factors that might influence the growth and uniformity of the hydrothermal conversion layer, including the optimised Zr or Ti concentration in the sputtered coatings, pre-treatment of these surfaces, and the parameters controlling the hydrothermal treatment (such as steam pressure, temperature, as well as treatment time).

4. Conclusions

1. Hydrothermal treatment in an autoclave results in the accelerated growth of oxide on sputtered Al-Zr and Al-Ti coatings.
2. The generated oxide layer was found to have a needle structure at the top, and a thinner compact oxide film close to the sputtered coating. Both Zr and Ti enrichment were detected in this compact oxide film while negligible amounts (if any) were present in the needle top layer.

3. Potentiodynamic polarization showed a reduction in anodic activities for the treated Al-Zr and Al-Ti coating, compared to pure Al after a similar treatment.
4. The compact oxide film was critical to reduce electrochemical activities on the treated Al-Zr and Al-Ti coatings.
5. Sputtered Al-Zr coating showed better corrosion resistance compared to sputtered Al-Ti coating after the same hydrothermal treatment.
6. Zr concentration had insignificant effect on the electrochemical behaviour of sputtered Al-Zr coating both before and after hydrothermal treatment; while the electrochemical behaviour of sputtered Al-Ti coating after hydrothermal treatment was slightly dependent on Ti concentration.

Data Availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical and time limitations.

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Figure Captions

Figure 1: RF-GDOES elemental depth profile of (a) Al-12Zr and (b) Al-12Ti magnetron sputtered surfaces after hydrothermal treatment showing the conversion layer, and the underlying magnetron sputtered coating.

Figure 2: SEM secondary electron micrographs of the (a) Al-12Zr sputtered coating, (b), (c) Al-12Zr surface after hydrothermal treatment, and (d) Al-8Zr surface showing uneven coverage by the hydrothermal conversion layer. Arrows in (a) pointing at growth defects in sputtered coating and in (d) at regions of non-uniform coverage by hydrothermal conversion coating.

Figure 3: SEM secondary electron micrographs of non-uniform regions in conversion layer after hydrothermal treatment of (a) Al-8Zr sputtered coating, and (b) Al-12Ti sputtered coating. Arrows pointing at regions of non-uniform coverage by hydrothermal conversion coating.

Figure 4: Bright field transmission electron micrographs of the cross-section of the hydrothermally treated (a) Al-12Zr, and (b) Al-12Ti sputtered coatings showing needle, and compact oxide morphology of the obtained conversion layers.

Figure 5: Bright field transmission electron micrograph of the compact oxide region in the conversion layer formed on Al-12Zr after hydrothermal treatment.

Figure 6: XPS spectra recorded from different regions of the hydrothermal conversion layer obtained by ex-situ RF-GDOES sputtering followed by in-situ Ar⁺ sputtering in the XPS. (a) Al-12Zr showing Al 2p, Zr 3d and O 1s photopeaks, and (b) Al-16Ti showing Al 2p, Ti 2p and O 1s photopeaks. Legend: Black – Recorded spectrum, Gray – Residuals, Green – Envelope, Others – Fitted peaks

Figure 7: Potentiodynamic anodic polarisation curves for the reference AA1090, and Al-Zr sputtered coatings of different Zr concentration (a) before, and (b) after hydrothermal treatment.

Figure 8: Potentiodynamic anodic polarisation curves for the reference AA1090, and Al-Ti sputtered coatings of different Ti concentration (a) before, and (b) after hydrothermal treatment.

Figure 9: Potentiodynamic cathodic polarisation curves for the reference AA1090, and Al-Zr sputtered coatings of different Zr concentration (a) before, and (b) after hydrothermal treatment.

Figure 10: Potentiodynamic cathodic polarisation curves for the reference AA1090, and Al-Ti sputtered coatings of different Ti concentration (a) before, and (b) after hydrothermal treatment.

Figure 11: Secondary electron SEM images of the Al-12Zr surface after potentiodynamic anodic polarisation showing (a) severe corrosion of the sputtered coating surface and the underlying AA1090 substrate, and (b) crystallographic pitting in the underlying AA1090 substrate.

Figure 12: Secondary electron SEM images of the (a) Al-4Zr surface, and (b) Al-16Zr surface after hydrothermal treatment and potentiodynamic anodic polarisation showing lateral corrosion of the Al-4Zr surface (pointed with arrows) and corrosion of underlying AA1090 substrate, and higher localised inwards corrosion to the underlying AA1090 substrate for the Al-16Zr surface through the sputtered coating.

Figure 13: Potentiodynamic polarization tests on hydrothermally treated Al-12Zr sample showing the selected potential values where the tests were terminated.

Figure 14: Scanning electron microscopy micrographs of the typical surface morphology, and related cross section images resulting from potentiodynamic polarisation of hydrothermally treated Al-12Zr coating to the selected potential values shown in Figure 16. (a), (b) Spot A: -600 mV, (c), (d) Spot B: 0 mV, and (e), (f) Spot C: +550 mV vs. saturated Ag/AgCl reference electrode.

Figure 15: Schematic showing the growth mechanism of the conversion layers on reference pure Al and the Al-Zr/Ti sputtered coatings under hydrothermal conditions highlighting the differences in the uniformity of the conversion layer due to difference in wetting of the surfaces.

Table Captions

Table 1: Targeted and measured concentration (using SEM-EDS) of Ti and Zr (in wt.%) in the magnetron sputtered coatings used in this study.

Table 2: Hydrothermally generated conversion layer thickness on pure Al and sputter deposited Al-Zr and Al-Ti coatings as a function of Zr, or Ti concentration measured using RF-GDOES sputtering.

Table 3: Relative atomic concentration of different elements in the three regions of the hydrothermal conversion layers on Al-12Zr, and Al-12Ti measured using TEM-EDS.

Table 4: Open circuit potential values for the pure Al, magnetron sputtered Al-Zr and Al-Ti coatings before and after hydrothermal treatment measured in a 0.1 M NaCl solution against an Ag/AgCl reference electrode.

Figure 1: RF-GDOES elemental depth profile of (a) Al-12Zr and (b) Al-12Ti magnetron sputtered surfaces after hydrothermal treatment showing the conversion layer, and the underlying magnetron sputtered coating.

Figure 2: SEM secondary electron micrographs of the (a) Al-12Zr sputtered coating, (b), (c) Al-12Zr surface after hydrothermal treatment, and (d) Al-8Zr surface showing uneven coverage by the hydrothermal conversion layer. Arrows in (a) pointing at growth defects in sputtered coating and in (d) at regions of non-uniform coverage by hydrothermal conversion coating.

Figure 2: SEM secondary electron micrographs of the (a) Al-12Zr sputtered coating, (b), (c) Al-12Zr surface after hydrothermal treatment, and (d) Al-8Zr surface showing uneven coverage by the hydrothermal conversion layer. Arrows in (a) pointing at growth defects in sputtered coating and in (d) at regions of non-uniform coverage by hydrothermal conversion coating.

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Figure 3: SEM secondary electron micrographs of non-uniform regions in conversion layer after hydrothermal treatment of (a) Al-8Zr sputtered coating, and (b) Al-12Ti sputtered coating. Arrows pointing at regions of non-uniform coverage by hydrothermal conversion coating.

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Figure 4: Bright field transmission electron micrographs of the cross-section of the hydrothermally treated (a) Al-12Zr, and (b) Al-12Ti sputtered coatings showing needle, and compact oxide morphology of the obtained conversion layers.

Figure 4: Bright field transmission electron micrograph of the compact oxide region in the conversion layer formed on Al-12Zr after hydrothermal treatment.

Figure 5: Bright field transmission electron micrograph of the compact oxide region in the conversion layer formed on Al-12Zr after hydrothermal treatment.

Figure 6: XPS spectra recorded from different regions of the hydrothermal conversion layer obtained by ex-situ RF-GDOES sputtering followed by in-situ Ar^+ sputtering in the XPS. (a) Al-12Zr showing Al 2p, Zr 3d and O 1s photopeaks, and (b) Al-16Ti showing Al 2p, Ti 2p and O 1s photopeaks. Legend: Black – Recorded spectrum, Gray – Residuals, Green – Envelope, Others – Fitted peaks

Figure 7: Potentiodynamic anodic polarisation curves for the reference AA1090, and Al-Zr sputtered coatings of different Zr concentration (a) before, and (b) after hydrothermal treatment.

Figure 8: Potentiodynamic anodic polarisation curves for the reference AA1090, and Al-Ti sputtered coatings of different Ti concentration (a) before, and (b) after hydrothermal treatment.

Figure 9: Potentiodynamic cathodic polarisation curves for the reference AA1090, and Al-Zr sputtered coatings of different Zr concentration (a) before, and (b) after hydrothermal treatment.

Figure 10: Potentiodynamic cathodic polarisation curves for the reference AA1090, and Al-Ti sputtered coatings of different Ti concentration (a) before, and (b) after hydrothermal treatment.

Figure 11: Secondary electron SEM images of the Al-12Zr surface after potentiodynamic anodic polarisation showing (a) severe corrosion of the sputtered coating surface and the underlying AA1090 substrate, and (b) crystallographic pitting in the underlying AA1090 substrate.

Figure 11: Secondary electron SEM images of the Al-12Zr surface after potentiodynamic anodic polarisation showing (a) severe corrosion of the sputtered coating surface and the underlying AA1090 substrate, and (b) crystallographic pitting in the underlying AA1090 substrate.

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Table 1: Targeted and measured concentration (using SEM-EDS) of Ti and Zr (in wt.%) in the magnetron sputtered coatings used in this study.

Target wt.% of Zr or Ti	Measured Zr wt.%	Measured Ti wt.%
4	1.5	4.3
8	6.1	6.2
12	11.5	10.2
16	16	14.6

Table 2: Hydrothermally generated conversion layer thickness on pure Al and sputter deposited Al-Zr and Al-Ti coatings as a function of Zr, or Ti concentration measured using RF-GDOES sputtering.

Sample name	Zr concentration wt. %	Conversion layer thickness nm	Standard deviation nm	Sample name	Ti concentration wt. %	Conversion layer thickness nm	Standard deviation nm
AA1090	0	1303	167	AA1090	0	1303	167
Al-4Zr	1.5	948	41	Al-4Ti	4.3	747	40
Al-8Zr	6.1	609	5	Al-8Ti	6.2	715	81
Al-12Zr	11.5	513	7	Al-12Ti	10.2	569	26
Al-16Zr	16	554	6	Al-16Ti	14.6	356	32

Table 3: Relative atomic concentration of different elements in the three regions of the hydrothermal conversion layers on Al-12Zr, and Al-12Ti measured using TEM-EDS.

Region	Zr/Al	Standard deviation	O/(Al+Zr)	Standard deviation	Ti/Al	Standard deviation	O/(Al+Ti)	Standard deviation
Sputtered Coating	0.02	-	0.02	-	0.05	-	0.04	-
Compact Oxide	0.06	0.01	2.15	0.22	0.15	0.02	1.70	0.08
Needle Oxide	0	-	1.67	0.15	0.00	-	1.78	0.08

Table 4: Open circuit potential values for the pure Al, magnetron sputtered Al-Zr and Al-Ti coatings before and after hydrothermal treatment measured in a 0.1 M NaCl solution against an Ag/AgCl reference electrode.

Sample name	Concentration		As received		Hydrothermally treated		Sample name	Concentration	As received		Hydrothermally treated		
			OCP	Standard deviation	OCP	Standard deviation			OCP	Standard deviation			
wt. %		mV vs Ag/AgCl						wt. %		mV vs Ag/AgCl			
AA1090	0.00		-645.20	73.71	-1289.65	54.66	AA1090	0.00		-645.20	73.71	-1289.65	54.66
Al-4Zr	1.5		-725.76	57.73	-1271.60	97.53	Al-4Ti	4.3		-726.90	89.93	-593.34	34.06
Al-8Zr	6.1		-738.19	84.33	-756.78	92.14	Al-8Ti	6.2		-721.54	92.83	-650.23	30.67
Al-12Zr	11.5		-648.54	55.12	-805.17	138.61	Al-12Ti	10.2		-748.92	10.79	-563.08	43.82
Al-16Zr	16		-640.98	54.13	-784.96	126.95	Al-16Ti	14.6		-655.27	27.98	-481.79	31.36