

TRIVALENT CHROMIUM CONVERSION COATINGS ON Al and Al-Cu ALLOYS

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“Trivalent chromium conversion coatings on Al and Al-Cu alloys”

A thesis submitted to the University of Manchester for the degree of Doctor of Philosophy

Jiantao Qi / 9th November, 2015

Trivalent chromium conversion coatings formed on Al and Al-Cu alloys has been investigated using high-resolution, analytical electron microscopy, atomic force microscopy, ion beam analysis, glow discharge optical emission spectroscopy, Raman spectroscopy, X-ray photoelectron spectroscopy, electrochemical impedance spectroscopy, potentiodynamic polarization and electrochemical noise analysis.

These coatings on the electropolished Al and sputtering-deposited Al consist of a chromium- and zirconium-rich outer layer and a thinner, aluminium-rich inner layer. Zirconium and chromium are presented in chemical states consistent with ZrO_2 , $\text{Cr}(\text{OH})_3$, $\text{Cr}_2(\text{SO}_4)_3$, CrF_3 and CrO_3 or CrO_4^{2-} . However, negligible amounts of hexavalent chromium species occurred in both coatings formed in de-aerated solution. On AA2024-T351 alloys, the coating above the second phase particles was thicker than that on the matrix due to the increased localized alkalinity. Moreover, the localized corrosion and copper enrichment of the matrix occurred at the coating base. The presence of copper resulted in a thinner coating at the matrix compared with superpure aluminium.

An Fe(III)-containing D30 desmutter can effectively remove the protruded particles generated by alkaline etching. Moreover, a thinner oxide film on the D30-treated surface was evidenced to promote the coating initiation on the matrix. Further, the coating comprised the concentrated zirconium oxyfluorides and decreased contents of aluminium and copper. Coated alloys displayed a significantly enhanced corrosion protection, especially the cathodic inhibition. In terms of coating post-treatments, the water immersion (40 °C, pH 5) soon after conversion treatment revealed a simple but effective process to improve the fluoride enrichment in coatings and to enhance corrosion protection of freshly-developed coatings.

Increasing concentration of solid-solution copper in sputtering-deposited alloys, in a range of 2, 24, 40 and 64 at.%Cu, significantly promotes the coating growth kinetics and an evident and a thicker corrosion layer by substrate dissolution was observed on Al-40 at.%Cu alloys. In addition, the relationship of copper-rich deposits with Cr(VI) transformation was demonstrated by Raman spectroscopy.

Declaration

No portion of the work referred to in this thesis has been submitted in support of an application for another degree or qualification of this or any other university or other institution of learning.

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Chapter 1 INTRODUCTION

Aluminium alloys are widely employed in engineering structures owing to their advantageous mechanical and physical properties. The outstanding high strength-to-weight ratio results in aluminium alloys being extensively used in the aerospace industry. The alloying with copper and magnesium, on the other hand, leads to an increased susceptibility to localized corrosion, especially pitting corrosions.

Chromate conversion coatings (CCCs), which are regarded as one of most effective surface treatments, are extensively applied to improve the corrosion resistance of the Al-Cu alloys. However, Cr (VI) is a high risk substance posing a threat to human health and the environment due to the toxicity and carcinogenic hazard, and research in this field is, therefore, is directed towards finding a suitable replacement whilst maintaining performance.

One promising candidate treatment uses a trivalent chromium bath, consisting of zirconium hexafluoride and trivalent chromium salts. It is necessary to understand the formation and composition of the trivalent chromium conversion (TCC) coatings on selected substrates, and the mechanism of Cr(III)/Cr(VI) transformation and corrosion protection enhancement by this trivalent chromium conversion coating motivated this project.

In this present study, a commercial trivalent chromium bath, SurTec 650, was used to prepare the trivalent chromium conversion coatings on superpure aluminium and AA2024-T351 alloys. The following examinations include: high resolution, analytical electron microscopy; atomic force microscopy; scanning Kelvin probe force microscopy; ion beam analysis; glow discharge optical emission spectroscopy; Raman spectroscopy; and X-ray photoelectron spectroscopy. Corrosion protections were investigated by the electrochemical impedance spectroscopy, potentiodynamic polarization and electrochemical noise analyses. The optimal process of this conversion coating was offered with the underlying mechanism.

The report consists of nine chapters:

- Following this introductory chapter, Chapter 2 is a brief literature review including the background of materials and conversion coatings and key unsolved problems.

- Experimental procedures and methodologies employed are described in Chapter 3.
- Chapters 4 and 5 provide the characterization of TCC coatings on superpure aluminium and AA2024-T351 alloys. This includes the coating growth, hexavalent chromium transformation mechanism and corrosion protection performance.
- The effect of altering key parameters of the conversion process on coating composition and its corrosion protection is fully discussed in Chapters 6 and 7. This includes the alloy pre-treatment and coating post-treatment respectively.
- Sputtering-deposited aluminium and aluminium-copper alloys are used to investigate. The influence of copper on the growth kinetics and chemical components of TCC coatings is discussed in Chapter 8.
- Finally, Chapter 9 summarises main conclusions that have been drawn from results; and includes suggestions for future work.

Chapter 2 LITERATURE REVIEW

2.1 Background of Aluminium and AA2024-T3 Aluminium Alloy

2.1.1 Composition and microstructure

Superpure aluminium, with 99.99% purity, is primarily applied as a reference material in the laboratory. The major impurities in aluminium include copper, iron and silicon in tens of ppm by weight [1]. The relatively low density and good corrosion resistance provided by the air-formed film give superpure aluminium remarkable properties [2].

AA2024-T3 alloy has been extensively used in the aerospace, defence and electronic manufacturing due to the high strength to weight ratio and damage tolerance. The nominal components are listed in Table 2.1, where the major alloying specification has 3.8~4.9 wt.% copper and 1.2~1.8 wt.% magnesium. This alloy is solution heat-treated, cold-worked, and naturally aged at ambient temperatures to a substantially stable condition represented by 'T3'. In terms of a special set of additional digits, the designation of 'T351' means that further strength was received after a stretching treatment [3]. With respect to the microstructure complexity, the coarse intermetallic compounds, dispersoids (0.05-0.5 μm dimensions) and fine precipitates (up to 0.1 μm dimensions) are formed during the alloy casting, homogenization by solid state precipitation and natural age hardening respectively. The primary three forms of particles include Al_2CuMg (S-phase), Al_2Cu (θ -phase) and $(\text{Al,Cu})_x(\text{Fe, Mn})_y\text{Si}$ (α -phase) particles, where these particles exhibited a multiphase clustering of more than one composition. [4, 5] Further, dispersoid-free periphery phases around particles were revealed as a real part of alloy microstructure [6]. The concentrations of the soluble elements available and their ratios play an important role in determining the heterogeneous precipitation during alloying. For example, Al_2CuMg (S-phase) is primarily formed since the $\text{Cu/Mg} > 2$ and $\text{Mg/Si} > 1.7$; while the latter Mg/Si ratio is close to 1.7, the Mg_2Si and CuAl_2 (θ -phase) are in equilibrium [7].

In terms of the dominant form of S-phase particles, Buchheit et al. revealed that approximately 60% of particles are of this type. This was achieved with scanning electron microscopy and electron beam microanalyses with accelerating voltages of 20 and 30 kV [5].

By contrast, Hughes et al. [6] applied electron probe microanalysis (EPMA) mapping to assess the chemical composition of 82, 000 phase regions in 18, 000 particles. Their results revealed the S phase particles with the fraction of the total particles being ~40% that corresponded to ~2.83% of the total area. This fraction variance is attributed to the presence of S-/θ-phase clusters that were all calculated as S-phase type in the early report. In terms of the metallurgy process, S phase particles nucleate heterogeneously on the dislocation lines as laths in the early stage of the ageing process of the Al-Cu-Mg alloys. Additionally, when this alloy is aged at the elevated temperature, the nanosized Cu-Mg co-clusters are presented as fine dispersions in the matrix grains [8].

Furthermore, Hughes et al. [9] used the EPMA mapping to classify the nine types of clusters on the basis of the variation of the primary alloying components and the level of the incorporated silicon impurity. For the intermetallic particles, α phase particles constituted ~47% of the total particles and ~39% particles in the form of S-/θ-phase particles were predominately clustered. The remaining ~14% of the total particles were Al₃(Cu, Fe, Mn) without silicon, which was in good agreement with the SEM/EDX analyses by Chen et al [10]. Additionally, ~77% cathodic domains were assessed with combination of the θ-phase particles. In addition, an Al-enriched periphery phase was investigated and shown to comprise higher contents of Cu, Mg, Fe and Mn compared to the matrix; this zone possibly correlated with the trenching corrosion around the particles after corrosion [6, 11].

Notably, the clustering of S and θ phase particles was revealed to be popular along the rolling direction of the AA2024-T3 alloy by SEM/EDX analyses [10]. Furthermore, Luo et al [4] used an elliptical model of the shape-based classification to reveal the two forms of the S phase and θ phase particles, including the single and clustered particles. The average long axis/short axis ratios for the single S phase, clustered S phase, single θ phase and clustered θ phase particles were measured at ~1.69, 0.29, 1.08 and 4.32 respectively. Thus, the clustered S-phase particles were much more spherical compared to the single S phase particles, and the single θ-phase particles are more spherical shapes than the clustered θ phase particles.

2.1.2 Surface morphology and pre-treatment

A thin alumina oxide film is presented on the macroscopic surface of aluminium and aluminium alloys. The thickness of this film present on superpure aluminium depends on the

formation conditions and is generally of the order of several nanometres [12, 13]. In terms of the structure of the thin oxide films, various investigations have been done with different proposed structures. For instance, Fehlner and Mott [14] assumed that this amorphous film (predominantly composed of Al_2O_3) has a glassy network with five- and six-membered rings at room temperature. However, Pryor [13] suggested 'the glassy structure' failed to consider any structural implications of the substantial number of excess aluminium ions. Furthermore, the crystalline $\gamma\text{-Al}_2\text{O}_3$ was revealed to coexist with the amorphous alumina when the temperature of aluminium oxidation was at $\sim 450^\circ\text{C}$ and above. The formation of crystalline alumina was attributed to the inward diffusion of oxygen ions, which is in good agreement with Snijders's experimental results [15].

Moreover, the air-formed oxide film with residual and mechanical flaws is not a "perfect" corrosion barrier, where the former type is associated with impurity segregation and the latter is related to gross structural defects. Wood et al. [16] decorated these flaws with copper deposits by means of cathodic polarization at $1\ \mu\text{A}/\text{cm}^2$ in potassium chloride solution containing 1 g/l copper sulphate. Flaws traced by copper were evidently observed under optical microscopy. Pitting corrosion is preferentially induced around active flaws in the oxide film during exposure to corrosive chloride solution [17]. Thompson et al. [1] employed transmission electron microscopy on the transparent stripped anodic films prepared by the ultramicrotome, and directly revealed the flaws of size $\sim 73\text{-}200\ \text{nm}$ above metal ridges at the metal/film interface. It was suggested that these arise from the influence of iron and/or copper impurities. In addition, the corrosion of the ultramicrotomed section of the high purity aluminium in the double distilled water bath revealed the presence of residual flaws. For example, the flaws of the grain boundaries and cellular boundaries served as the cathodic sites to develop bubble-feature deposits in the form of aluminium hydroxides. These flaws were associated with the impurity segregation in the aluminium substrate. [18]

In terms of surface pre-treatments, the selection depends on the experimental objectives. For instance, the mechanical grinding and/or polishing with the subsequent degreasing generates the same surface with the bulk composition to be used to examine the behaviour of the microstructures on the initial formation of the conversion coating [19]. By contrast, chemical/electrochemical pre-treatments were used to remove the surface oxides and any deformed layers to provide a clean surface for the successive coating formation [20, 21],

where the removal of the second phase particles was determined by the deoxidation solution [22, 23].

For superpure Al, a comparative study of the effect of pre-treatments on the surface topography has been conducted by Shimizu et al. [24], using transmission electron microscopy and atomic force microscopy. A characteristic cellular texture with a dimension of 100 nm and a network of ridges in height of ~20 nm were examined on the aluminium surface after electropolishing in a perchloric acid-ethanol bath at temperatures below 10 °C at 100 mA/cm² current density. Subsequently, the etching treatment of electropolished Al in the 1.5 ml HF-10ml H₂SO₄-90 ml H₂O solution for 30 s can produce a distinct cellular texture in excellent agreement with the enrichment of the cathodic impurity segregations at the cellular boundaries [25-27]. Moreover, a ~1.5 nm thick copper-rich layer beneath the air-formed film on electropolished aluminium revealed a significant difference with the bulk composition. With respect to mechanical polishing with a 0.05 µm Al₂O₃ in water, the high-resolution AFM and TEM examinations revealed that the surface was not microscopically flat with the presence of scratches and the protuberance of aluminium oxide polishing particles. By contrast, the ultramicrotomed sections generated by a diamond knife revealed a fine aluminium surface that was microscopically smooth to within 1 nm over a scanned area of several microns. This novel approach allowed AFM to fully examine the highly localized processes, such as pit initiation.[28]

The network patterns on the Al after the electropolishing pre-treatment were suggested to depend upon the crystallographic orientation by Shimizu et al [24]. Further, Konovalov et al. [29] used an electropolishing solution (70 vol.% ethanol, 10 vol.% 2-butoxyethanol, 13.8 vol.% water and 6.2 vol.% perchloric acid) to clean the surface of polycrystalline and monocrystalline Al rods and recorded the topography texture by atomic force microscopy. The applied voltage up to 50 V from the polycrystalline anode to cathode revealed the severe damage of the surface, and preferential etching was observed at the high-energy grain boundary that was attributed to the charge-transfer-control dissolution. In contrast, the distinct topographies of (1 1 1), (1 1 0), and (1 0 0) Al single crystals were examined under the applied voltages of 20, 30 and 40 V. The highly-ordered patterns of the (1 1 0) Al surface was observed at low voltages of 20 and 30 V with the two-dimensional dislocations. At 40 V, the isolated island defects were detected in the absence of the dislocations. The variance of

surface patterns of the single aluminium crystals under applied voltages was suggested to relate the different chemical adsorptivity of the molecules on different crystalline faces [30].

Alkaline etching and acidic desmutting were extensively used to clean the aluminium alloys due to the effective and economic concerns from industry. The effect of these pre-treatments has been well studied by several research groups [20-23, 31-35]. Liu et al [35] used transmission electron microscopy, Rutherford backscattering spectroscopy and X-ray photoelectron microscopy to examine the etching rates on the magnetron sputtering-deposited Al-30 at.%Cu alloys after alkaline etching treatments for 0, 15, 30 and 45 seconds. The results revealed a copper-enriched layer in the etched products of the hydrated alumina in the form of nanoparticles, which were mainly present as either Cu^0 or Cu^1 species. The thicknesses of the loss of the Al-30 at.%Cu alloys after etching treatment for 15, 30 and 45 s were measured at ~9, 39 and 58 nm respectively, and the etching rates were $\sim 0.7 \text{ nm s}^{-1}$ in the first 15 s, 1.8 nm s^{-1} between 15 and 30 s, and 1.3 nm s^{-1} until 45 s. The enhanced cathodic reaction and etching rates correlated with the formation of copper-rich nanoparticles. In addition, Lunder et al. [20] investigated the effect of alkaline etching on the pitting corrosion of aluminium alloy. For as-received alloys, a thicker oxide on the matrix and a possible layer of matrix alloy over the cathodic intermetallic particles provided a higher resistance against pitting. By contrast, the etching pre-treatment dissolved this protective layer and increased the cathodic areas by protruded second phase particles. Consequently, the cathodic reaction rates were increased and this indicated the enhanced corrosion activity.

Hughes et al. [22] used SEM, TEM, EDX, XPS and RBS to examine the morphologies and composition differences after deoxidizing AA2024-T3 alloy by various acid treatments. The acid treatment of HNO_3 , H_2SO_4 and H_3PO_4 alone exhibited no preferential removal of particles, which contained a similar composition to the alkaline-etched surface. Further, the combination of the H_2SO_4 -HF and H_3PO_4 -HF treatment revealed an enhanced dissolution of iron, magnesium and manganese to leave the insoluble copper-rich smuts, and a clean surface in the absence of copper smuts displayed after the HNO_3 -HF treatment. The desmutting rates in the presence of HF addition showed a significant increase by 2.5 orders of magnitude compared to the situation of the single acids. Moreover, the addition of oxidant $\text{Na}_2\text{S}_2\text{O}_8$ into the solution as the HNO_3 -HF- $\text{Na}_2\text{S}_2\text{O}_8$ and H_3PO_4 -HF- $\text{Na}_2\text{S}_2\text{O}_8$ promoted the silicon removal from the alloy surface. The improved deoxidation effect in the presence of the oxidants is in

excellent agreement with the situation of the Fe(III)/HF/HNO₃ solution on the AA7475-T7651 alloys [23]. In summary, the distinct three-stage process of the deoxidation to remove the etched oxides includes (i) the preferential dissolution of components of the etched products, e.g. the single mineral acid of HNO₃, (ii) the beginning etching of the underlying alloys soon after the complete removal of surface oxides that remain after alkaline etching, e.g. the combination of H₂SO₄-HF, and (iii) the cleaning of second-phase particles at a higher etching rates of alloying components, such as the HNO₃-HF, HF-Na₂S₂O₃ and HNO₃-HF-Fe(III) solutions.

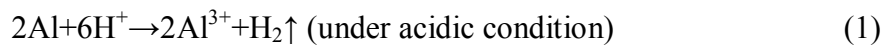
Little et al. [34, 36] employed cyclic voltammetry (CV) in a deaerated, pH=8.4 borate buffer solution to quantitatively assay the Cu distribution and concentration of AA2024-T3 alloys after the NaOH/HNO₃ treatments. In Figure 2.1, the Cu coverage was assessed by the copper oxidation reaction peaks and peak areas. The Cu⁰→Cu^I and Cu^I→Cu^{II} oxidation peaks were presented at about -0.1 V_{SCE} and between 0 and 0.1 V_{SCE} respectively. The current and the total charge of Cu(0)/Cu(I) peak exhibited a linear correlation with dependence on the etching treatment times of alloys (Fig. 2-1(b)). In this sense, the peak current of Cu(0)/Cu(I) oxidation was compared with that of pure Cu to assess the fraction of copper coverage over the alloy substrate after pre-treatments. For example, the fraction of copper on the alloy surface after the etching treatment for 5 min was assessed at ~0.233. This is because the peak areas of the Cu(0)/Cu(I) oxidation of pre-treated alloy and the pure copper were $\sim 3.74 \times 10^{-7}$ and 1.61×10^{-6} C/cm² respectively. The assessment of copper coverage by the CV method is in agreement with the results by the areas of the individual XPS peaks in the Cu 2p_{3/2} photoelectron regions. Davenport and Liu [37] used this CV method to investigate the effect of nitric acid desmutter on the etched alloy. They demonstrated the absence of copper oxidation peaks on the etched-desmuted Al-0.2Cu and Al-1Cu alloys, and this indicated the complete removal of detectable copper by HNO₃ desmutting. The behaviour of two high purity Al-Cu alloys was used to simulate that of the matrix of AA2024-T351 alloy. By contrast, a well-defined presence of Cu(0)/Cu(I) peak on etched-desmuted AA2024 alloys showed the independent correlation with the copper accumulation by the prolonged etching treatment. It indicated that all detectable, electroactive copper after etching and desmutting were located at particles rather than the matrix.

2.2 Corrosion Behaviour of Aluminium and AA 2024-T3 Alloy

Pitting, a form of localised corrosion, is a critical premonition of the failure of the corrosion-protective film on aluminium and aluminium alloys, especially in the aggressive chloride environment. There are four distinct aspects of pitting corrosion in halide environments: (i) processes occurring at the interface between the passive film and corrosive solution; (ii) processes occurring within the passive film in the absence of the visible microscopic morphology changes; (iii) initiation and formation of the metastable pits at a lower potential than the pitting potential, and then pits repassivate under such a lower current than that required for the stable pit growth (10^{-2} A/cm); and (iv) the stable pit growth, above the critical pitting potential. The presence and concentration of chloride ions play an important role in pit nucleation, growth and propagation [38].

2.2.1 Corrosion of pure aluminium

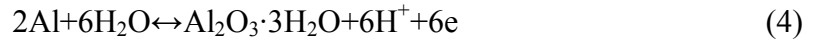
Aluminium is a thermodynamically active base metal, so that an air-formed oxide film develops on the surface in an oxygen-containing environment (air, water). However, a pit is initiated at selected locations where oxide film deterioration exists either by a mechanical scratch or by a chemical attack such as chloride and fluoride. Aluminium dissolution occurs during pitting nucleation in the following manner:



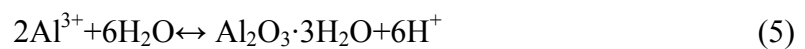
The two ionic species, Al^{3+} and AlO_2^- , have been used by Pourbaix in constructing the potential-pH diagrams for the aluminium-water system at ambient temperature as shown in Figure 2.2 [39, 40]. During the aluminium dissolution in the presence of a strong acidic environment ($\text{pH} < 4$), Al^{3+} cation dominates (reaction (1)) whereas AlO_2^- is the predominant ion in the high pH region ($\text{pH} > 9$, reaction (2)). The equilibrium reaction (3) between the Al^{3+} and AlO_2^- ions is outlined with a dashed line in Fig. 2.2.



$\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, generated by the reaction (4), is regarded as the stable aluminium phase between pH 4 and 9 [41].



Further, the pit propagation always correlates with the local acidity and in the aqueous and near-neutral environments, a stable thin layer of gibbsite, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, can be developed over the macroscopic metal surface by reaction (5).



In the Pourbaix diagram of potential-pH plots, three regions are identified for aluminium as follows: (i) the immune state in the form of aluminium metal; (ii) the passive state, represented by the region of either gibbsite or boehmite to form a coherent film to halt corrosion on the surface; (iii) the corrosive state, represented by the regions of the presence of Al^{3+} , $\text{Al}(\text{OH})^{2+}$ and AlO_2^- ions. In addition, the regions of the corrosive state can be expanded by increasing the temperature of alkaline solution, revealing the more favourable formation of AlO_2^- aluminate ions. Hence, the effective corrosion protection of applied inhibitors and coatings on the surface shall make aluminium in the region either of immunity or passivation of aluminium in the Pourbaix diagram [41].

2.2.2 Corrosion of AA2024-T3 alloy

Electrochemical differences within AA2024 are the result of Cu and Mg rich alloying components which form heterogeneous size and spatial distributions of second phase particles within the matrix. Consequently, the susceptibility of AA2024-T3 alloy to localised corrosion is promoted by such galvanic couplings of the second phase particles and the aluminium matrix [42, 43]. Notably, S phase particles initially served as the anodes in 0.1 M NaCl solution and then became the cathodes due to the severe dealloying corrosion with copper-rich remnants. In addition, the periphery zones around S phase particles displayed trenching corrosion once the particles were ennobled and became cathodic sites. This was similar to that of the cathodic α/θ -phase particles [4]. In terms of the pre-treatments, the

alloy surface demonstrated poor corrosion resistance after alkaline etching and acidic desmutting, which were attributed to the deterioration of the air-formed film and the significant protrusion of particles [20].

2.2.2.1 Mechanism of localised corrosion

The dominant cathodic reaction around the second phase particles at the open-circuit corrosion potential is the oxygen reduction reaction (ORR), $2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^- \rightarrow 4\text{OH}^-$, which leads to a local pH increase. The locally enhanced alkalinity by the galvanic couplings of particles relative to the matrix promotes the dissolution of the neighbored periphery to generate local trenching around the particles [44].

Jakab et al [36] used a rotating disk electrode of AA2024-T3 to reveal the relationship between the kinetics of the oxygen reduction reaction (ORR) and the coverage of Cu-rich particles and re-plated copper by the methods of Koutecky and Levich [45]. Charge-transfer, mass-transfer, and mixed regimes were revealed during the ORR on AA2024-T3 in the form of a four-electron process. The charge-transfer ORR reaction rate increased linearly with copper coverage, while the mass-transfer-controlled ORR rate revealed a complex function of copper coverage and a complex function of the inverse of boundary layer thickness. Thus, the reduction of copper coverage (OCP at -0.8 to -0.9 V_{SCE}) revealed a considerable limitation of the ORR on copper-rich sites. However, if the corrosion potential of the alloy is extremely negative, decreasing copper coverage has only a slight effect on controlling the corrosion rate. In this case, the barrier coatings were suggested to be the best strategy to inhibit the ORR of AA2024-T3 alloy [46].

2.2.2.2 Effect of the intermetallic particles

The composition and coverage of the intermetallic particles (IMCs) play an important role in the electrochemical behaviour of AA2024-T3 alloy. Schmutz and Frankel [43] employed scanning Kelvin probe and in-situ atomic force microscopy to study the behaviour of the alloy particles in 0.1 M and 0.5 M NaCl solutions. They revealed that S phase particles, as the dominant IMCs, displayed a noble Volta potential in air, indicating the active nature relative to the matrix. Correspondingly, S phase particles were anodically dealloyed to leave the copper sponges behind after a certain period in the chloride solution, therefore, becoming the

cathodic sites relative to the matrix. In addition, the in-situ AFM contact examination was suggested to cause surface abrasion resulting in the immediate dissolution of the S phase particles because of a destabilization of the surface film. By contrast, trenching corrosion of the matrix was displayed around α - θ -phase particles in the chloride solution. These conclusions were in good agreement with other literature [37, 47].

The copper redeposition during the corrosion process of AA2024-T3 alloy was observed at the lip of a pit in the flow direction of a neutral 5 wt.% salt-spray exposure for one week [48]. Further, Buchheit et al [42] used a rotating Pt-ring-disk collection experiment and stripping voltammetry to present the compelling evidence of the generation of Cu ions by the dissolution of the S- Al_2CuMg phase particles in 0.5 M chloride solutions. Their results revealed that copper ions were yielded either under the open-circuit conditions (OCP of $\sim -0.930 \text{ V}_{\text{SCE}}$), or by the slightly anodic or cathodic polarization ($\pm 0.050 \text{ V}$ relative to the OCP). Furthermore, the processes associated with Cu ion generation were identified as shown in Figure 2.3, including (i) the dealloying of the second phase particles, (ii) the nonfaradaic liberation of mechanically and electrically isolated metallic Cu clusters by the physical coarsening of the dealloyed particle, and (iii) the oxidation of the electrically isolated Cu clusters. Moreover, the degree of solution aeration correlated with the copper ion generation, and the absence of copper ions under the deaerated chloride solutions revealed a significant role of copper oxidant in the generation of copper ions. This process of copper dissolution, detachment and redeposition in the the Al_2CuMg -bearing alloys significantly decays the corrosion resistance of alloy surface and may lead to the failure of conversion coatings applied on this substrate.

Ilevbare et al. [49, 50] used the mixed solution of 0.1 M Na_2SO_4 and 0.005 M NaCl (pH 3, 6, and 10) and the near-neutral 0.5 M NaCl solution to study the localized corrosion around the alloy particles. They revealed the types of attacks in the categorization of the pitting on the matrix and particles, trenching at the adjacent periphery around particles, and the matrix etching. The galvanic couplings between the matrix and the particles determined the attack rates. In open-circuit conditions, corrosion within the intermetallic particles was localized at the particles themselves and did not spread into the matrix even after the prolonged immersion in the corrosive electrolyte. The finely polished and exposed S phases served as anodes, while α and θ phase particles were the net cathodes. Compared to the stable pits in

the S phase particles, the metastable pitting was observed at the cathodic α phase particles due to the sufficiently low pitting potential at the OCP of AA20204 alloys. For the matrix, the stable pits formation correlated with the presence of the large intermetallic clusters, possibly in the form of copper deposits, which revealed good consistency with the report by Buchheit [42].

In terms of the mechanism of trenching corrosion around the cathodic α -/ θ -phase particles, there exhibited two trenching models of the anodic and cathodic types [50, 51], where the latter is based on the effect of increased pH. In comparison, the anodic trenching model was a complex function of the cathodic kinetics of the particles; the effect of chloride concentration; the matrix dissolution rate; and the particle/matrix metallurgy. By contrast, the trenching mechanism with the dependence on the chloride concentration, particle type and size is hard to explain by the alkaline trenching model. For example of the anodic trenching, the trenches around the cathodic particles were relatively narrow in the low-pH solutions with some absence of trenches. Further, θ -phase particles revealed high susceptibility to trenching in dilute chloride solutions, where the oxygen reduction kinetics was low and the pH increase was limited. In addition, the trenching corrosion was also investigated around α -phase particles in the concentrated chloride solution. Thus, this anodic model can rationalize the effect of chloride concentration; pH value; and the absence of some trenches around the cathodic particles.

2.2.2.3 Chemistry of copper and its dissolution

Copper is more noble relative to aluminium, however, Cu^+ and Cu^{2+} ions can be generated by the electrochemical oxidation of copper in naturally-aerated solutions. Moreover, copper ions can form complexes with chloride and sulphate ions during the corrosion process of copper. This formation of copper complexes revealed no significance on the copper enrichment on the substrate [42]. In addition, the dissolution of copper to form CuCl_2^- ions is dependent on the interfacial potential and immersion time in the chloride solution, especially in the short period of 20 seconds near +40 mV_{SCE} [52]. Polarization curves in the anodic part were independent of the solution pH value, which indicated the pH-independent dissolution of copper to form complexes [53].

In terms of the cathodic reduction during the copper dissolution, the hydrogen evolution and standard potentials are given in reactions (6, 7), and the oxygen reduction and potential are displayed in reactions (8, 9). The open-circuit potential of copper in the chloride-containing solution revealed a higher potential than the standard potential of the H^+/H_2 reaction. When the copper was slightly polarized in the negative direction of the open-circuit potential, the cathodic reaction was primarily determined by the reaction (9) of the mass-transport-controlled process. By contrast, hydrogen evolution (reaction (7)) was present at lower potentials [52].

$$E_{H^+/H_2} = -0.0591 \text{ (pH)}, V_{SHE} \quad (6)$$



$$E_{O_2/H_2O} = +1.229 - 0.0591 \text{ (pH)}, V_{SHE} \quad (8)$$



Concerning the effect of fluoride on the copper dissolution, a reduced concentration of copper ions was examined in the deaerated corrosive condition by means of the inductively coupled plasma-mass spectroscopy (ICP-MS) [54]. Further, the individual concentration of oxygen and fluoride in the solution was shown to play a first-order role in the dissolution kinetics of copper. Furthermore, the formation of CuO on the surface can effectively reduce the chemical attack by dilute HF [55]. Concerning the kinetics of copper corrosion in fluoride-containing solution, Potvin et al. [56] used the rotating disk electrodes to reveal that the diffusion of the Cu^{2+} ions from the electrode to the bulk solution determined the rate of dissolution when the rotating angular velocity is close to zero. In the theoretical limit of an infinite rotating velocity, the process of charge transfer dominates the dissolution kinetics. In addition, the fluoride ions showed a relatively weaker bonding with copper cations to form copper-fluoride complexes according to the hard-and-soft-acids-and-bases (HSAB) theory [56-59].

In terms of the source of copper redeposition on the alloy surface in 0.5 M NaCl solution, the copper in solid solution and S-phase particles were revealed as the two major sources to equally contribute to the copper redistribution by the copper solid state and/or liquid phase transport mechanisms [42, 60]. Further, Buchheit et al. [5] studied the copper behaviour of S-phase particles in AA2024-T3 exposed to the naturally-aerated 0.1 M NaCl solution at room

temperature by means of SEM/EDS analyses. Two types of S phase particles were observed. Some particle was remained in a large and intact shape with the presence of induced pitting at their periphery once ennobled by dealloying corrosion. In comparison, the active type of S phase particles decomposed into small Cu clusters (~10 to 100 nm dimensions), which detached from the alloy surface and were carried away either by the mechanical action of growing hydrous corrosion products or by the moving solution. This non-Faradaic liberation of copper from the alloy may correlate with copper redistribution in pitting process by potentials, which were hundreds of millivolts negative of the reduction potential for Cu. It is in good agreement with the report by Dimitrov et al [61], who investigated that the electrolyte convection of 0.5 M NaCl can significantly enhance the Cu enrichment and redistribution process.

With respect to corrosion protections on aluminium and aluminium alloys, conversion coatings have been widely used as a pre-treatment layer to provide the inner barrier in the case that the outer coating was completely damaged. The conversion process involves the reactions between the substrate and bath to form the coating in a chemical/electrochemical process, such as anodizing and chromate conversion treatment. This coating thickness is generally accepted to range from 100 to 500 nm. Figure 2.4 shows the structure of a typical three-layer coating system on an aluminium alloy. [62] The innermost layer is formed by a pre-treatment of the conversion coating to improve the bonding strength of the outer primer with the substrate and to provide the final corrosion protection. As the principal corrosion-protection layer, the primer is composed of a pigmented organic resin matrix in the middle of the coating system. The top decorative layer is paint with the ability to prevent corrosion of the materials. Conversion coatings used on Al alloys include the chromate conversion coating (CCC), zirconium-based conversion coating, anodizing coating and trivalent chromium conversion (TCC) coating.

2.3 Chromate Conversion Coating (CCC)

2.3.1 Background

Chromate conversion coating (CCC) surface treatment has been employed for more than ninety years since Bauer and Vogel formed this protective conversion coating on aluminium

alloys in a dichromate-based solution in 1915 [63]. The comprehensive understanding of the CCC composition and corrosion protection mechanism has been obtained in the last twenty years or so. CCC is regarded as the most effective coating system so far for aluminium alloys. However, the carcinogenetic toxicity of Cr(VI) component to human beings limits the use in the household application. The chromate conversion coating bath comprises the Cr^{6+} salt (CrO_3 or $\text{Na}_2\text{Cr}_2\text{O}_7$), F^- salt (NaF or KF) and $[\text{Fe}(\text{CN})_6]^{3-}$ salt for one accelerator. For the CCC process, the specimens were simply immersed in this hexavalent chromium bath at room temperature for a specific duration, followed by the deionized water rinsing, drying by a stream of cool air and air ageing for a period [64].

2.3.2 Nature and coating growth

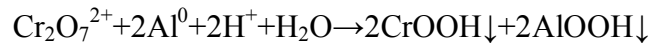
The nature of CCC formation is generally accepted to be an electrochemical process on aluminium and its alloys [18, 27, 63, 65-68]. Distinctly, the chemical process is one component with the prolonged CCC treatment in the report by Zhang et al. [69], who used the aluminium wire electrode arrays to examine the electrochemical activity during the CCC formation by the net currents. They revealed two characteristic formation stages of the aluminium in the hexavalent chromium bath. The first period of 30 s of CCC formation was regarded as an electrochemical process by the measurable net currents. After this electrochemical period, the net currents of electrochemical activity were undetectable, revealing the chemical process of CCC formation in the prolonged treatment.

On pure aluminium, Brown et al. [18, 27, 65] studied the CCC development in a typical solution containing CrO_3 and NaF components. They revealed that the initial sites of the deposits of CCC were the flaw sites on the surface, such as dislocations and grain boundaries. These flaws served as the cathodic sites with respect to the surrounding matrix because of the impurity accumulation at these flaw sites. Furthermore, the pre-existing metal ridges of impurity enrichment were suggested to contain the residual cracks of nanometre dimensions in the thermal oxides to play a role in the ‘easy path’ for the mass transport [70]. The overall reaction for the CCC growth on the pure aluminium is as follows:



This fluoride-containing solution sufficiently thins but does not completely remove the air-formed oxide film to provide the appreciable electron tunnelling for mass transport in a thickness of 14 Å [71]. Consequently, the dissolution of aluminium and the cathodic reactions of hydrogen evolution near the metal ridges led to the local pH increase to promote the hydroxide deposits of chromium species. In terms of the cathodic reactions, the reduction of hexavalent chromium to trivalent chromium preferentially occurred near the metal ridges to form the deposit of CCC. The anodic sites were located between the pre-existing ridges. In the developed CCC, the presence of the aluminium hydroxide at the coating/substrate interface was evidenced by analysing Al KL_{2,3}L_{2,3} in the Auger measurement [19].

Over aluminium alloys, the formation process of CCC is by a redox reaction of chromate species in the bath with dependence on alloy components. The dissimilarities of surface composition and reactivity of constituent particles and the matrix led to the complication of the mechanism of CCC formation on the alloy. A hydrated chromium oxide gel was formed in the chromate/fluoride solutions by the overall reactions as follows [66, 67]:



After CCC treatment for 5 seconds, Kulinich et al. [19] revealed a denser CCC on the second phase particles and the absence of chromium signal in the matrix, consistent with other literature [72-75]. The reduction of Cr(VI) to Cr(III) preferentially exhibited on the cathodic particles of θ and α types and little or no CCC formed on the alloy matrix. After CCC treatment for 30 seconds, a uniform coating was investigated over the entire Al matrix surface. In terms of the S-phase particles, the cathodic and anodic galvanic couplings with respect to the aluminium matrix gave rise to the duplex role in the chromate bath. The presence and absence of chromium signals on the S-phase particles were both revealed by Auger measurements. The anodic S-phase particles initially underwent the severe dealloying to form the noble copper-rich sponges, and then fast deposition of the CCC occurred. Consequently, the inhomogeneity of CCC displayed between the particles and matrix of AA2024 alloys.

2.3.3 Composition and structure

Treverton et al. used XPS analyses in conjunction with ion-beam etching to examine the components of CCC on aluminium, which mainly comprised the hydrated chromium oxide, $Cr_2O_3 \cdot xH_2O$ ($x=1$ or 2), with the presence of the remnant ferricyanide on the top layer [66]. Further, Wood et al. [76] used the secondary ion mass spectrometry to identify that the CCC on pure Al was primarily composed of the amorphous type material, probably of hydrated chromic oxide with a small amount of included dichromate anion. In addition, a complex oxyfluoride was suggested to exhibit in the inter-cellular region of CCC.

Kendig et al. [77] employed X-ray absorption near edge spectroscopy to reveal the presence of a significant ratio of unreacted hexavalent chromium in the CCC on Al 2024-T3 and 3003-H14 alloys. The Cr(VI) component in the CCC revealed the dependence on the treatment time in the chromate bath, where more Cr(VI) species were reduced in the initial period to the trivalent chromium in the form of $Cr(OH)_3$ rather than Cr_2O_3 . After CCC treatment of 300 seconds, a limit ratio of Cr(III)/Cr(VI) concentration was also observed at approximately 4:1. The presence of the soluble Cr(VI) species rationalized the self-sealing properties of deteriorated chromate coating in chloride solutions.

Figure 2.5 show the proposed three stages of the sol-gel mechanism for CCC formation on Al [78, 79], consisting of hydrolysis, polymerization and condensation of Cr^{3+} . During the reaction process, Cr^{6+} species were reduced at the cathodic sites, while oxygen reduction and hydrogen evolution led to local pH increase on the activated Al surface to promote the hydroxide deposition. Consequently, a chromium hydroxide ($Cr(OH)_3$) polymer played a role in the inner backbone with edge- and corner-sharing octahedral units of Cr^{3+} cations. The labile Cr^{6+} reservoir built up in the outer coating layer along the $Cr(OH)_3$ deposition. Finally, the freshly-formed CCC was a well-hydrated gel within the first period of 24 h after coating treatment. After aging for more than 24 h, the gel coating became decreasingly receptive to the organic overcoats, but this CCC was used for the stand-alone corrosion protection film.

For a better understanding of the composition and structure of the CCC on the individual particle and the overall surface of AA2024-T3 alloy, researchers developed different models in the latest decades [72-75, 80]. For instance, Hughes et al. [80] provided the three-layer structure of CCC as shown in Figure 2.6, where the outer layer was composed of $CrOOH$ with a significant presence of $Fe(CN)_6^{3-}$ and few chromate species. A mixture of

$\text{Cr}_2\text{O}_3 \cdot \text{CrOOH}$, F^- and $\text{Fe}(\text{CN})_6^{3-}$ anions displayed in the middle region of coating, while the inner layer comprised $(\text{Cr,Al})\text{OF}$ and Al_2O_3 . Figure 2.7 shows the other explanation of the compositional structure of the CCC by Vasquez [72]. Their results revealed (i) CCC was of chemically and topographically heterogeneous composition, (ii) CCC composition varied laterally with the distribution and morphology of the alloy particles, (iii) a thinner CCC exhibited on Cu-enriched particles due to the ferricyanide absorption on these particles to reduce the aluminium availability, and (iv) the chromate of the CCC on the regions over the Cu-rich particles was not available to repair the damaged CCC region.

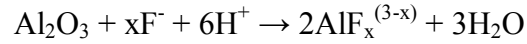
2.3.4 Factors influencing CCC formation

2.3.4.1. Fluorine ions

Valand et al. [81] used a potentiostatic step method to examine the influence of fluorine ions on a high purity Al electrode in the deaerated sodium acetate solution ($\text{pH}=5.25$) containing fluoride ions ranging from 5×10^{-5} to 10^{-2} M. Prior to the electrochemical examination, aluminium electrodes were usually stabilized after overnight at a certain potential, such as at $1.0 \text{ V}_{\text{SCE}}$. Subsequently, several potentiostatic steps of less than 5 s duration were applied to examine the current densities of aluminium electrode with increasing the fluorine concentration. The results revealed that both rates of the anodic and cathodic reactions increased with addition of NaF in the bath. The replacement between fluoride in solution and oxygen in the oxide was suggested because of the relative smaller size of fluorine ($r_{\text{F}}, r_{\text{O}^{2-}} = 1.36$ and $1.40 \text{ \AA}$). Consequently, the ionic and electronic conductivity of the air-formed oxide increased to promote the electrode reaction kinetics. Further, Zhang et al. [69] found that the corrosion rate of pure Al at the open-circuit condition in the chromate solution of Cr^{6+} , $\text{Fe}(\text{CN})_6^{3-}$ and F^- components was three orders of magnitude greater than the situation without fluorine ions. Accordingly, evident mud-crack morphology of CCC in the former case was investigated in scanning electron micrographs, while no apparent change of morphology displayed in the latter case. In this sense, the separate fluoride ions promoted the electrochemical reactions during CCC formation.

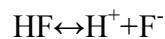
In terms of the chemical reactions between fluorine and oxide film, the role of fluoride is to undermine the air-formed film to provide the appreciable electron tunnelling for the

solution/aluminium reactions. This activation of substrate surface by the fluorine ions permits the coating nucleation and lateral growth on the overall matrix. The fluorine/substrate reaction acts initially at material flaws as follows [71, 76, 82].



Shimizu et al. [71] used an equation of potential barrier height at the interface between aluminium substrate and the air-formed film by DiQuarto et al. [83] to quantify the variance of tunnelling of electron in local film thickness. The local variance of the air-formed film on the aluminium of thickness of only a few angstroms during the chemical attack by HF significantly gave rise to the difference of local tunnelling probability of electrons by the exponential thickness dependence. Thus, the homogeneous CCC formed on the surface with holidays or voids through the coatings because the tunnelling of electrons at these sites was always insignificant. These explanations of voids in the CCC are in good agreement with the results by Brown et al [27, 65, 84].

With respect to the alumina oxides, the fluorine ions revealed much aggressive than CrO_4^{2-} , PO_4^{3-} ions, and were more aggressive towards the aluminium substrate than Cl^- ions, especially in acidic solution [76]. The transfer equilibrium between HF and F^- ion depends on the solution pH values in following reaction:



At pH=1.5, HF dominates in fluoride species and the transformation balance in the manner of $(\text{HF})=(\text{F}^-)$ occurs at pH 3.2 [39]. Katzman et al. suggested that the pH-sensitive transfer of HF and F^- ion is well associated with the CCC thickness at different pH conditions. For example, more aluminium and less chromium of a thinner coating were examined on the surface and in the depth of the CCC by Auger electron spectroscopy, when the bath pH values increased up to the range of 3.5-4.8[67].

2.3.4.2. Hexafluorizirconate ions

Chidambaram et al. [82] investigated the role of hexafluorozirconate ions during the growth of CCC over aluminium alloy, using contact angle measurements, scanning electron microscopy, energy dispersive spectroscopy and X-ray photoelectron spectroscopy. Their results revealed that ZrF_6^{2-} ion was not directly involved in thinning and/or removing the native oxide film as the similar situation of the free fluorine ion. The interfacial tension was decreased after the reaction with the ZrF_6^{2-} ion and then to increase the surface hydrophilicity to form a fresh Al-Zr-F-O based hydrated layer, activating the surface. Consequently, the interaction between the electrolyte and alloy substrate was enhanced to develop a uniform chromate coating. In terms of the reaction mechanism between hexafluorozirconate ions and the air-formed oxide, the alloying element of copper was hypothesized to play a catalytic role in their reactions to produce the active nodules, comprising ZrO_2 and K_3AlF_6 components.

2.3.4.3. Ferricyanides $[\text{Fe}(\text{CN})_6]^{3-}$

Ferricyanide ion is well-accepted as an accelerator during CCC formation [68, 69, 80, 85, 86]. Xia et al. used Raman and infrared spectroscopy to investigate the structure of ferricyanides and the mediator mechanism in the CCC [86]. They revealed the air-dried CCC in the compositional structure of a $\text{Fe}^{3+}\text{-CN-Fe}^{3+}$ polymer, where the $\text{Fe}(\text{CN})_6^{3-}$ physisorbed on $\text{Cr}(\text{OH})_3$ and $\text{Fe}(\text{CN})_6$ species. The inclusion of $[\text{Fe}(\text{CN})_6]^{3-}$ species increased the oxidation of aluminium in alloys, and then Cr (VI) was fast reduced in the presence of $[\text{Fe}(\text{CN})_6]^{4-}$ ions. Thus, a redox mediation action for $[\text{Fe}(\text{CN})_6]^{3-/4-}$ correlated to the increased oxidation of aluminium and reduction of Cr(VI) to Cr (III). In terms of the redox effectiveness, the rate of CCC growth kinetics was enhanced by such mediators as follows: $\text{Fe}(\text{CN})_6^{3-} > \text{IrCl}_6^{2-} > \text{V}^{3+} > \text{Fe}^{3+}$. The standard potential for the redox series, however, displayed a lack of good consistency. For example, the standard potential of $\text{IrCl}_6^{3-/2-}$ mediator revealed higher than that of $\text{Fe}(\text{CN})_6^{3-/4-}$ series, while the redox effectiveness of such mediator series was converse. This discrepancy revealed that the growth kinetic of CCC film was a complex function of mediator redox, the alloy components and the kinetics of the Cr(VI)/Cr(III) redox reaction.

By contrast, Zhang et al. [69] used aluminium arrays to examine the breakdown potential distribution of the CCC grown in the solution with and without $[\text{Fe}(\text{CN})_6]^{3-}$ addition. A positive shift of $\sim 0.07 \text{ V}_{\text{SCE}}$ in the median breakdown potentials was attributed to whether the $[\text{Fe}(\text{CN})_6]^{3-}$ ion was presented in the bath, which revealed great significance on the

electrochemical reaction in the initial period of 30 s rather than the situation of prolonged treatment of 120 s. Moreover, this chemical addition into the chromate bath correlated with the improved corrosion protection of the coated alloys in chloride solutions, which is consistent with other literature [80, 85]. In terms of the reaction of these cations with copper-bearing particles, Hagans et al. [85] investigated the electrochemical behaviour of the alloys at the open-circuit condition in the chromate bath with the presence and absence of cyanide addition. The reference of the open-circuit potential evolution of the bare alloy was in the boric-borate electrolyte (pH=9.25) without the addition of 3 mM $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$ (ferro- and ferri-cyanide, respectively). In comparison, a reduced duration of the initial period and the positive ~ 150 mV OCP at the steady-state stage was observed in the electrolyte with the addition of ferricyanide. Further, the situation of addition of ferrocyanide species displayed an elongated period of the initial stage and a negative ~ 200 mV OCP at the steady-state stage in comparison to the reference. These results revealed the capability of ferrocyanide ions to react with the surface copper to form an insoluble copper-ferrocyanide complex to inhibit the CCC deposition kinetics.

2.3.4.4. Cu influence

Liu et al. [87-89] used the magnetron sputtering method to simulate Al-Cu binary alloys with a range of alloying concentrations over pure aluminium substrate, and then to examine the thickness of CCC growth and substrate loss by transmission electron microscopy and Rutherford backscattering spectroscopy. They revealed the enrichment of alloying elements of copper on the Al-Cu substrate by the acidic etching of the chromate solution to reach the critical level at ~ 40 at.% after treatment of several minutes to lead to the coating detachment. Furthermore, this disrupted adhesiveness of CCC on Al-Cu substrate may correlate with the incorporation of copper nano-particles into the coating region [89]. Further, the evidence of the nanosized copper particles was also observed in the cross-sections of the sputtering Al-30 at.%Cu alloy after alkaline etching in the transmission electron micrographs [35]. In terms of alloying influence on CCC growth kinetics, the substrate loss in the initial period of 6 min was relatively fast and the subsequent thinning rate of substrate was ~ 9.3 , 6.2, 6.0 and 5.4 nm/min for the sputtering-deposited Al, Al-2.3 at.%Cu, Al-1.9 at.% Au and Al-20 at.%Au alloys respectively. Alloying present in the substrate decreased the coating thickness and metal consumption as well. Moreover, the average ratio of chromium atoms relative to that of

oxidized aluminium atoms in the developed CCC was $\sim 0.25\text{-}0.33$, indicating the low growth efficiency of coating materials.

2.3.4.5. Air ageing effect

Hughes et al. [80] used the corrosion current density of coated alloys to represent the corrosion protection of CCC with and without air ageing, where the potentiodynamic polarization was employed at a scan rate of 1 mV/s. A significant decrease of corrosion current density of CCC after air ageing for the first 40 h ($\sim 0.04 \mu\text{A}/\text{cm}^2$) was revealed at the reduced $\times 10$ factors in comparison to the chromate coating without air ageing ($\sim 0.4 \mu\text{A}/\text{cm}^2$). In terms of the prolonged air ageing, the cracks by drying the coating decreased corrosion protection. This demonstrated that the appropriate period of the air ageing can improve the corrosion protection of the coated alloys as recommended for 24 h hardening periods of chromate conversion coatings [90].

Furthermore, Liu et al. [91] revealed the sufficient impedance effect on the further CCC growth by air ageing in the laboratory air for one hour. A reduced growth rate of CCC was also observed when the coating was either aged in the humid air or immersed in water and then was immersed in the chromate bath again. This comparative examination of CCC growth behaviour by such intervening factors identified the role of the water-bearing coating in the growth process for the transport of reactant and product species. For instance, the air ageing sufficiently reduced the probability of the water-bearing component across the coating to impede the coating growth kinetics. In addition, Frankel et al. [92] provided a diffusion-controlled model of the soluble chromate release process. The post-treatment of heating and air ageing for the longer period with the resultant lower diffusion coefficients rationalizes the decrease of the absorbance of UV-visible spectra at 340 nm that was evidenced to linearly correlate with the concentration of Cr(VI) [93, 94].

2.3.5 Corrosion resistance performance

Corrosion protection of CCC is remarkable for the self-healing capability; that is, the soluble chromate species can transport and migrate to scratch sites to impede corrosion occurrence over the fresh substrate in a corrosive environment [64, 95]. The Frankel group summarized

the protection mechanism of chromate and CCC against corrosion and revealed the role of the single Cr(VI) oxoanions as follows [92, 94-102].

(i) Cr(VI) ions were highly soluble and mobile in solution to migrate by itself to the vicinity of localised corrosion, and then were preferentially reduced to Cr(III) and irreversibly adsorbed at metal surfaces to inhibit oxygen reduction.

(ii) The Cr(III)-containing film can inhibit pit initiation of Al and dissolution of the active S phase particles in Al alloys.

(iii) This redox reaction modified the chemical composition of the surface with the passive oxides and passivated the particles by adsorption and buffering.

(iv) Cr(VI) ions reduced the surface zeta potential by adsorption on aluminium oxides to halt adsorption of the chloride ions.

The corrosion protection mechanism of chromate conversion coating includes:

(i) CCC was a good barrier of the hydrophobic Cr(III) hydroxide and promoted the surface adhesion and mechanical properties.

(ii) The presence of Cr(VI) oxoanions in the chromate conversion coating provided a time-release source in the corrosive solution, and then migrated to repair defects to inhibit corrosion on the exposed substrate. A higher pH value favoured the kinetics of Cr(VI) release.

(iii) CCC sufficiently inhibited anodic and cathodic reactions. The inhibition of the oxygen reduction reaction at the cathodic Cu-rich particles much contributed to the overall corrosion inhibition.

2.3.6 Promising alternatives to CCC

The use of Cr (VI) conversion coatings is highly-regulated by the environmental legislation due to the toxic and carcinogenic risk to human beings and being harmful to the

environments. Researches revealed that the static presence of Cr^{3+} or Cr^{6+} cannot directly lead to DNA damage and cancer, but rather that the molecular debris involved with the reduction process of Cr(VI) to Cr(III) led to the critical damage in the DNA [64, 103-105]. According to the Restriction of Hazardous Substances (RoHS) organization, the maximum level of hexavalent chromium is 1000 ppm [106].

In terms of the promising alternatives of the inorganic species, Kendig and Buchheit [64] reviewed the considerable efforts of replacements and suggested the alternative elements on the base of the periodic table in Figure 2.8 as follows:

- Mo, V, Mn and Tc elements that are the reducible hypervalent transition metals with the highly soluble and mobile oxoanions in aqueous solution.
- Zr, Hf, Ta, Ti and Y elements in the form of the noble transition metal oxides and Si, Ge, P and Te elements to deposit the covalent oxides. The process is based on the sol-gel chemistry.
- Deposit coatings as a type of a barrier layer, including boehmite and hydrotalcite and rare-earth metal. The process is by the simple immersion in the bath.

Considering the future development of nanotechnology, the self-organizing chemistries and biomimetic technologies of coatings represent the promising research direction. Kulinich et al. [104] also revealed that the increasing research in Cr(VI)-free coatings includes the stand-alone chemistry and combination for the organosilane-based chemistries, the electroactive polymers, sol-gel coatings, and inorganic conversion coatings systems. Although a number of such non-chromate coatings displayed the similar corrosion resistance to that of CCC under certain conditions, the details of the formation and the large scale processing require much study in the future. To date, the promising replacement is the combination of surface treatment with the reduced copper-rich particles, the barrier coatings of an appreciable thickness and an inhibitor addition in the corrosive environment [105].

2.4 Zirconium-based Conversion Coating

2.4.1 Background

The zirconium-based conversion coating is one alternative to replace the CCC in practice. The bath generally is regarded as one hexafluorozirconate solution and the titanate, hydrofluoric, organic acids and Cu-/Si-containing additions were used to reach the special objectives [107-113]. The organic polymer addition as in the commercial Alodine 2840 solution was to obtain corrosion resistance and to improve the bonding strength [107]. The presence of the hydrofluoric acid or potassium fluoride in the bath was used to rapidly activate the surface to promote the fast deposition of zirconium and titanium hydroxide [110]. The small quantities of Cu- and Si-containing addition were used in the TecTalis solution (Henkel Corp.) to form the thicker conversion coating around the copper deposits on the surface [113]. The Zr-based bath was processed at 30-40°C and at the pH ranges from 2 to 5.

2.4.2 Formation and structure

Zr-/Ti-based coatings preferentially formed around cathodic sites, such as α phase particles, due to the local alkalization by the oxygen reduction in the presence of the chemical attack by fluorine ions [107, 108]. The passivation of cathodic sites by developed coating resulted in a limitation of a good quality coating [107]. Moreover, Andreatta et al. [108] used the scanning Kelvin probe force microscopy and scanning electron microscopy associated with SEM/EDX analyses to examine the influence of the surface microstructure on the coating formation. The underlying mechanism in the coating formation process was illustrated in Figure 2.9. After the preferential coating formation at the intermetallic particles in the initial treatment for 30 s, the lateral coating in relatively extending areas around these particles was evidenced by the further decrease of the Volta potential variance of particles relative to matrix. The complete coating coverage over the whole surface was revealed after the coating treatment for 300 seconds as evidenced by the complete elimination of the Volta potential variance between the intermetallic compounds and surrounding matrix. Notably, the cathodic intermetallic particles were covered by a thicker coating than that over the matrix, and this was consistent with the report that a thicker Zr-based coating formed on copper deposits on the alloy surface.[113]

In terms of composition and structure, Scram et al. [114] used the AES, XPS and SIMS analyses to reveal one two-layer coating structure, consisting of inner aluminium oxide and outer coating layer of zirconium oxide and fluoride. The polymer addition in the bath

contributed to the top layer of coating surface as the polymer film. Furthermore, the coverage area by the polymer was much larger than that of underlying oxide. In terms of the deposition mechanism of polymer addition, the nucleation was located around the particles, where the hydroxide ions generated by oxygen reduction enhanced the condensation reaction as follows [107]:



After the nucleation, a rapid two-dimensional (2-D) growth of polymer developed over the aluminium alloy, while a limited growth of Zr-Ti oxide was observed. Increasing the dipping treatment times in the bath may cause the polymer formation directly along alloy substrate. Notably, the surface defects along extrusion die line may play a role in polymer nucleation as the situation of the cathodic particles, and then the 2-D growth by the prolonged treatment was observed on the alloy substrate.

Furthermore, Yi et al. used the SEM, EDX, XRD, FTIR and X-ray photoelectron spectroscopy analyses to investigate the composition and structure of the coatings generated in the bath containing H_2TiF_6 , H_2ZrF_6 , NaF with the addition of tannic acid used to provide a golden colour [112]. They revealed that the duplex coating structure mainly consists of an inner Na_3AlF_6 component and the main layer of mixture of metal-organic complex. The primary components of this coating were the Na_3AlF_6 and organic complex of Ti and Al with the presence of a minor concentration of alumina, titanium oxide and fluoride. The metal-organic complex formed by the reaction of the gallic acid with titanium and aluminium cations in the solution. And the gallic acid was yielded by the hydrolysis of tannic acid and contained the carboxyl group and phenolic hydroxyl group on the ortho position to react with metal cations of Ti^{4+} and Al^{3+} . The illustration of this duplex coating structure is shown in Figure 2.10. The formation process of these golden conversion coatings includes the initial nucleation, the subsequent deposition of Na_3AlF_6 crystals on the surface and the lateral formation of metal-organic complex on the surface.

2.4.3 Chemistry of Zr (VI) complex

Zirconium (VI) at VI-B group has 8 coordination numbers in aqueous solutions and the Zr-based bath contains the ZrF_6^{2-} compounds. The Zr-complex chemistry plays a great role during the coating formation. For example, the same concentration of H_2ZrF_6 solution with the H_2TiF_6 solution revealed the less acidity due to the relatively smaller dimension of Ti(VI) ions (coordination number of 6). However, this influence of solution acidity displayed no significance on the polarization resistance of AM60 alloy. The difference of the complex chemistry of Zr(VI) and Ti(VI) ions in the aqueous solutions influenced the slope of logarithm of polarization resistance ($\text{Log } R_p$) relative to the zirconium and titanium concentration (pZr and pTi respectively) [110].

The solubility of zirconium hydroxide influenced coating morphologies and formation process [110, 113]. It was refined as $\log K_{sp}^\circ = -62.46 \pm 0.10$, considering contributions of Zr^{4+} , ZrOH^{3+} and $\text{Zr}(\text{OH})_4$ (aq) [115]. In terms of the pH-dependent deposition of zirconium suspensions, Romyantsev et al. [116] used the dynamic light scattering principle (DLS) and the laser diffraction principle measurement methods to measure the deposit size in dimension ranging from ~ 1 to $2000 \mu\text{m}$ respectively. A further evidence of pH-sensitive deposits was revealed by the zeta-potential and scanning electron micrographs. Their results revealed that a stable mono-disperse colloidal dispersion as the form of sub-micron particles occurred at the pH range from 3 to 4. There exhibited a proportional relationship of particle size with the pH levels. At near pH 4, a bi-modal distribution of the mixture of sub-micron particles and large agglomerates was obtained. Over pH 4.5, large agglomerates formed immediately.

2.4.4 Factors influencing Zr-based conversion coating

Effect factors on the formation of Zr-based conversion coating include the bulk concentration, pH value, concentration of the free fluorine, solution convection, after-rinsing water temperature and surface microstructure [109, 111, 114]. For example, the agitation of the bath was investigated to influence on the coating growth as evidenced by the decreased layer deposition on the matrix with increased stirring rates. Further, an increase of the cathodic current density were revealed by means of potentiostatic polarization on the α phase particles with the increased agitation of the Zr-/Ti-based bath [109].

2.4.4.1. Surface metallurgy of cathodic particles

Lunder et al. investigated the cathodic activity of α -Al(Fe,Mn)Si particles present in AA6060 alloys by means of the various surface analytical methods to examine the affecting parameters on Zr-based coating formation in a fluorotitanate-zirconate solution. The preferential coating formed at and in the vicinity of these cathodic α -phase particles, attributed to the formation of local alkaline diffusion layer by the water and dissolved oxygen reduction to encourage the pH-sensitive deposition of zirconium and titanium hydroxides. However, a small reduction of cathodic activity on the α -phase particle was revealed during the conversion treatment to build up the persistent alkaline diffusion layer to produce an extensive oxide deposits on the particles. Thus, the variance of coating thickness on the AA6060 alloy surface gave rise to the inefficient corrosion protection. In addition, the iron impurity levels in the alloys were expected to influence the coating weight in a given conversion coating process on the different alloys [109].

2.4.4.2. Pre-treatment with controlled hydroxyl fraction

Taheri et al. [117] used X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) to examine the formation mechanism and the interfacial bonding of Zr-based conversion coating on the pure zinc samples after pre-treatment by alkaline, neutral and acidic solution. They demonstrated the fraction of initial hydroxyl by pre-treatments determined the final hydroxyl fraction formed on the Zr-based conversion layer. Consequently, this affected the interfacial bonding properties between the polymer and metal substrate. In addition, the hydroxyl fraction on the zinc sample after deionized (DI) water treatment for 30 min at 25 °C was about 42% with a thicker zirconium-conversion coating. This indicates that the prior DI water immersion provided the sufficient hydroxyl fraction to promote the coating deposition and to offer good adhesion for the successive polymer treatment.

Furthermore, the Taheri research group [118] investigated the influence of such surface conditioning of aluminium alloys on the Zr-based conversion coating with the same methodologies. The more hydroxyl fraction of AA6014 alloy was revealed to encourage the zirconium conversion coating formed. This was suggested to relate to the initial coating

formation process, where the chemical undermining of air-formed film was induced by the free fluorine attack to form Al-F complex and then to detach into bulk solution. In fact, the major interaction of free fluorine ions with the air-formed film occurred with the hydroxyl ligand on the oxide surface. Thus, the fluorine absorption and detachment process of the Al-F complex were both encouraged by the higher hydroxyl fraction on the surface to allow the more time for the coating deposition stage. The reference specimens were pre-treated with ultrasonically degreasing in ethanol for 300 seconds, and the 46% hydroxyl fraction in the surface chemistry was revealed to well develop a conversion coating as evidenced by the relative shorter duration (~60 s) of the initial fall of the open-circuit potential. In contrast, the longer duration (>70 s) of the initial OCP drop and poorer coating formation on AA6014 alloys were observed on the surface after thermally heating in air for 24 h at 275 °C and treatment in nitric acid with ~13 and 22% hydroxyl fractions respectively.

2.4.4.3. pH value

During the coating initiation, the interfacial pH environment became alkaline to favour the precipitation of zirconate and titanate cations especially around cathodic intermetallics in the Zr/Ti based bath. Lunder et al. [109] examined the open-circuit potential during the coating formation on the AA6060 alloys when increasing the bath pH from 2.9 to 4.0. A ~50 mV positive OCP shift revealed the more stable and thicker coating formation. In contrast, Verdier et al. [110] examined the polarization behaviour of the zirconium-based conversion coating formed on AM60 alloy (6%Al-Mg) in the fluorine-containing solution in the acidity range from 2 to 7. The results revealed no significant influence on polarization resistance of the zirconium conversion coating in a given process. Further, the more dilute solutions were the most effective in the conversion coating formation. This discrepancy with the early literature was attributed to the contribution of the fluorine ions to the electrochemical reactivity with the alloy substrate. The concentrated fluorine ions even damaged the early Zr-/Ti-complex deposits to decrease corrosion protection of this conversion coating [110, 119].

2.4.4.4. Additives into the bath

Fluoride salts added into the bath can enhance the dissolution of the native alumina oxide over surface to promote the growth of the coating. However, the fluoride addition in the bath

revealed a detrimental side effect [110]. The increased amount of fluoride concentration into bath solution led to a more aggressive solution with respect to magnesium alloy, resulting in less chance for zirconium or titanium depositions over the surface.

In terms of the copper component addition in a small quantity into a commercial zirconium based solution (TecTalis, Henkel Corp.), Adhikari et al. [113] used the TEM/EDX analyses to reveal the improved conversion coating growth of a ~30 nm thick coating, which was higher than that formed in the copper-free solution (~20 nm thickness). In addition, one enriched Cu layer of up to 50-60 wt.% copper was observed at randomly distributed locations and clusters at the coating/substrate interface.

2.4.5 Corrosion protection

This conversion coating is deemed as one barrier film to passivate the aluminium and/or magnesium substrate and to reject the chloride ions away from the surface. Yi et al. used the potentiodynamic polarization test in 3.5 wt.% NaCl solution to reveal the improved corrosion resistance by the golden Zr/Ti based conversion coatings after the treatment for 25 min. Support of this is the decreased $\sim \times 20$ corrosion current densities and a significant increase (~296 mV) of the variance between the corrosion potential and pitting potential [112].

This improvement of corrosion protection by the zirconium conversion coatings was in good agreement with other literature [108, 113, 120]. Andreatta et al. provided the further evidence of the passivating nature of zirconium conversion coatings by examining the OCP evolution during immersion of the AA6016 alloys after the conversion treatment for 90 and 300 s in the 0.1 M NaCl solution. Support of this fact is that the duration of the first OCP plateau was approximately 20 and 32 h, while the OCP of the bare alloy displayed the continuous fall in the initial duration of 10 h that correlated with the corrosion process [108]. In addition, the coating inhomogeneity over the surface was revealed at and in the vicinity of particles. However, this did not impart the improvement of zirconium-based conversion coatings on AA6060 alloys as evidenced by the polarization behaviours of the uncoated and coated alloys in 0.1 M NaCl solution [109]. For the pitting corrosion of zirconium-coated alloy in 3.5 wt.% NaCl solution for seven days, the reduced number of pits for the specimens treated in 5, 10 and 20 g/l zirconium oxychloride solution revealed the long-term corrosion

protection by this passivating film on magnesium AZ31D substrate.[120] In terms of the comparability with the paint, Adhikari et al. [113] revealed the good long-term corrosion protection of coated steel in 0.5 M NaCl solution, where the zirconium conversion coating formed after more than 30 s. The successive paint treatment revealed the continuously high impedance even up to 120 days in the corrosive solution.

For the bath solution of the component of polyacrylic acids, Nordlien et al. [107] found that the polymer layer preferentially deposited at the regions with a high concentration of surface defects such as the extrusion die lines. This presence of the polymer deposits inhibited the growth of the coating oxides with the prolonged treatment, and thus the coating was not able to give a complete coverage over AA6060 aluminium, leading to the decreased corrosion protection.

2.5 Anodic Coating

2.5.1 Background

Anodizing is used to produce the protective and decorative films on valve metal surfaces (e.g. Al) by the electrolytic oxidation, where the metal part is the anode electrode of an electrical circuit. Anodizing changes the microscopic texture of the surface and the crystalline microstructure of the metal near the surface into amorphous or microcrystalline alumina. The role of the anodic coatings on metal surfaces is to increase the corrosion resistance and wear resistance, and to enhance the adhesion for paint primers. Compared with most types of paint and metal plating, the anodic films are much stronger but also brittle and susceptible to cracking from the thermal stress. The latter can be improved by applying the suitable sealing substances.

2.5.2 Formation and morphology

During the anodizing process under the electric field, the overall reactions between the aluminium substrate and electrolyte occurred in the reaction (10), although there exhibited the extent of penetration of the electrolytic cations into the surface of the anodic film [121].



In terms of the separate reactions during the anodic film growth, the aluminium dissolution played a role in the anodic reaction (11) to produce the aluminium anions that egressed outward under the electric field, which was evidenced by the presence of aluminium ions in the aluminium-free electrolyte after the anodizing process. Accordingly, the cathodic reductions of water and oxygen (reactions (12) and (13) respectively) occurred at the impurity sites to increase the local alkalinity.



After the initial development of the barrier-type anodic film, two interfaces inside and outside the substrate determined the further growth as the following reactions (14) and (15). The alumina anodic film proceeded along the egress of aluminium anions and ingress of hydroxide and oxygen cations through the formed oxides [122].



(at the metal/film interface the inward moving oxygen anions react with the metal)



(at the film/electrolyte interface the outward moving aluminium cations react with water)

The nature, concentration and temperature of the electrolyte and the current density and voltage at the electrical circuit gave rise to the formation of two different types of film morphologies, including a regular array of parallel-sided pores and a relatively thin and intact barrier layer adjacent to the metal substrate [121, 123-125]. The prevalent sulphuric acid electrolyte and chromic acid solution were widely used in aircraft industry, while the oxalic acid solution was for architectural application and phosphoric acid electrolyte was used as pre-treatment for adhesives or organic paints. In terms of the formation mechanism of the porous-type anodic film on Al, it initiated along the locally thickening oxide regions associated with the substrate substructure. Further, the concentrated current led to the Joule

heating at the thin region and on pore bases to promote the significant dissolution of anodic film. Concerning the effect of the electrolyte, larger dimensions of the porous layer, barrier layer and cells were yielded in the milder phosphoric electrolyte compared to the case of sulphuric acid under the applied constant current density. In addition, the pore and cell size and barrier layer thickness revealed a function of the anodizing voltages [126-129].

The composition of the anodic film was identified by Rutherford backscattering spectroscopy (RBS) by Skeldon et al. [122]. They revealed the Al_2O_3 component exhibited at the inner region and the outer region of this alumina was contaminated with electrolyte anions. Support of this fact is that the formula of the out anodic layer formed in the borate electrolyte revealed the consistency of $(\text{Al}_{1.9\pm0.03}\text{B}_{0.14\pm0.03})\text{O}_3$ with the boron present as B_2O_3 . The mass densities of the inner and outer layers were similar by RBS analyses. Furthermore, the type of incorporated electrolyte anions with dependence on the adsorption and mobility influenced the resultant levels on the surface of the anodic film. It was evidenced by the restriction of molybdenum incorporation by the presence of tungsten anions, which revealed the preferential adsorption and incorporation during the anodizing process of aluminium in their mixed electrolyte.

2.5.3 Electrochemical behaviour

Due to the duplex structure with the outer porous layer, the absorption and penetration of aggressive substances in the chloride solution led to the poor corrosion resistance. The post-treated sealing process was well accepted to decrease the porosity to improve the corrosion protection and to provide a durable decorative finish [130].

Hao et al. [130] reviewed the present types and performance of sealing methods applied in the industry, including the hydrothermal sealing (HTS), steam sealing, dichormate sealing, nickel acetate sealing and cold nickel fluoride sealing. The hot water sealing process above 85°C transferred the aluminium oxide into the more stable boehmite within micropores as $\text{Al}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow 2\text{AlO}(\text{OH})$ (boehmite). The surface did not show this boehmite evidence. In contrast, the incorporated precipitates into the porous layer along the formation of the stable boehmite were used by other processes to synergistically increase corrosion protection. The best performance of corrosion protection was offered by the nickel acetate sealing at 90°C as

evidenced by the long-term resistance of standard salt spray test of 3,000 h and less than 1 mg/dm² of weight loss in standard acid dissolution test. However, the reduced abrasion resistance and eco-friendly concern to cause allergic contact dermatitis limited the application. The promising alternative sealing process shall consist of the eco-friendly metal salts, passivating inhibitors, buffer and surface cleaners. In addition, the electrochemical sealing process of the electrolytic colouring and electrophoretic coatings provided the other potential candidate replacement.

Yu et al. [131] employed the potentiodynamic polarization and scanning electron microscopy to investigate the corrosion performance of the anodic films on 1070, 2024 and 7075 aluminium alloys after sealing in boiling water, stearic acid, potassium dichromate and nickel fluoride to examine the pH effect of corrosive environments. Their results revealed the orders of corrosion performance of sealing processes with dependence upon the pH values of the corrosive media as follows: In the neutral solution, nickel fluoride sealing and stearic acid sealing > dichromate sealing and water sealing; for the acidic solution, stearic acid sealing > dichromate sealing and water sealing > nickel fluoride sealing; for the basic solution, nickel fluoride sealing > stearic acid sealing > dichromate sealing > water sealing. Notably, the organic sealing in the stearic acid provided good corrosion protection both in the acidic and alkaline environments, indicating a promising alternative replacement.

In addition, the quality control of sealing processes included the extremely simple dye spot test and fixed frequency admittance measurements and acid dissolution test according to standards ISO 2143 and 2931 [132, 133], which were commonly applied in the production line. Electrochemical impedance spectroscopy (EIS) combining an equivalent circuit (EC) technology was widely used in the research to provide the more sensitive details of the quality level in comparison to standard seal quality control tests [134-137].

In terms of the EC efficiency in the anodic film, Gonzalez et al. [136] reviewed the present models used in the equivalent circuits (ECs) and offered one refined EC model as shown in Figure 2.11, where two parallel circuit branches were used. One parallel branch consisted of the resistance R_{pw} and capacitance C_{pw} elements represented the electrochemical properties of the walls of cells in the anodic films. Further, the application of the electrochemical elements in ECs representing the pore filling by the resistance R_p and capacitance C_p well indicated the

effect of sealing and/or ageing post-treatments. The inner branch of resistance R_b and C_b represented the electrochemical properties of the barrier layer over the substrate. Considering the unsealed case, the conductive solution in the pore and large resistance R_{pw} shortened this circuit branch and were eliminated in the corresponding ECs. Except for the resistance of the electrolyte, R_{sol} , between the reference electrode and coated alloys, one distinct resistance R_1 was with the physical significance of the intermediate layer formed by diffusion from the outside electrolyte at boiling temperature. As the exposure time increased in the chloride solution, the hydration of the alumina filling in the pores developed, leading to the decrease of the capacitance as evidenced by the decreased C_p value. Their results revealed that the refined ECs offered the information of transformations through the anodic film thickness, as well as of the electrical properties, the integrity of the barrier and porous layers and of the effect of influencing factors on sealing and ageing.

2.6 Trivalent Chromium Conversion (TCC) Coating

2.6.1 Background

Cr (III) was revealed to be less toxic than Cr (VI) by the EPA organization and the trivalent chromium bath is a promising alternative for the hexavalent chromium process (Table 2.2) [138]. Pearlstein and Agarwala (at NAVIAR, Patuxent River, Maryland) first used the trivalent chromium compounds on aluminium alloys in 1994 to reveal a long-term corrosion resistance of 96 hours in 5 wt.% NaCl salt spray by this Cr(III) conversion coatings [139, 140]. In terms of the bath composition, the Agarwalar group used a mixture of Cr_2O_3 , Na_2SO_4 and Na_2SiF_6 and the fresh bath was a one-week stand before use. To date, the bath generally contains the hexafluorozirconate (ZrF_6^{2-}), trivalent chromium salt ($Cr(OH)_3$ or $Cr_2(SO_4)_3$), one fluoride salt (NaF) at pH 3.8~4 adjusted by the addition of sodium hydroxide (NaOH) [141-145].

2.6.2 Formation and structure

Trivalent chromium anion can form coordination compounds of coordination number six. Thus, a polymeric film of the coordination complexes formed on the surface by pH-driven deposition. The nature of this film was expected to be the basic chromium species with

fluorozirconate branching [139, 141, 146]. The probable hydrolysis and deposition of chromium compounds formed by increasing the local pH and analogous compounds were formed with sulphate are shown in Figure 2.12. After this hydrolysis, the resultant release of free hydrochloric acid was consistent with the observed decrease in pH with time.

Chen et al. [147] studied the formation of TCC coatings on AA 5052 (AlMg2.5) for different immersion times, and revealed that an immersion period of 30-300s resulted in the main stage of coating growth investigated by the open-circuit potential evolution as follows: the non-steady region (0-30 s), growth region (30-300 s), and steady region (300-600 s). Coatings formed for 300 s had a uniform structure, but the obvious cracks were generated on the surface after immersion for an extended time of 600s. Coatings cracks were regarded to relate the proceeding dissolution reaction during a conversion period by authors.

Guo et al. [148] investigated the presence of the spherical nodules (0.2 μm in diameter) over the TCC coating surface, which is similar to the situation of CCC and Zr-based conversion coating [110, 149]. These nodules were suggested to correlate with the initial precipitation of the conversion reaction to promote the further growth [149]. They revealed the coating thickness in the range of 40-120 nm, which was much thicker than the cases of zirconium-based conversion coating without trivalent chromium component. Moreover, a two-layer coating structure was identified to comprise zirconium-chromium mixed oxide over the inner layer of aluminum oxide or oxyfluoride. The line profiles of analytical TEM/EDX across the TCC coating region revealed ~ 10 wt.% chromium and ~ 40 wt.% zirconium. They used the dilute Harrison's solution, a mixture of 0.05 wt.% NaCl and 0.35 wt.% $(\text{NH}_4)_2\text{SO}_4$, to investigate the potentiodynamic polarization. The TCC coating displayed a protective barrier layer to suppress the oxygen reduction reaction on the aluminium alloy surface, while the anodic polarization curves showed no significant influence before and after coating treatment on the alloy after etching and desmutting.

Li et al. [150] investigated the formation and structure of the trivalent chromium coating using X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy, and revealed that the coatings (50-100 nm thickness) formed over most of the alloy surface and were primarily composed of hydrated zirconia ($\text{ZrO}_2 \cdot 2\text{H}_2\text{O}$). The formation of the coatings under the open circuit conditions was suggested to involve two steps. (i) The dissolution of the air-formed

oxide was promoted by fluorine to form AlF_6^{-3} complex to make the reactions occurrence of the hydrogen evolution and/or oxygen reduction on the bare metal surface to lead to the subsequent increase of the local pH. (ii) The subsequent pH-driven hydrolysis of ZrF_6^{2-} formed a hydrated zirconia along the precipitation of trivalent chromium hydroxides. The coating was biphasic with a hydrated zirconia overlayer and a fluoroaluminate interfacial layer ($\text{K}_x\text{AlF}_{3+x}$) (illustrated in Figure 2.13).

2.6.3 Effect of pre- and post-treatment

In general, the basic etching and acid desmutting were applied to degrease the alloy surface and provide a certain rough surface to promote the coating growth. Furthermore, the electrochemical behaviour of the etched-desmuted aluminium alloys revealed an increased corrosion resistance as evidenced by the 200 mV negative shift of the breakdown potential compared to the as-received specimens [148]. The extent of these pre-treatments can also have a significant effect on the conversion coating formation [148, 150-152].

Guo et al. [148] used two types of gentle desmutters to remove the dark etching products on AA2024-T3 alloys, consisting of 20% (v/v) liquid TrucoSumt-go NC (named process I) and the 72 ml/l HNO_3 -30g/l Sanchem 1000 solution (named process II). The process I solution contained the ferric sulfate, bifluoride, nitric acid and small amount of sulphuric acid with a low etch rate. In contrast, the process II contained the sodium bromate and nitric acid to offer a low Al matrix etch rate and revealed the efficiency in the removal of the oxide layer and intermetallic particles. The surface roughening in the form of hundreds of connected etch pits by the process II for 3 min displayed a comparable extent to the 5-min treatment by the process I, which contained a smaller silicate amount over surface. Furthermore, the successive TCC coatings formed over alloys after both treatments presented the similar morphologies and compositions of Cr/Zr ratio of 1:4 in weight. They concluded that the silicate enrichment by pre-treatments had no significant influence the TCC formation and composition as well.

In terms of TCC coating post-treatments, Li et al. [150] used the 2-min tap water rinse to stabilize the freshly-developed coatings over the metal substrate. The tap water at pH ~ 6.8 possibly encouraged the nature of hydroxide components compared to the ultrapure water

(pH=5.8). Furthermore, the authors suggested that this post-treatment played an important role in the reproducible experiments; however, the reason is still unknown. In addition, the air ageing and baking at the high temperature were used to improve the corrosion protection of TCC coatings. The experimental temperatures are selected as room temperature, 55, 100, and 150 °C. The resultant analyses by EIS indicated that the 2× increases in the charge-transfer resistances were at 55 and 100 °C; however, 150 °C aging extensively induced the cracking over the surface and, consequently, decreased the corrosion resistances. The longer period of the room-temperature aging enhanced the charge-transfer resistance and they revealed the stable coating thickness even after such post-treatments. Notably, the presence of surface cracks and the increased hydrophobic property were also observed with increasing the periods of air ageing and the temperature of baking treatment. This mechanism of the improved corrosion protection by the ageing post-treatments either in the air or in the baking temperatures correlated with the reduced hydrated channels and coating defects in the freshly-developed TCC coatings as shown in Figure 2.14 [153].

2.6.4 Evidence of Cr (VI)

Iyer et al. [141] used the UV-visible spectroscopy to conduct the comprehensive Cr(VI) detection on bare aluminium substrates, as-deposited coated aluminium panels, corroded panels, and in both new and depleted coating solutions. They revealed that there exhibited no evidence for Cr(VI) in the solution, either fresh or used, even when exposed to oxidizing chemicals, and the TCC coatings did not contain chromate, as-deposited or corroded, unless such species form in a transient, non-detectable state. Thus, they implied that there were two possible types of Cr(VI) formation under the aggressive acid/oxidative conditions. One possibility was for either in the form of a transient species or the possible formation at the metallic chromium content. The other suggestion was for the transient formation of Cr(VI) species during the acid treatment.

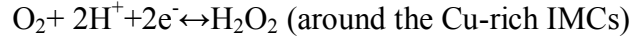
Rochester and Kennedy [154] used the 1,5-diphenylcarbazide chemical in the spot tests to titrate whether or not a coloured complex (pink-violet) forms to provide the evidence of the presence of Cr (VI). This reaction for the presence of Cr (VI) was extremely sensitive at the upper limit of the absorbency index per gram atom of chromium of ~40, 000 at 540 nm but was relatively noble to the Cr (III). Notably, the reddish-violet colour was investigated for

TCC coating-treated articles after the salt spray test, indicating the presence of hexavalent chromium. They supposed that the transformation of Cr(III)/Cr (VI) reactions occurred by the strong oxidants during this corrosion process.

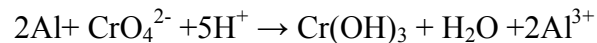
Guo et al. [155] used the artificial scratch cell consisting of one TCC coated panel and one noncoated panel in 0.5 M sodium chloride to examine the possibility of self-healing property of TCC coating. The XPS analyses revealed that a small amount of Cr (VI) as the form of CrO_4^{2-} was presented on the noncoated surface of the artificial scratch cell after 14-day immersion in this NaCl solution. Furthermore, the inductively coupled plasma-optical emission spectroscopy (ICP-OES) analyses of the used electrolyte identified the evidence of chromium in the sodium chloride solution. Their results revealed that the TCC coating was capable to release chromium into the solution and the mobile chromium species in the possible form of CrO_4^{2-} ions migrated to the uncoated surface. Further, there was no evidence of zirconium release in the electrolyte and noncoated panel. By contrast, Cr (VI) was not investigated by XPS analyses in freshly-developed TCC coatings on AA2024-T3 alloy, where specimens were dried in the compressed air at room temperature for at least 1 hour.

The effectiveness of Raman spectroscopy analyses on the hexavalent chromium examination has been extensively studied in the chromate conversion coating process. And a fingerprint evidence of $840\text{-}904\text{ cm}^{-1}$ shift was the evidence of hexavalent chromium species, although Raman vibrational shift cannot distinguish the actual formula of underlying compounds [78, 156-158]. In terms of Raman examination for the transient Cr(VI) in TCC coatings on AA2024, Li et al. [150, 159] revealed that no Cr(VI) species were detected in freshly-developed TCC coatings, but the presence of a 880 cm^{-1} Raman shift was presented both in the coatings after more than 1h air drying and in all coatings after immersion in air-saturated Na_2SO_4 or NaCl solutions from 1-14 days. This Raman shift indicated the presence of Cr(VI) oxides, which was in the similar form to the case of hexavalent chromate conversion coatings. Furthermore, the distribution of transient Cr(VI) species displayed inhomogeneous and concentrated in and around the corrosive pits, and the absence of the peak at the distinct Raman shift was found on the terrace outside the pits and indicated no significance of Cr(VI) oxides. Moreover, the addition of hydrogen peroxides into the trivalent chromate bath revealed the increased intensity of the Cr(VI)-O peak at 860 cm^{-1} shift in the developed TCC coatings, indicating the oxidation effectiveness on the Cr(III)/Cr(VI) transformation. Thus,

they hypothesized that the dissolved oxygen in the TCC coatings became reduced at the cathodic Cu-rich IMCs sites to produce hydrogen peroxide, H_2O_2 , which then migrated to oxidize $\text{Cr}(\text{OH})_3$ to chromate (CrO_4^{2-}) in the manners as follows.



In terms of chemical environments for the transient Cr(VI) oxides, they revealed the role of Cu-intermetallic compounds in and around pits to promote such transformation compared to the situation of the copper-free matrix on the terrace sites. In the former case, the present $\text{Al}(\text{OH})_x^{3-x}$ ions, generated by the pH-driven deposition, were suggested to interact with the transiently formed Cr(VI) to form a mixed oxide of Al(III)/Cr(VI) [160]. On the remote terrace away the pits, the covalent and polymeric Cr(III)/Cr(VI) oxide was supposed to account for the chemical stability of the TCC coatings (as illustrated in Figure 2.15). Concerning the self-healing properties of the TCC coatings, the scratched TCC coatings before and after immersion in the mixed solution of sodium chloride and hydrogen peroxides were examined by Raman spectroscopy. The observation of the hexavalent chromium at 843-861 cm^{-1} Raman shifts in the coatings and around pits in the scratched area correlated with the presence of the transient CrO_4^{2-} species, which formed through the Cr(III) oxidation by H_2O_2 . The hexavalent chromium had some mobility and was released into the solution to react at the corroded sites on the aluminium alloys in the following manner to self-heal the corrosion.



2.6.5 Corrosion protection

TCC coatings are regarded as one of the promising alternatives for the CCC and it has been identified that this Cr(III) coating effectively impedes corrosion as a passivate film, although not fully reaching the level of Cr(VI) coatings [64, 161]. TCC coatings (typically 20-400nm thickness) served as a barrier and not as an inhibitive coating [148, 154, 155, 162, 163].

Guo et al. [155] used an artificial scratch cell, consisting of one TCC coated article and one uncoated alloy, to examine the active corrosion inhibition of the TCC coatings exposed in 0.5 M NaCl electrolyte (Figure 2.16). The TCC coated alloys displayed no intentional defects after immersion in NaCl solution to reveal the effective corrosion protection by the single TCC coating (Figure 2.17). Further, the electrochemical impedance spectroscopy (EIS) and the equivalent circuit (EC) model were used to investigate the corrosion protection, where the EC model represented the physical significance of coating structure in Figure 2.18. C_{coat} and R_{po} symbols represented the coating capacitance and corrosion resistance of the hydrated channels or defects through coating respectively. R_{corr} and C_{dl} were the charge-transfer resistance and one double-layer capacitance at the coating/metal substrate respectively. In addition, R_s was the electrolyte resistance between the electrode and coating surface. The increased twice charge-transfer resistance of the uncoated surface in the cell sealed with the other TCC coated alloy panel was found in comparison to the situation of uncoated cell controls, identifying the active corrosion protection by the TCC coatings. The mechanism of the active corrosion protection by the TCC coatings was suggested to relate two possible reasons. One possibility was involved with the transient formation of Cr(VI) and the other suggestion was associated with the non-Faradaical release of Cr (III) into solution such as by means of the chemical dissolution. For the latter hypothesis, a certain organometallic Cr (III) species in the type of highly soluble $[\text{Cr}(\text{NH}_3)_6]^{3+}$ species possibly formed in the chloride-containing solution (pH $\approx$ 5.8) and then detached from the coating into electrolyte [164]. In comparison to the situation of the nonTCC cell controls, the lower C_{dl} values of the TCC coated surface at $\sim 3.5 \mu\text{F}/\text{cm}^2$ indicated the better capacitance of the coating/substrate interface. This was also in good agreement with the improved corrosion protection by TCC coatings.

Li et al. [150, 165] compared the electrochemical behaviour of TCC coatings over aluminium alloys of AA2024-T3 alloy, AA6061 alloy and AA7075 alloy in the air-saturated 0.5 M Na_2SO_4 solution and a mixed solution of 0.5 M Na_2SO_4 and 0.05M NaCl, using the potentiodynamic polarization and electrochemical impedance spectroscopy. For the equivalent circuit model, they refined the capacitances of C_{coat} and C_{dl} with the constant phase elements to fit the nonideal capacitances as evidenced by the phase angle of less than 90° in Figure 2.19. The order of the charge-transfer resistances and coating resistances in the TCC coatings over these alloys revealed as follows, AA6061>AA7075>AA2024. The impedance

of the constant phase element was refined as $Z = (j\omega)^{-n}Q^{-1}$, where the larger ratio n was associated with the increased heterogeneity of the TCC coatings. The most homogenous TCC coatings were revealed over AA6061 alloys as evidenced by the largest ratio n_{coat} and n_{dl} at 0.93 and 1 respectively. In addition, the charge-transfer resistances were used to estimate the coating porosity, analogous to a defect parameter. Given the assumption of electrochemical inert coating, the equation (16) was used as follows.

$$P = \frac{R_{p,bare}}{R_{p,TCC}} \times 10^{\frac{-|\Delta E_{corr}|}{b_a}} \quad (16)$$

$R_{p, bare}$ and $R_{p,TCC}$ represented the charge-transfer resistances of the bare substrate and TCC coated substrate with ΔE_{corr} for the difference of the corrosion potentials and b_a for the anodic Tafel slop for the bare alloy. The porosity index P revealed an apparent decrease with a same order in both two electrolytes, AA2024>>AA7075>AA6061. For example, the porosity for TCC coated AA2024 was highest, which indicated the poorest corrosion protection and was in good agreement with the smaller R_{po} values. Furthermore, the corrosion current density of i_{corr} was significantly impeded on all specimens in both solutions in compared to the corresponding situation of the uncoated control in the polarization plots. By contrast, the coatings on AA6061 and AA2024 alloys primarily functioned as a cathodic inhibitor against corrosion, and both the anodic and cathodic inhibitions were investigated in the coatings on AA7075. The inhibitive mechanism was attributed to the physical blocking of the deposited TCC coatings on the Al-rich sites (oxidation) and cathodic reductions around Cu-rich particles.

Delaunois et al. [166] compared the corrosion protection of TCC coatings with and without post-oxidation treatment. They revealed that the single TCC coatings without oxidation treatment offered very good protection on the aluminium 1050 against pitting and filiform corrosion. One optimal process in their study comprised a 10-minute immersion in the trivalent chromium bath without post-oxidation. Li et al [153] studied the effects of aging time and temperature on the corrosion-protective performance of the TCC coating over the AA2024-T3 alloy. They proved that hydrated channels and or defects in the freshly-developed TCC coating were improved by baking treatment at the higher temperature to provide better the physical barrier inhibition (Figure 2.14). The best improvement of

corrosion inhibition was after the 7-day-room-temperature aging with the acceptable hydrophobicity property.

In terms of the solution chemistry effect on the TCC coating process, Nickerson et al [167] compared three series of TCC solutions containing one baseline control and two modified TCC-I and TCC-IC solutions, using the neutral salt fog (NSF), SO₂ salt fog, accelerated paint adhesion, surface electrochemical analyses. Prior to the coating treatment, the reduced period of the acidic deoxidation was revealed to provide a better surface to form TCC coatings against corrosion during the NSF experiments of all three solutions. Further, TCC-IC treatment for 10 min performed the best corrosion protection as evidenced by the absence of corrosion after the 21-day NSF tests and the highest overall coating resistances by EIS tests, followed by a lesser extent TCC-I treatment for 5 min and the baseline TCC coating treatment for 10 min. Concerning the durability of TCC coating with the primer and paints, the painted alloys with TCC conversion coatings of these three types were investigated by the NSF and acidified salt spray in SO₂. They revealed a good corrosion performance on TCC-I treatment, while the degradation of corrosion protection was observed on the painted TCC-IC specimens. Considering the SEM/EDX analyses, no significant chemical variances of zirconium and chromium components were observed on these three TCC coatings, revealing the similar coating compositions. These modified TCC-I and TCC-IC solutions with the improved corrosion protection were probably attributed to either the addition of some components into the coating or the alteration of coating deposition process.

2.7 Key Unsolved Issues

- Understanding of TCC coating chemistry and the growth kinetic, especially for the relationship with the copper chemistry in the Al-Cu alloy.
- Relationship between the composition and structure during the coating formation.
- Bath chemistry and changes during the coating formation.
- Cr (VI) evidence and formation mechanism on superpure Al and Al-Cu alloys.
- Optimal process of TCC coatings including methodologies to reduce Cr(III)/Cr(VI) transformation and to improve corrosion protection.

2.8 Introduction to Present Work

Electron microscopies have been used to investigate morphologies and thickness of trivalent chromium conversion coatings to study growth kinetics. SEM-/TEM-/EDX and GDOES profiles identified the elemental types and in-depth distribution of TCC coatings. AFM was employed to examine the presence of cracks on the coating surface in the open-air environment. RBS and NRA analyses quantified elemental concentrations. XPS and Raman spectra analysed the elemental valence near the coating surface and in depth respectively. In addition, potentiodynamic polarization, electrochemical impedance spectroscopy and electrochemical noise analyses were employed to detect the electrochemical behaviour.

In this present work, the following shows the systematic research tree:

- The growth mechanism of TCC coatings on superpure Al and the chemistry of chromium components with and without the air ageing treatments.
- The effect of alloy microstructure on the coating initiation and growth, and the particular attention paid on the initial growth of TCC coatings formed in the period of 5 and 15 seconds on AA2024-T351 alloys.
- The effect of surface pre-treatments on the coating formation, including mechanical polishing, etching and desmutting in chemical solutions.
- The effect of post-treatments, including the deionized water immersion with dependence on temperature and pH values and the addition of sulphite salts to improve the chromium chemistry.
- The effect of copper in alloys on the coating formation and composition on the sputtering-deposited Al-Cu alloys of different copper concentration.

Figure captions 2.1-2.19

Figure 2.1 The copper assay by the cyclic voltammetry method (a) in deaerated borate buffer over 40 min NaOH pre-treated, unpretreated, and 40 min NaOH+30 s HNO₃-pre-treated AA2024-T3 alloy, and (b) the linear correlation of Cu(0)/Cu(I) oxidation peak area against Cu oxidation peak height from NaOH-treated AA2024-T3 alloys after the indicated etching times.

Figure 2.2 The potential-pH Pourbaix diagram and the graphical presentation of the various equations for aluminium-water system at 25°C [39]. All ionic activities and gas pressures have been set arbitrarily at 10⁻⁶ g ion/l and 1 atm respectively.

Figure 2.3 The schematic illustration of a process for copper redeposition by the dissolution of large Al₂CuMg and Al₂Cu intermetallic particles in Al alloys. The particle dealloying process included (i) the anodic polarization by the adjacent matrix, (ii) the formation of detached metallic Cu clusters along the particle remnant coarsens, (iii) the oxidation of the detached clusters, and (iv) the precipitation or reduction of copper ions that stimulated the secondary pitting.

Figure 2.4 The schematic illustration of a typical coating system on aluminium matrix.

Figure 2.5 (a) the schematic representation of the hydrolysis-polymerization-precipitation mechanism for Cr(OH)₃ backbone formation, and (b) the condensation of Cr(VI) on the Cr(III) backbone by nucleophilic attack of hydroxyl ligands in the backbone.

Figure 2.6 Illustration model for the chromate conversion coating formed on AA2024-T3.

Figure 2.7 The refined model for the chromate conversion coatings formed on AA2024-T3 alloy.

Figure 2.8 The periodic table of the shaded elements, which compounds were considered as alternatives for the oxo-Cr⁶⁺ inhibitors.

Figure 2.9 Mechanism of deposition of Zr/Ti layer on AA6016 by SKPFM and SEM.

Figure 2.10 The structure of Zr/Ti-based conversion coating over aluminium alloy.

Figure 2.11 The equivalent circuit model for the physical significance of the anodic film.

Figure 2.12 The hydrolysis process of trivalent chromium chloride, which accelerated by the local pH increasing.

Figure 2.13 The proposed biphasic chemical structure of the TCC coatings on AA2024. The thickness values listed were those estimated from measurements made in vacuum.

Figure 2.14 Aging effect on TCC coating structure.

Figure 2.15 The schematic illustration of the mechanism for the transient formation of Cr(VI) in the TCC coating during immersion in the air-saturated solution.

Figure 2.16 The schematic drawing of the artificial scratch cell.

Figure 2.17 The plan-view macrophotography of the artificial scratch cell sheets in 0.5 M NaCl, (a) TCC-treated surface exposed for 21 days, (b) nonTCC surface exposed near TCC-treated surface for 21 days, (c) bottom nonTCC surface exposed in control cell for 14 days, and (d) top nonTCC surface exposed in control cell for 14 days.

Figure 2.18 The equivalent circuit model used for TCC and nonTCC surfaces in the artificial scratch cells and for control cells in the Harrison's solution.

Figure 2.19 The equivalent circuit model used for TCC coated alloy surface.

Table 2.1 The nominal composition in AA2024-T3 alloys

Component	Al	Cu	Mg	Fe	Mn	Si	Ti	Zn	Cr
Weight %	90.7-	3.8-	1.2-	Max	0.3-	Max	Max	Max	Max
	94.7	4.9	1.8	0.5	0.9	0.5	0.15	0.25	0.1

Table 2.2 Water quality criteria summary, concentration in µg/l

CAS	Priority Pollutant	Carcinogen	Fresh Acute Criteria	Published criteria		Recalculated Values using IRIS, aa of 9/90		Drinking Water MCL	Criteria Federal Register Notice
				Water & Organisms	Organisms Only	Water & Organisms	Organisms Only		
Cr VI	7440-47-3	Y	N	16	50	170	3,400	100	50 FR 30788
Cr III	1308-14-1	Y	N	1,700	170,000	33,000	670,000	100	50 FR 30788

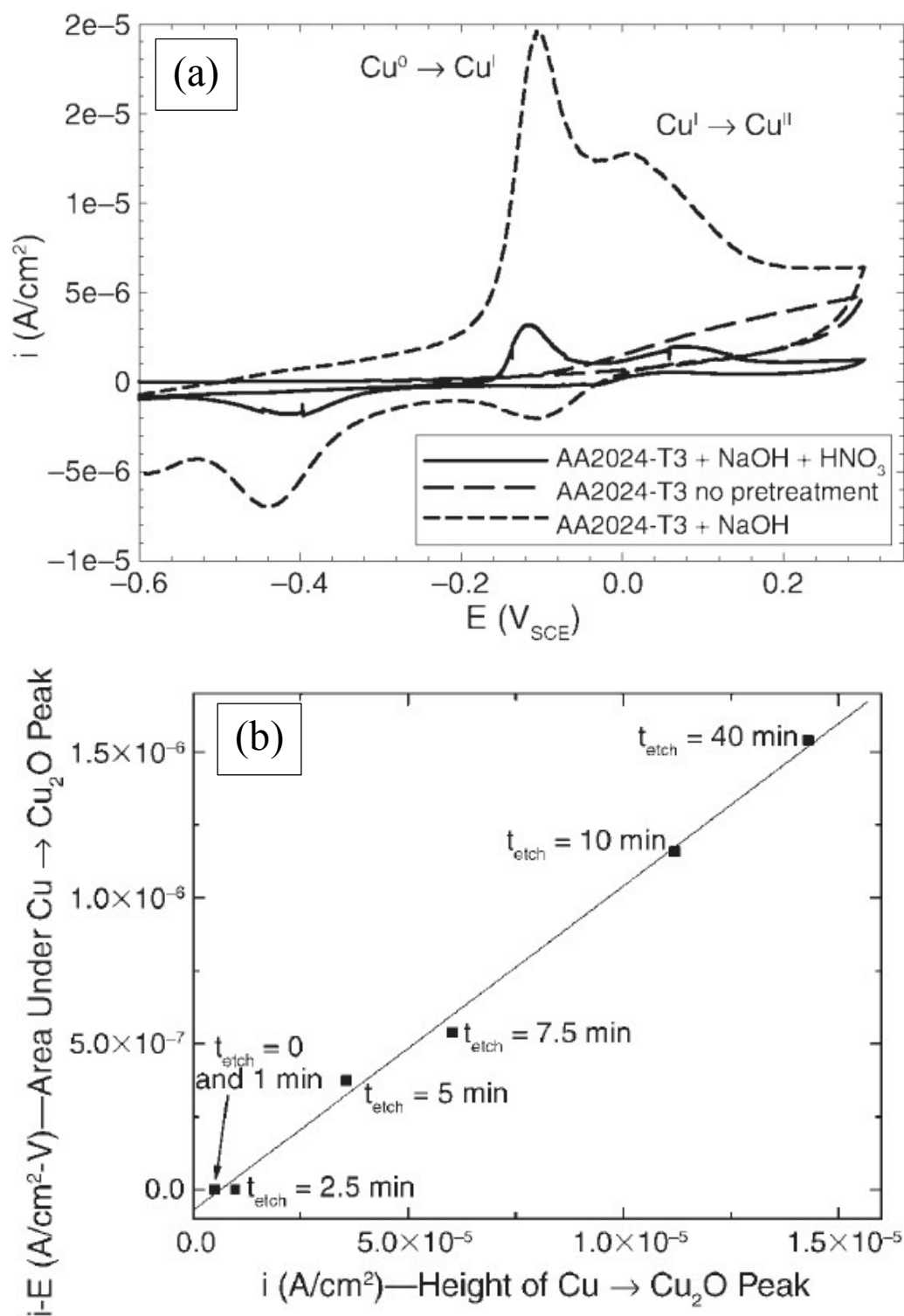


Figure 2. 1 The copper assay by the cyclic voltammetry method (a) in deaerated borate buffer over 40 min NaOH pre-treated, unpreatreaed, and 40 min NaOH+30 s HNO₃-pre-treated AA2024-T3 alloy, and (b) the linear correlation of Cu(0)/Cu(I) oxidation peak area against Cu oxidation peak height from NaOH-treated AA2024-T3 alloys after the indicated etching times

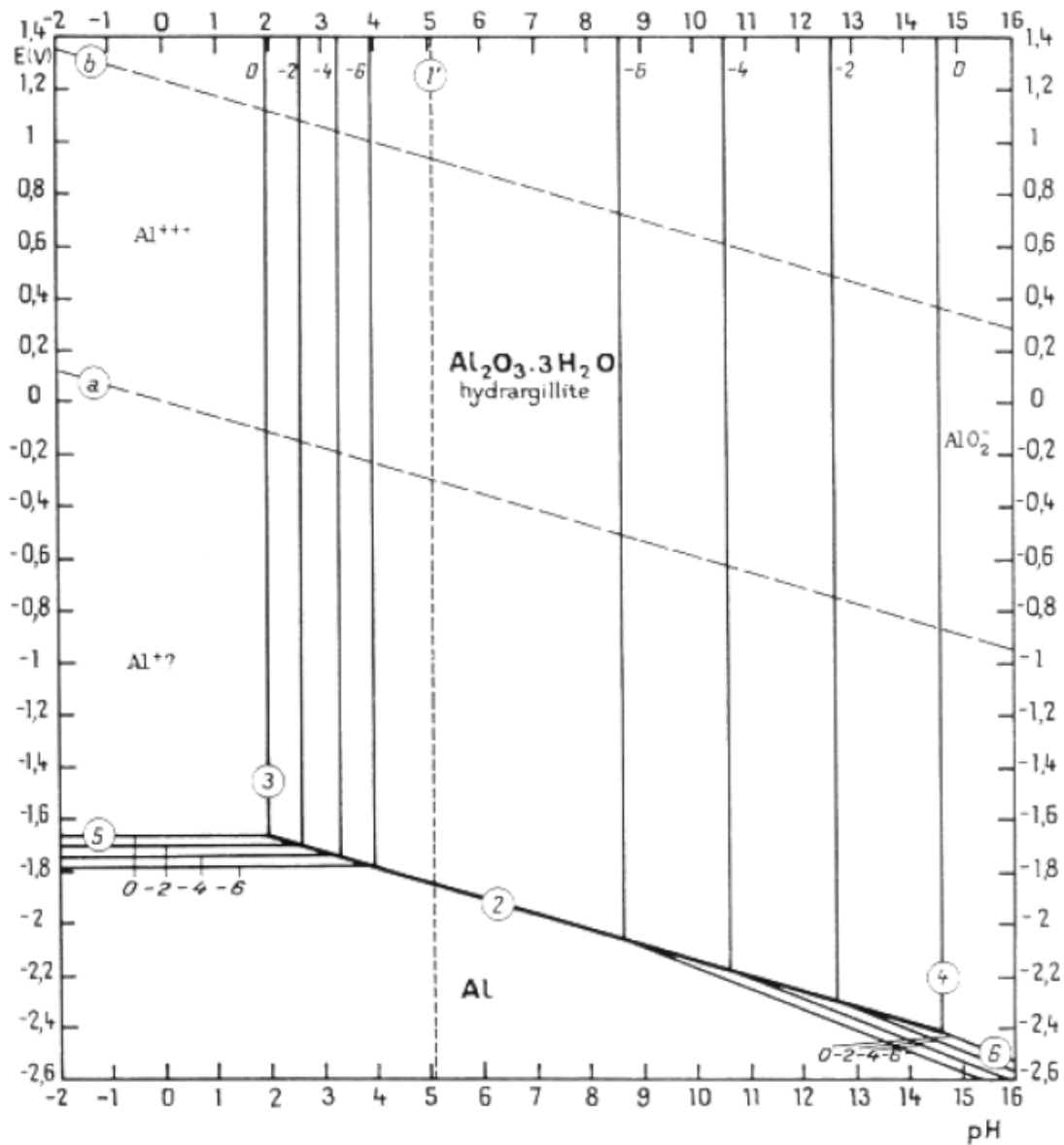


Figure 2. 2 The potential-pH Pourbaix diagram and the graphical presentation of the various equations for aluminium-water system at 25°C [39]. All ionic activities and gas pressures have been set arbitrarily at 10^{-6} g ion/l and 1 atm respectively.

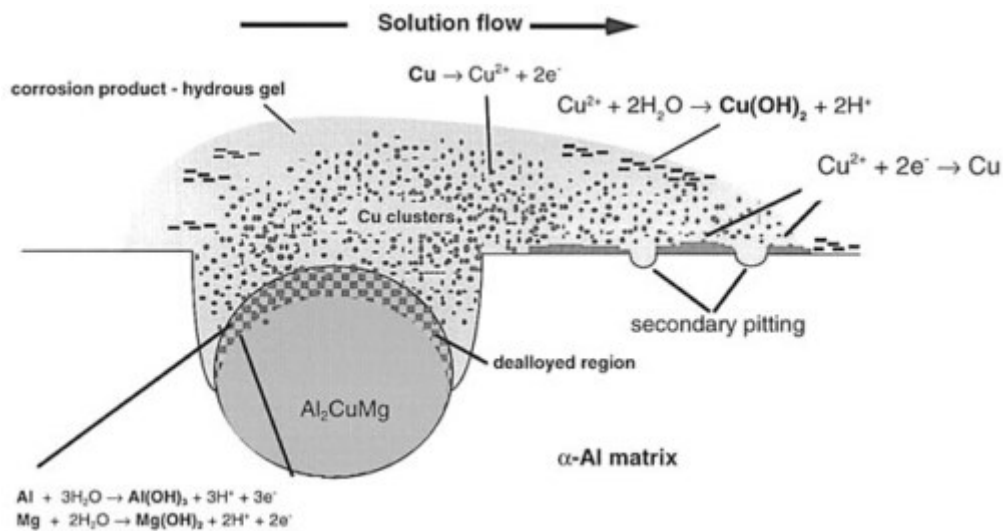


Figure 2. 3 The schematic illustration of a process for copper redeposition by the dissolution of large Al_2CuMg and Al_2Cu intermetallic particles in Al alloys. The particle dealloying process included (i) the anodic polarization by the adjacent matrix, (ii) the formation of detached metallic Cu clusters along the particle remnant coarsens, (iii) the oxidation of the detached clusters, and (iv) the precipitation or reduction of copper ions that stimulated the secondary pitting.

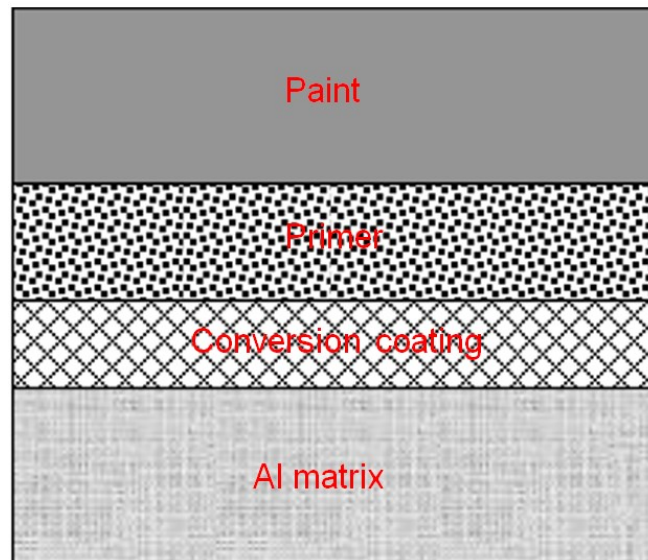


Figure 2. 4 The schematic illustration of a typical coating system on aluminium matrix.

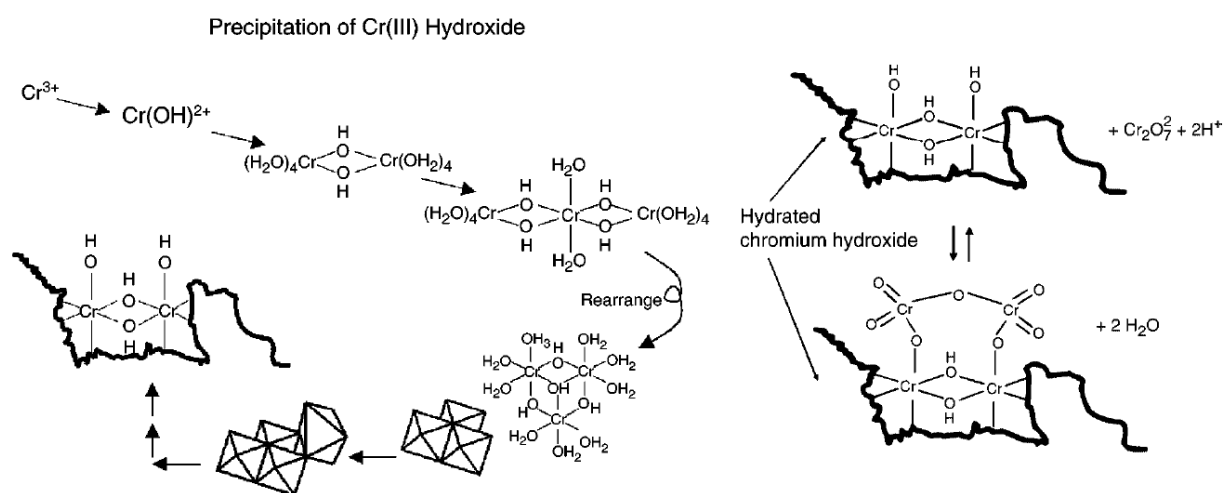


Figure 2. 5 (a) the schematic representation of the hydrolysis-polymerization-precipitation mechanism for Cr(OH)_3 backbone formation, and (b) the condensation of Cr(VI) on the Cr(III) backbone by nucleophilic attack of hydroxyl ligands in the backbone.

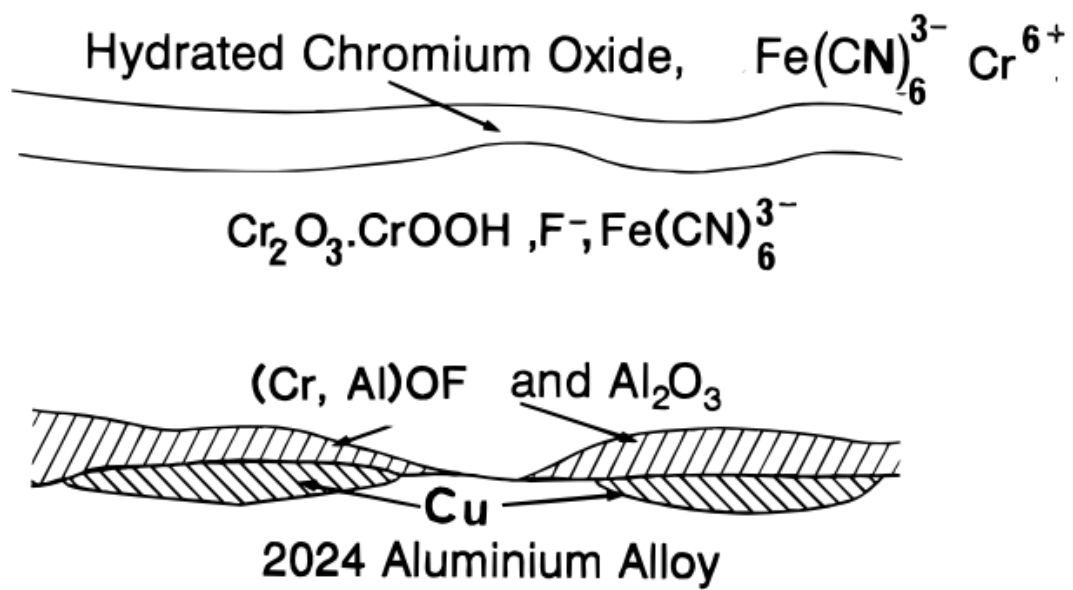


Figure 2. 6 Illustration model for the chromate conversion coating formed on AA2024-T3.

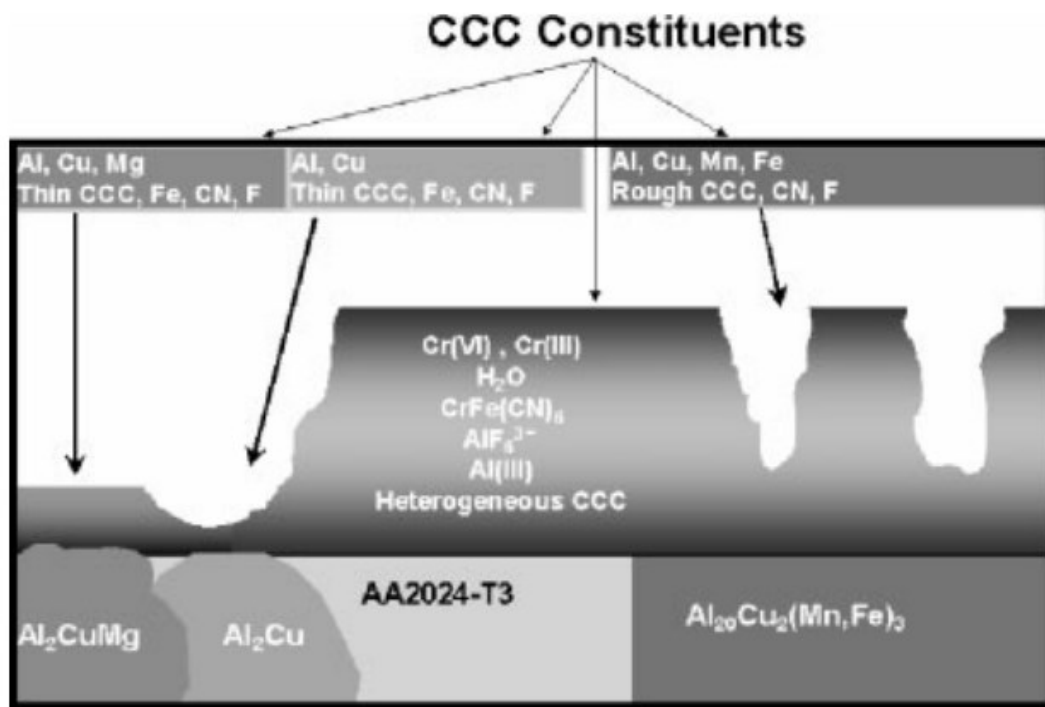


Figure 2. 7 The refined model for the chromate conversion coatings formed on AA2024-T3 alloy.

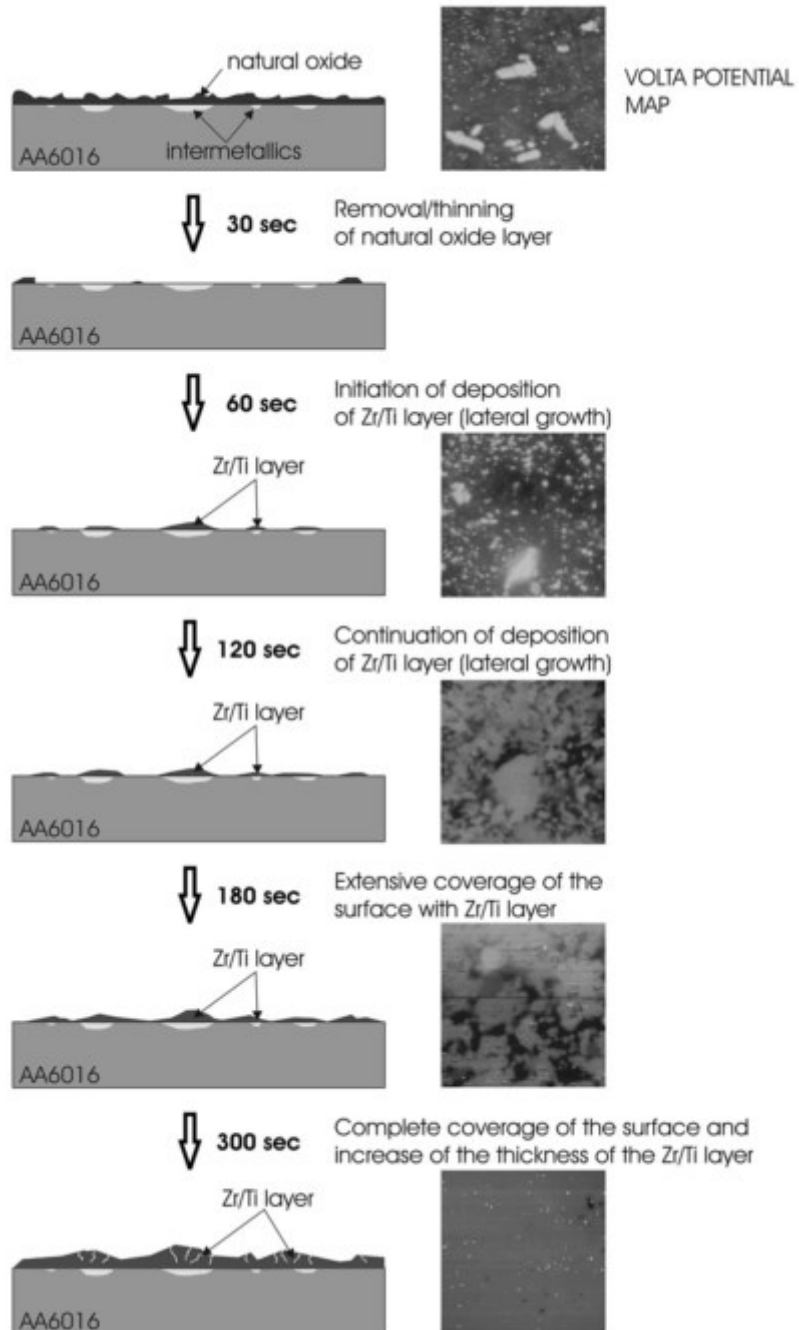


Figure 2. 9 Mechanism of deposition of Zr/Ti layer on AA6016 by SKPFM and SEM.

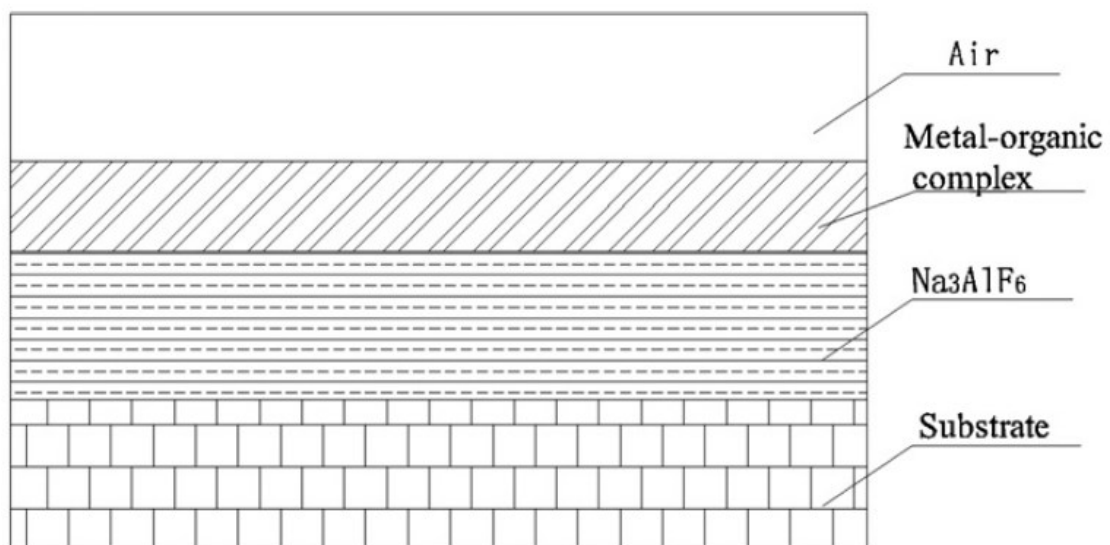


Figure 2. 10 The structure of Zr/Ti-based conversion coating over aluminium alloy.

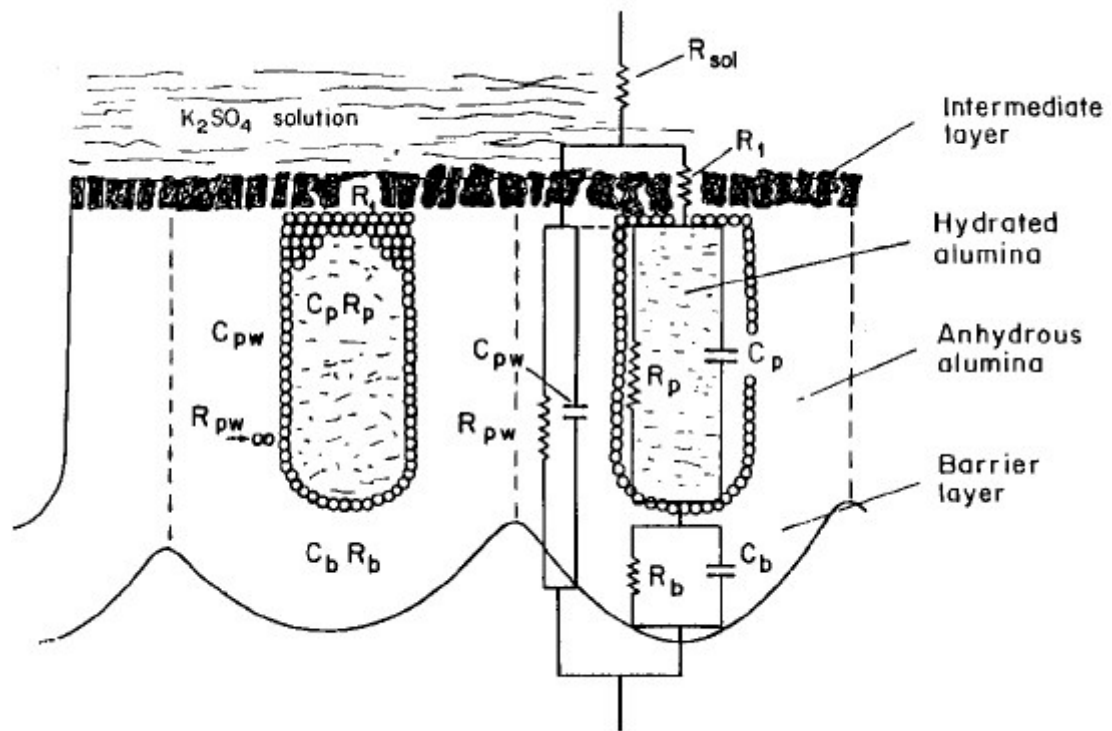


Figure 2. 11 The equivalent circuit model for the physical significance of the anodic film.

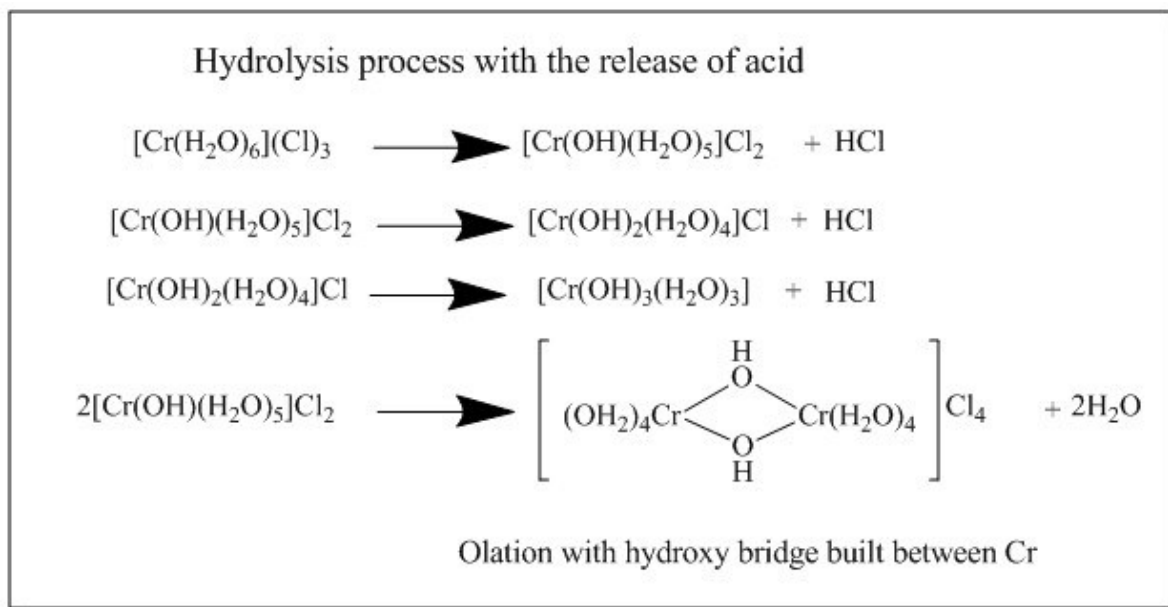


Figure 2. 12 The hydrolysis process of trivalent chromium chloride, which accelerated by the local pH increasing.

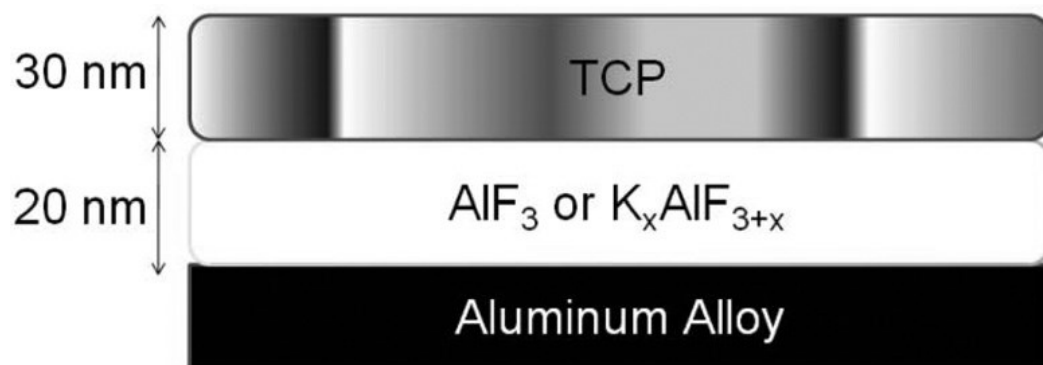


Figure 2. 13 The proposed biphasic chemical structure of the TCC coatings on AA2024. The thickness values listed were those estimated from measurements made in vacuum.

**Hydrated Channels
and Defects**

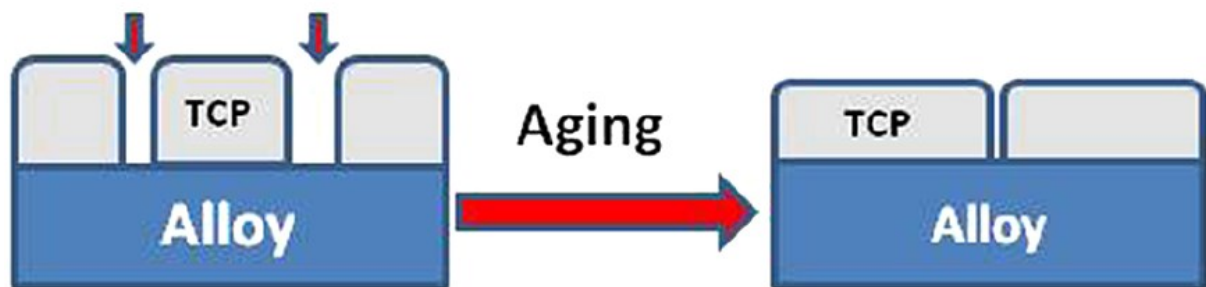


Figure 2. 14 Aging effect on TCC coating structure.

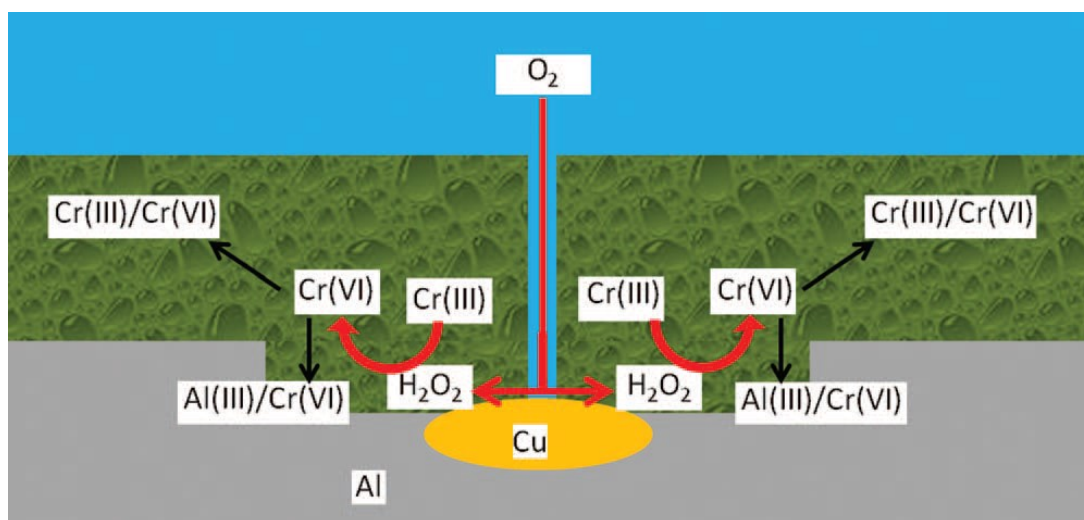


Figure 2. 15 The schematic illustration of the mechanism for the transient formation of Cr(VI) in the TCC coating during immersion in the air-saturated solution.

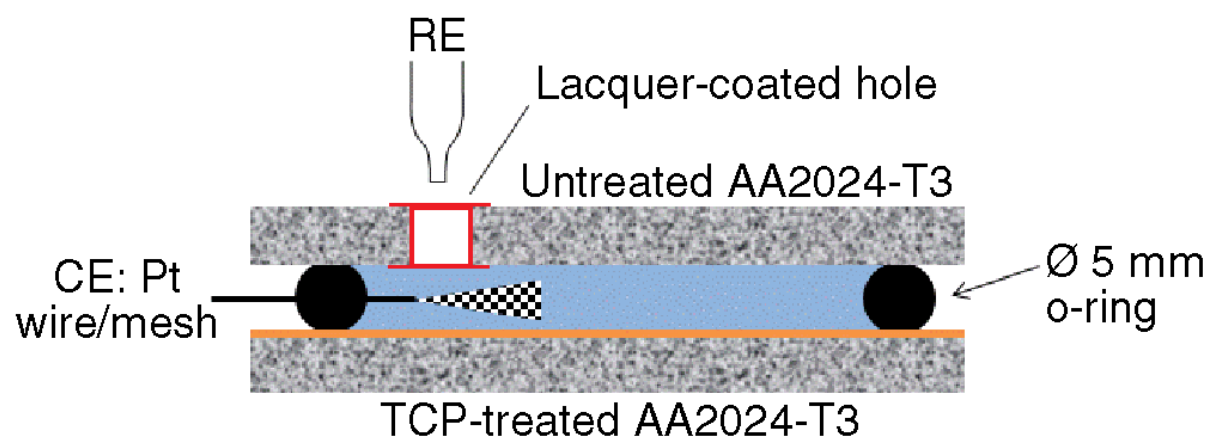


Figure 2. 16 The schematic drawing of the artificial scratch cell.

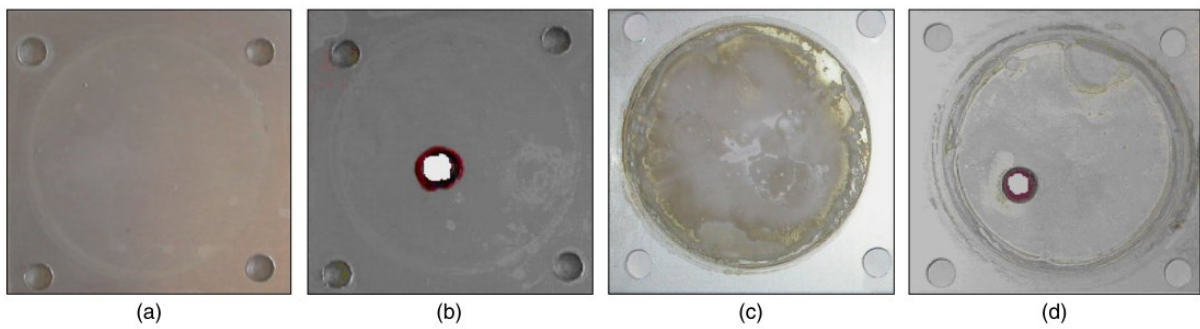


Figure 2. 17 The plan-view macrophotography of the artificial scratch cell sheets in 0.5 M NaCl, (a) TCC-treated surface exposed for 21 days, (b) nonTCC surface exposed near TCC-treated surface for 21 days, (c) bottom nonTCC surface exposed in control cell for 14 days, and (d) top nonTCC surface exposed in control cell for 14 days.

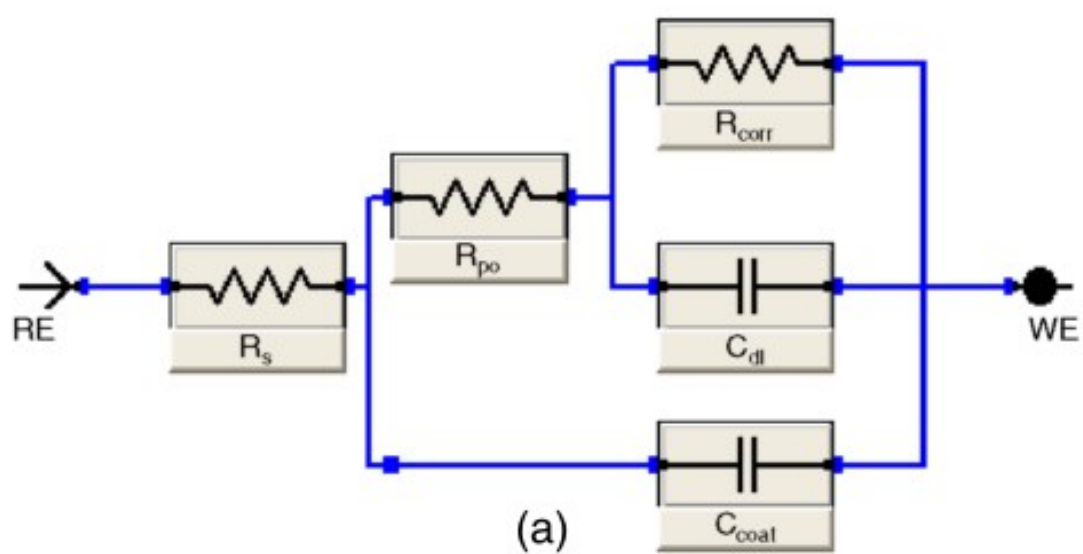


Figure 2. 18 The equivalent circuit model used for TCC and nonTCC surfaces in the artificial scratch cells and for control cells in the Harrison's solution.

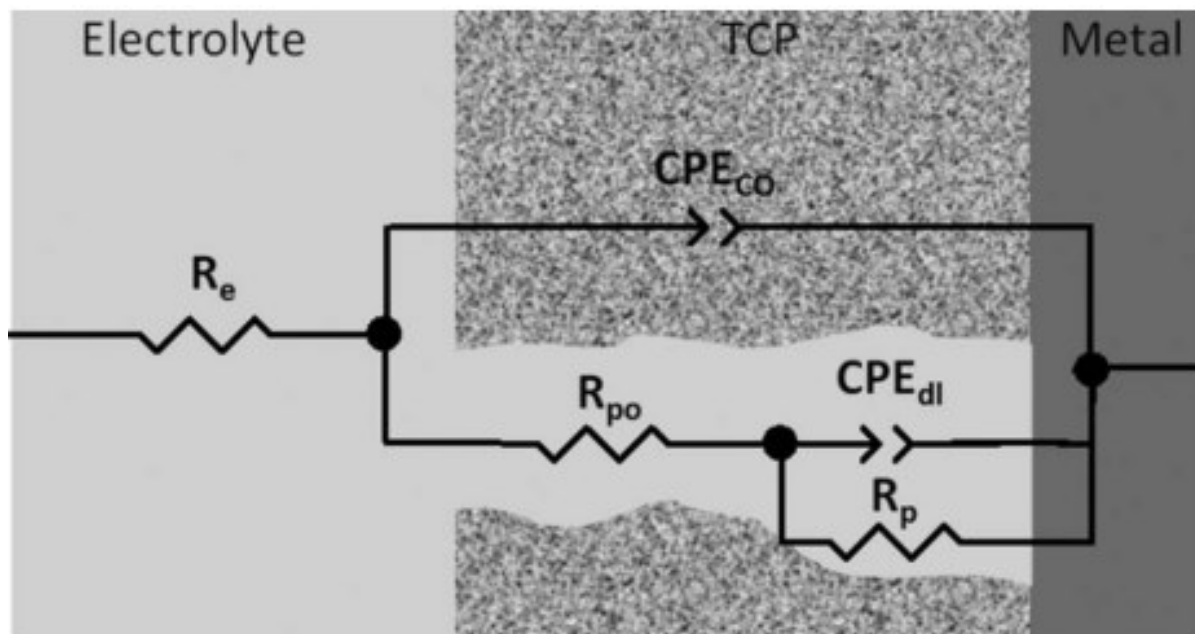


Figure 2. 19 The equivalent circuit model used for TCC coated alloy surface.

Chapter 3 EXPERIMENTAL PROCEDURE

3.1 Introduction

In this chapter, the experimental procedure, including specimen and solution preparation, experimental approaches and the surface analytical characterization, are described in detail. Sputtering-deposited aluminium and Al-Cu alloys were used to better investigate the influence of copper contents on the coating formation and Cr(III)/Cr(VI) transformation. Analytical methods for the coating morphology, coating composition, the chemical state examination and corrosion protection tests are briefly introduced.

3.2 Specimen and Solution Pre-treatment

3.2.1 Materials

Three forms of materials were employed for experiments.

(i) Superpure aluminium sheets of ~0.5 mm thickness and 99.99 wt.% purity, containing 50 ppm copper and 8 ppm Fe [168].

(ii) Cold-rolled AA 2024-T351 alloy sheets of ~1.5 mm thickness. The nominal composition is 3.8-4.9 wt.%Cu, 1.2-1.8 wt.%Mg, up to 0.5 wt.%Fe and 0.5 wt.%Si, 0.3-0.9 wt.%Mn and other impurities of less than 0.1 wt.% contents. The balanced component is aluminium of 90.7-94.7 wt.% [169].

(iii) Pure Al, Al-2 at.%Cu, Al-24 at.%Cu, Al-40 at.%Cu and Al-64 at.%Cu alloys were deposited by magnetron sputtering using an Atom Tech Ltd. System with aluminium and copper targets, which are both of high purity of 99.999%. The deposited layer thickness was 400-420 nm on an electropolished aluminium substrate. Prior to the coating treatment, the surface was simply cleaned by deionized water rinsing and then dried in a stream of cool air.

3.2.2 Solutions and reagents

All chemicals used in this study were analytical grade qualities and all solutions were prepared with deionised water ($>17 \text{ M } \Omega \cdot \text{cm}$ resistivity). The electropolishing bath for Al comprised perchloric acid (60 wt.%) and ethanol solution of volume ratio at 1:4 v/v. The alkaline etching solutions were 5 and 10 wt% NaOH and the acidic desmutting solutions were 50 v/v% HNO_3 and one commercial D30 solution (dilute 15 vol.%, from MacDermid Corp.). While the composition of the D30 solution was proprietary, it contained a mixture of ferric sulphate, sulphuric acid and nitric acid.

The trivalent conversion coating bath was a diluted SurTec 650 (SurTec Corp.) bath with the deionised water at 1:4 v/v ratio and the pH value was adjusted with 5 wt% sulphuric acid or 1 wt% sodium hydroxide solution to 3.9 prior to the conversion treatment. The SurTec 650 bath consisted of a mixture of ZrF_6^{2-} , Cr^{3+} , F^- and SO_4^{2-} components in an aqueous solution.

Chromium oxide (Cr_2O_3 , powder, $\geq 98\%$) and chromium fluoride tetrahydrate ($\text{CrF}_3 \cdot 4\text{H}_2\text{O}$, 97%) were purchased from Sigma-Aldrich (UK). Chromium sulphate hydrate ($\text{Cr}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$) was purchased from Alfa Aesar (UK). Iron (II) sulphate heptahydrate (99+%) was purchased from Fisher Scientific (UK).

3.2.3 Superpure aluminium preparation

Individual rectangular specimens, of $\sim 30 \times 24 \text{ mm}$ and $\sim 30 \times 12 \text{ mm}$ dimensions, were first degreased with acetone in an ultrasonic wave environment for 10 min; thereafter, the specimens were masked with the stop-off lacquer to provide exposed surface areas of ~ 6 and 3 cm^2 respectively, and then immersed in the electropolishing bath for 240 s at 20 V. Due to the highly-oxidising electropolishing solution, an ice bath mixed with the tap water was used to maintain the temperature of the polishing cell below 10°C . The solution was continuously stirred magnetically in order to inhibit localised heating. After the operation, the specimens were rinsed in the ethanol and deionised water for at least 15 s and dried in a cool air stream. Finally the specimens were stored in a desiccator over silica gel until required for the further study.

Aluminium rods of 150 mm length and 3 mm diameter were cut with a notch (approximately 8 mm deep) at one end of the rod. A crocodile clip was attached to the notched end of the rod. In order to ensure a good electric connection, a copper wire (~0.1 mm diameter) was attached to the crocodile clip and the aluminium rod with a heat shrink polyolefin tubing was then fitted over the copper line and aluminium rod. Specimens for the experiments were connected by the crocodile clip.

3.2.4 AA2024-T351 aluminium alloy preparation

AA2024-T351 aluminium alloys were prepared by cutting to dimensions of ~30×24 mm and ~30×12 mm with a foot-shear machine. The degreased and cleaned specimens were first mechanically ground using the SiC grit papers from 400, 800, 1200, 2400 to 4000 finish. A fine alloy surface was further polished in a polishing cloth using 3 and 1 µm diamond paste and 0.25 µm colloidal silica, where an organic lubricant was sprayed onto the polishing cloth. After polishing, the specimens were cleaned ultrasonically in acetone bath, rinsed in ethanol and deionized water and dried in a cool-air stream. In addition, the surface pre-treatment of alkaline etching and acidic desmutting was employed on the alloys after the mechanical polishing up to 4000 grit finish.

(1) Alkaline etching

Two selections of alkaline etching solutions were used, consisting of ~5 wt% sodium hydroxide solution for 60 s and ~10 wt.% NaOH solution for 30 s. The alkaline bath temperature was maintained at 60 °C in a water bath.

(2) Acid desmutting

Two solutions were individually employed, comprising a 50% (v/v) nitric acid (specific gravity 1.42) for 30 s at ambient temperature and the 15% (v/v) D30 solution for 90 s at 30 °C. The constant temperature of the desmutting solution was maintained by the heated water bath.

All pre-treatments were rinsed by deionized water. After this mixed pre-treatment, specimens were dried in a stream of cool air and stored in a desiccator over silica gel prior to the further study.

3.2.5 Ultramicrotomy

Ultramicrotomy is a technique developed from the biological sciences to prepare the electron transparent thin cross-sections for the electron microscopy [170]. The detail of the procedures used is provided below:

- (i) Mounting of the specimens in a 00 size BEEM polyethylene capsule filled with embedding resins of DDSA, MNA, DBMA and Agar 100 resins, and finally curing the resins in an oven at 60 °C for 24-48 h.
- (ii) Grinding the specimen embedded in the resin in the specific directions and steps according to the schematic diagram of Figure 3.1, using the 800 grit silicon carbide papers.
- (iii) Trimming with a glass knife in an ultramicrotome (LEICA EM UC6) by steps as shown in Figure 3.2.
- (iv) Sectioning using a diamond knife to generate sections of about 30 nm normal thicknesses, which were collected onto 400 mesh nickel grids in the deionized water and ethanol-based solutions and then stored in the grid box.

3.3 Trivalent Chromate Conversion Coating Process

Superpure aluminium and AA 2024-T3 alloys, prepared as illustrated in sections 3.2.3 and 3.2.4, were immersed in the dilute SurTec 650 (40 °C, pH 3.9) for a range of immersion times of 15, 30, 60, 90, 120, 300 and 600 s. After immersion, coated specimens were then immersed in the deionized water for 120 s, followed by the rinsing in deionised water and drying in a cool air stream. Prior to the examinations, specimens were left in the open-air laboratory for 24 h at the room temperature.

Scanning and transmission electron microscopies were used to examine top-view and cross-sectional morphologies. In addition, the elemental profiling in depth and quantitative ion beam analyses of coatings were used to identify the coating composition along the chemical status characterization by spectroscopy techniques.

3.4 Characterization Technologies

3.4.1 Scanning electron microscopy (SEM)

A Zeiss Ultra 55 FEG-SEM scanning electron microscope was used to investigate the surface morphology by the secondary electron and backscattering electron and the constituent elements before and after TCC coating treatment by means of energy dispersive X-ray (EDX) analysis, operated at accelerating voltages of 3 and 15 kV.

3.4.2 Transmission electron microscopy (TEM)

Morphologies and associated features of cross sections of TCC coated superpure aluminium and alloys were examined using a JOEL 2000 FX II transmission electron microscope with an accelerating voltage of 120V. In addition, an FEI Titan G2 80-200 S/TEM, operated at 200 kV, was also employed to detect cross-sectional micro-features and elemental distributions, using the elemental mapping of energy dispersive X-ray (EDX) analyses. For diffraction pattern analyses, a FEI Tecnai F30 instrument was carried out at 300 kV.

3.4.3 Glow discharge optical emission spectroscopy (GDOES)

Glow discharge optical emission spectroscopy (GDOES) has been extensively employed to generate depth profiles of constituent elements of coatings by detecting emissions from atoms in the argon plasma generated by sputtering [171-174].

A GD-Profilier 2 instrument (Horiba Jobin Yvon, France), operating at a radio frequency at 13.56 MHz with a copper anode of 4mm diameter, was used to determine elemental depth profiles. Emission responses from excited sputtered elements were investigated with a polychromator of focal length of 500 nm with 30 optical windows. Emission lines used contained 396.157 nm for Al, 324.759 nm for Cu, 383.834 nm for Mg, 339.203 nm for Zr,

425.439 nm for Cr, 589.600 nm for Na, 180.738 nm for S and 130.223 nm for O. A pressure of 635 Pa and power of 35 W were employed for elemental depth profiling, with a data acquisition time of 0.005 s. Plasma cleaning was employed on a sacrificial silicon panel to remove contaminations on the anode prior to such examination [175].

3.4.4 Atomic force microscopy and scanning Kelvin probe force microscopy

Atomic force microscope (AFM) and scanning Kelvin probe force microscopy (SKPFM) were used to record the coating topography and the potential variance on alloys before and after the coating treatment, using A Dimension 3100 microscope with Nanoscope 3a controller (Bruker, Santa Barbara, USA). The TESPA tapping mode probes and OSCM-PT conductive probes for surface potential examination were used. According to the scanned area and surface roughness, the scanning rate, ranging from 0.5 to 1 Hz, was adjusted manually. Finally, quantitative image data were carried out by the NanoScope off-line analysis software (Version 1.5).

3.4.5 Rutherford backscattering spectroscopy and Nuclear Reaction Analysis

Specimens were analysed by Rutherford backscattering spectroscopy (RBS) and nuclear reaction analysis (NRA), using ion beams provided by the Van de Graaff generator at the University of Namur, Belgium. RBS employed 2.0 MeV $^4\text{He}^+$ ions, with detection of scattered ions at 165° to the direction of the incident beam. Data were interpreted using the RUMP program. The carbon, oxygen and fluorine contents of specimens were assessed by nuclear reaction analysis (NRA) using the $^{12}\text{C}(\text{d},\text{p}_0)^{13}\text{C}$, $^{16}\text{O}(\text{d},\text{p}_1)^{17}\text{O}$ and $^{19}\text{F}(\text{d},\text{p}_{11,12})^{20}\text{F}$ reactions, employing 0.87 MeV $^2\text{H}^+$ ions, with detection of emitted protons at 150° to the direction of the incident beam. The oxygen contents were quantified using a reference specimen of anodized tantalum. Details of the analysis of ^{16}O by NRA can be found elsewhere [176-178]. The carbon content was estimated from the ratio of the yields of the $^{12}\text{C}(\text{d},\text{p}_0)^{13}\text{C}$ and $^{16}\text{O}(\text{d},\text{p}_1)^{17}\text{O}$ using literature values of the cross-sections for the respective reactions [176, 179]. Fluorine could not be quantified by NRA due to lack of data on the reaction cross-sections. The region of analysis by RBS and NRA was of ~ 1 mm diameter.

3.4.6 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectra were acquired on a Kratos Axis Ultra DLD spectrometer (Kratos Analytical, Manchester, UK) located in the School of Materials at the University of Manchester. The spectra were generated using monochromatic Al K α radiation ($h\nu=1486.6$ eV) at 150 watts with a base pressure 1.0×10^{-8} mbar, and charge neutralisation achieved by low energy electrons produced by passing a current of 0.18 amps through a linear filament located at the lower end of the electrostatic lens. Wide scan spectra were acquired from 1200 eV to 0 eV binding energy at 80 eV pass energy and 0.5 eV step size, and the data were quantified by measuring peak areas and using theoretical sensitivity factors [180], modified for the instrument geometry and the inelastic mean free path energy dependency [181]. The intensity/energy response of the instrument was determined following acquisition of spectra from copper, silver and gold [182]. High energy resolution spectra at 20 eV pass energy and 0.1 eV step size were acquired for chemical state determination, and peak fitting was employed to determine the position and intensity of overlapping photoelectron peaks. Charge referencing was relative to the hydrocarbon peak at 284.6 eV. Where photoelectron peaks from different elements overlap, for example Al 2p, Cu 3p and Cr 3s, peak fitting to the high energy resolution data was used to determine an effective relative sensitivity factor for quantification. All data processing was carried out using CasaXPS (Casa Software, Teignmouth, UK). The area of the XPS analysis was $\sim 700\times 300$ μm .

3.4.7 Raman spectroscopy

Raman spectra were obtained using a Renishaw 2000 Raman instrument with an argon laser (514 nm, 12.5 mW power excitation). Before carrying out the examination, the laser was calibrated using the silicon peak at 520 cm^{-1} . The integration time was 30 s, with 10 times accumulation to avoid the effect of stray light noise. The analysed area was ~ 1 μm in diameter.

3.5 Electrochemical Examination

A three-electrode system in one glass cell of volume of 500 ml was employed for all electrochemical measurements in a Solarton electrochemical workstation with a Modulab software controller. The cell consisted of a working electrode of exposed area of $\sim 2.25\text{ cm}^2$, a platinum wire counter electrode, and a saturated calomel reference electrode (SCE, 4 M KCl, 0.24 V vs NHE).

3.5.1 Cyclic voltammetry

The quantitative coverage fraction of the presence of the electroactive copper on alloys after pre-treatments was assessed by cyclic voltammetry tests in a saturated borate buffer solution, consisting of 8.17 g/l sodium borate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) and 7.07 g/l boric acid (H_3BO_3). The pH value of this saturated solution was ~ 8.4 and the nitrogen bubbling method for a period of 30 min was used to remove the solution oxygen prior to the test [34, 36].

Experimental tests proceeded as follows: (i) 10 min OCP measurement; (ii) 5 min potentiostatic scan at $-0.7 \text{ V}_{\text{SCE}}$; (iii) cyclic voltammetry scan from $-0.7 \text{ V}_{\text{SCE}}$ to $0.3 \text{ V}_{\text{SCE}}$, then scanning back to $-1.2 \text{ V}_{\text{SCE}}$ at a scanning rate of 1 mV/s ; (iv) 10 min potentiostatic scan at $-0.7 \text{ V}_{\text{SCE}}$; (v) repeated (iii) step; (vi) 20 min potentiostatic scan at $-0.7 \text{ V}_{\text{SCE}}$; (vii) repeated (iii) step. This last cyclic voltammetry scan was used to assess the copper coverage due to the minimum effect of the aluminium oxidation reaction in the literature. Further, the peak height of the $\text{Cu}(0)/\text{Cu}(\text{I})$ reaction was used to represent the copper levels, attributed to the linear correlation with this peak area. Thus, the fractional surface coverage of copper on alloys after pre-treatments was assessed from voltammograms in the following formula:

$$\theta_{\text{Cu, assessed}} = \frac{\text{Area under Cu(0)} \rightarrow \text{Cu(I) peak of specimens}}{\text{Area under Cu(0)} \rightarrow \text{Cu(I) peak of pure Cu}}$$

The peak height and area of $\text{Cu}(0)/\text{Cu}(\text{I})$ reaction on the pure Cu was measured as $\sim 1.61 \times 10^{-5} \text{ A/cm}^2$ and $1.61 \times 10^{-6} \text{ C/cm}^2$ respectively.

3.5.2 Polarization and electrochemical impedance spectroscopy (EIS)

Corrosion protection was assessed by potentiodynamic polarization and electrochemical impedance spectroscopy using the following procedures: (i) 30 min OCP measurement; (ii) EIS measurement from 10^5 to 10^{-2} Hz at the OCP level; (iii) 30 min OCP measurement to stabilize the surface condition; and (iv) potentiodynamic scans from $-1.0 \text{ V}_{\text{SCE}}$ (vs reference) to an anodic potential of $1.0 \text{ V}_{\text{SCE}}$ (vs reference) at a scan rate of 1 mV/s . All electrochemical measurements were repeated twice to ensure reproducibility. Electrolytes included the 3.5

wt.% and 0.05 M NaCl solution, 0.1 M Na₂SO₄ solution, and the mixture solution of 0.1 M Na₂SO₄ and 0.1 M NaCl, which selection depended on experimental objectives.

3.5.3 Electrochemical noise analysis (ENA)

The electrochemical noise analysis technique is powerful to assess the real-life corrosion performance on the bare aluminium alloy and inhibitor effectiveness [183-185]. The evaluation of the real-life performance of TCC coatings formed for 60, 120 and 300 s was investigated by this powerful tool to understand corrosion process and protection effectiveness.

For the electrochemical noise measurements, shielded cables were used to reduce the external noise influence and two identical samples were used while a saturated calomel electrode was used as reference electrode. A Concerto (Capcis-Intertek) multichannel potentiostat was used to reduce aliasing influence during oversampling noise data at 5 Hz and recording at 1Hz. The fast Fourier transforms (FFT) calculated the noise data by the in-house developed software, acquiring 1023 Hz segments of 1000 points at each iteration [185, 186].

Figure captions 3.1-3.2

Figure 3.1 The schematic illustration for the grinding process of the specimen embedded in the resin in specific directions and steps by 800 grit papers of (a) the side-view of the ground tip, and (b) the top-view of the ground tip

Figure 3.2 The schematic illustration for the trimming process of well-grinded specimens, where B letter means the distance finish between 1 to half screen square in ultramitrotomy.

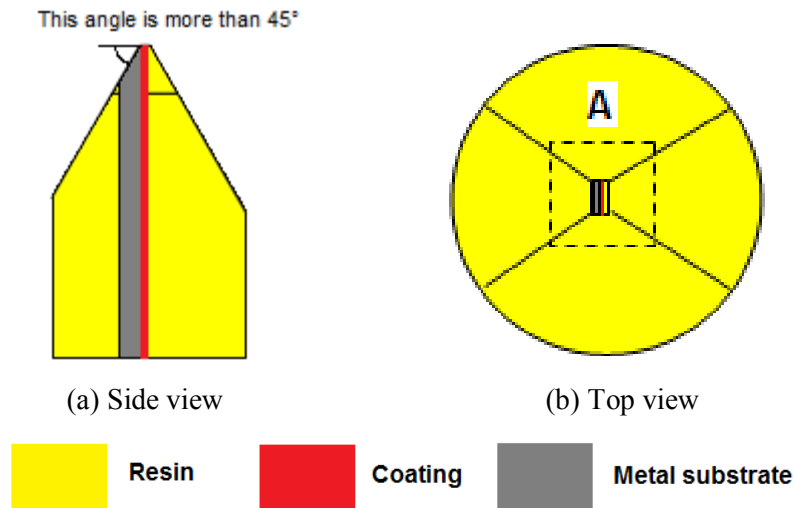


Figure 3. 1 The schematic illustration for the grinding process of the specimen embedded in the resin in specific directions and steps by 800 grit papers of (a) the side-view of the ground tip, and (b) the top-view of the ground tip

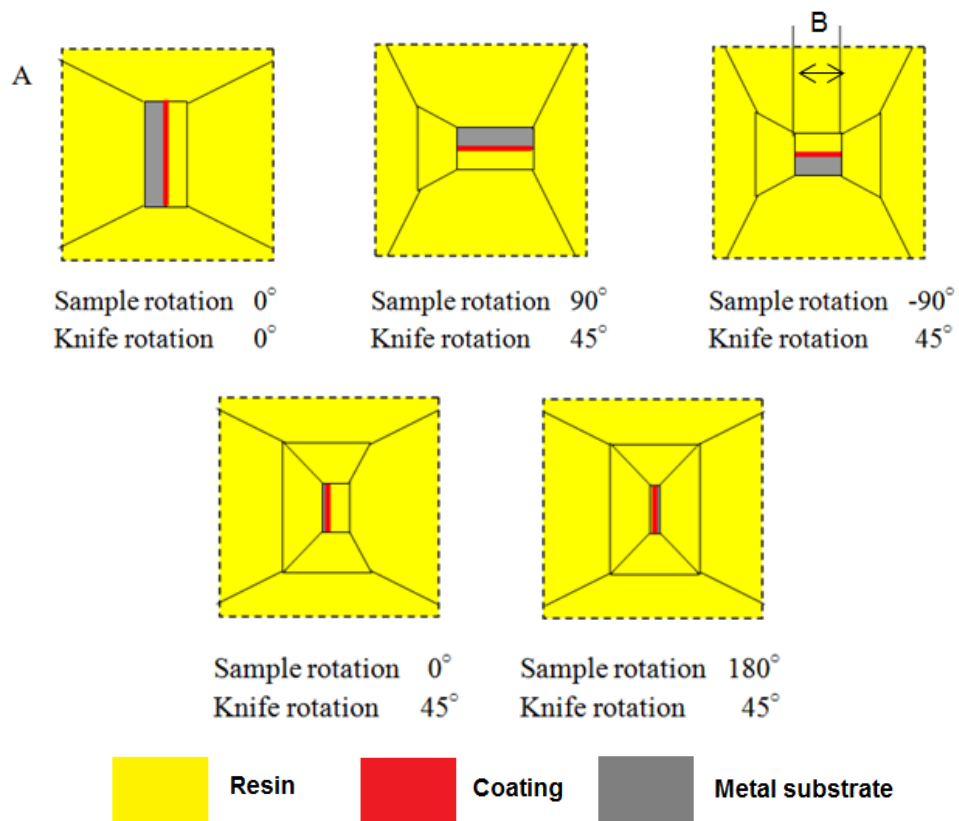


Figure 3. 2 The schematic illustration for the trimming process of well-grinded specimens, where B letter means the distance finish between 1 to half screen square in ultramicrotomy.

Chapter 4 TRIVALENT CHROMIUM CONVERSION COATINGS ON ALUMINIUM

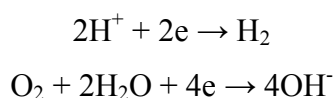
This chapter comprises three main parts, including the introduction, results and discussion, and the summary. After the first introduction part, the second part of results consists of (i) open-circuit potential measurement, (ii) the coating morphology and growth kinetics, (iii) the coating composition determined by GDOES, TEM/EDX, RBS and NRA, (iv) the chemical states of coating species by XPS and Raman spectroscopy, (v) electrochemical impedance spectroscopy, and (vi) the effect of air ageing treatment and (vii) sodium sulphite on Cr(VI) reduction.

Accordingly, the discussion covers (i) the formation and composition of TCC coatings, (ii) the growth mechanism and kinetics of TCC coatings, (iii) Cr(VI) transformation mechanism, and (iv) the effect of air ageing and sodium sulphite on Cr(VI) reduction.

4.1 Introduction

A TCC coating bath generally contains ZrF_6^{2-} , Cr^{3+} and SO_4^{2-} components in an aqueous solution with a pH of 3.8-4.0 for coating development at a temperature of 40°C [139, 141]. The bath is similar to those used for the formation of zirconium-based conversion coatings, but with an addition of trivalent chromium salts [155]. The resultant coatings on aluminium alloys have been reported to provide a level of corrosion protection similar to that of chromate-based conversion treatments [167].

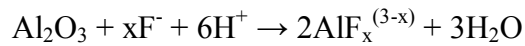
The coatings are considered to form by precipitation of an outer chromium- and zirconium-rich layer due to an increase in pH of the coating solution at the sites of the cathodic reactions:



The pH at the TCC coating surface can increase from 3.9 to 4.8 according to measurements using a tungsten microelectrode [187]. At the same time, aluminium is oxidized, forming an inner alumina film across the aluminium surface:



The alumina film dissolves by reaction with hydrofluoric acid [118]:



The dissolution of the film is balanced by formation of fresh alumina at the aluminium/alumina interface. A high electric field is maintained across the alumina layer, which enables the migration of Al^{3+} and O^{2-} ions within the alumina and continued oxidation of the aluminium [188]. At the same time, the reduced film thickness permits electron tunnelling to support the cathodic reactions [71]. The precipitated TCC coatings have been reported to contain hydrated chromium and zirconium oxides [148, 150], which may play a role as a hydroxide ion conductor with ligand exchange with fluorine to rationalize the enrichment of fluorides in the inner TCC coatings [189].

Despite the absence of Cr(VI) species in the TCC coating bath, recent research has reported that Cr(VI) species are present in the coatings after ageing in air or following a corrosion test [141, 150, 154, 159]. Additionally, Rochester et al. [154] found evidence of Cr(VI) species in a TCC coating on a zinc substrate after a salt spray test. They suggested that Cr(III) species in the coating were oxidized to Cr(VI) by atmospheric oxygen during the test. Iyer et al. observed the transient formation of Cr(VI) in a TCC coating on a AA 2024-T3 alloy under acidic/oxidative conditions [141]. Further, Li et al considered the possibility of oxidation of Cr(III) species by hydrogen peroxide formed around Cu-rich particles in the alloy by the reduction of dissolved oxygen in the sodium chloride solution [159]. The degradation of Cr(VI) components by the prolonged air ageing treatment has been revealed in the chromate conversion coatings on the AA2024-T3 alloy by the X-ray photoelectron spectroscopy analysis [80], motivating our research to examine this effect on reduction of transient Cr(VI) in the TCC coatings.

In terms of Cr(VI) or the Cr(VI)-O band, Raman spectroscopy revealed a ‘fingerprint’ evidence of the vibrational Raman shift between 840-904 cm^{-1} , while the peak position of the Cr(III)-O band was around 520-580 cm^{-1} [78, 159]. The presence of other metal oxides (e.g. Al and Zr) and the effect of water loss by drying the coatings gave rise to small variance of these shifts of special Raman peaks [190]. In addition, the quantitative analysis of the Cr 2p spectra by X-ray photoelectron spectroscopy revealed that a single Cr(VI) peak (579.6 eV) existed as well as five individual Cr(III) peaks (575.7, 576.7, 577.5, 578.5 and 578.9 eV) following the methodologies by Biesinger et al. [191, 192] This chemical shift relates to their electron structure, for example, the single Cr(VI) peak is assigned to the absence of unpaired electrons.

In the present work, specimens, with dimensions of either 30 × 24 mm or 30 × 12 mm, were cut from 99.99% aluminium sheet of ~0.3 mm thickness and rinsed with acetone, ethanol and deionized water, each for 5 s. Individual specimens were then electropolished at 20 V for 240 s in a 20% (v/v) perchloric acid (60 wt%) and 80%(v/v) ethanol mixture below 10°C, followed by rinsing in deionized water and drying in a stream of cool air. They were then immersed in naturally-aerated SurTec 650 solution (1:4 v/v deionized water, pH=3.9 (adjusted with 1% NaOH or 5% H₂SO₄)) at 40°C for times from 15 to 1200 s. After removal from the coating bath, the specimens were immersed in deionized water at 40 °C for 120 s and then rinsed in deionized water, dried in a cool air stream, and finally aged in laboratory air for 24 h. Coatings were also formed in a solution that was de-oxygenated, by bubbling nitrogen for 1 h, in order to determine the influence of dissolved oxygen on the formation of Cr(VI) species.

High-resolution analytical electron microscopy was combined with glow-discharge optical emission spectroscopy (GDOES), atomic force microscopy (AFM), Rutherford backscattering spectroscopy (RBS), nuclear reaction analysis (NRA) and X-ray photoelectron spectroscopy (XPS). The corrosion protection was examined by electrochemical impedance spectroscopy in 0.1 M Na₂SO₄ solution alone and in a mixed solution of 0.1 M Na₂SO₄ and 0.1 M NaCl. The study focuses on the composition and morphology of the resultant coatings, and provides evidence for the formation of Cr(VI) species in the absence of copper-rich, second phase particles in the substrate.

4.2 Results

4.2.1 OCP measurements

The open-circuit potential of electropolished aluminium during immersion for 1200 s in the naturally-aerated SurTec 650 solution is shown in Fig. 4.1. The potential displays an initial rapid fall and a gradual rise to a relatively steady value. The minimum and final potentials are -1.54 and -1.50 V (SCE) respectively. Repeated measurements gave similar results. Figure 4.1 also shows the open-circuit potential recorded in a deoxygenated solution. The potential displays a similar general trend to that of the naturally-aerated solution, but with slightly higher minimum and final potentials of -1.51 and -1.45 V (SCE), which may correlate with the impeded oxygen reduction in the deaerated solution. The open circuit potential of the coated specimens after several seconds of immersion in the coating bath is far below the Cr(III)/Cr(VI) equilibrium potential ($\sim -1 \text{ V}_{\text{SCE}}$), indicating that direct oxidation of Cr(III) ions on the aluminium substrate should not occur.

4.2.2 Coating morphology and growth kinetics

Figures 4.2 (a, b and c) display secondary electron scanning electron micrographs of the surface of the TCC-coated aluminium after treatments of 15, 120 and 600 s respectively, with subsequent post-treatment consisting of immersion in deionized water at 40°C for 120 s, rinsing in deionized water and ageing in air for 24 h. After 15 s, most of the surface is relatively featureless, although occasional areas reveal deposits of material with a nodular appearance (Fig. 4.2(a)). EDX analysis of the deposits indicates an atomic ratio of chromium to zirconium of ~ 3 , which compares with a ratio of $\sim 0.47 \pm 0.03$ in the adjacent coating material determined by later RBS analysis. A previous study of the role of hexafluorozirconate on the formation of CCC on aluminium alloys also revealed the presence of nodules at the coating surface with a similar morphology to those of Fig. 4.2(a), although the reason for their formation was not identified [82]. Further, the formation of a deposit at the bottom of the vessel containing the coating solution was observed after treating several specimens. Following collection and drying of the deposit, SEM examination revealed particles with a larger dimension (several microns in diameter) relative to those on the coating surface and these particles were zirconium-rich, with an atomic ratio of chromium to

zirconium of ~ 0.1 . It has been noted previously that zirconium species in solution can develop large agglomerates at pH 4.5 from a stable colloidal dispersion [116]. After treatment for 120 s, in addition to the previous features, cracking and detachment of the coating are evident (Fig. 4.2(b)). The detachment was much more extensive after treatment for 600 s, with the surface revealing both small and large areas where the coating has been lost (Fig. 4.2(c)). The increased magnification image of Fig. 4.2(d) shows the details of a region of the local detachment. About 2% of the aluminium surface was affected by detachment of the coating for times up to 300 s. However, by 600 s, the coating had detached from $\sim 25\%$ of the surface. Comparison of specimens coated for 600 s that had not been rinsed in deionized water following formation of the coating revealed localized detachment of the coating of similar appearance to the small regions in Figs. 4.2(c) and Fig. 4.2(d). However, the large regions of detachment were absent, which indicates that the freshly formed coating is weakly adherent to the aluminium substrate.

The topographies of the electropolished aluminium and the TCC coatings formed for 15 and 300 s are displayed in the atomic force microscopy images of Figs. 4.3(a-d). The specimen treated for 15 s received a post-treatment consisting of immersion in deionized water at 40°C for 120 s, rinsing in deionized water and ageing in air for 24 h. However, the specimen treated for 300 s was examined immediately after formation of the coating, i.e. without rinsing, immersion or ageing. The aluminium substrate in the non-coated condition reveals a furrowed surface due to the electropolishing pre-treatment (Fig. 4.3(a)), consistent with the earlier reports on the morphology of (110) surfaces [29, 65]. Following treatments for 15 and 300 s, a thin coating has formed, with the furrows of the original surface being faintly evident (Fig. 4.3(b,c)). Nodular deposits with similar dimensions and features to those revealed by SEM observation (Fig. 4.2(a)) occur locally as individual or lines of particles, possibly attributed to the preferential absorption of Cr(III) cations at cathodic sites. After 300 s, cracks were also observed at some locations in the coating (Fig. 4.3(c,d)). The cracks were formed either during the formation of the coating and the subsequent drying of the specimen in cool air or in the brief interval between forming the coating and the examination by AFM.

Bright field transmission electron micrographs of cross-sections of the coated aluminium following treatments in the TCC bath for 15, 60, 120 and 300 s and the standard rinsing, immersion and ageing post-treatment are shown in Figs. 4.4 (a,b,c,d) respectively). At each

of these times, the aluminium surface is covered by a coating of relatively uniform thickness that increases with increase of the immersion time. The coating has a fine texture and contains crack or fissures. The latter may result from the sectioning of the coating and dehydration of the coating in the microscope. An ~ 2 nm-thick region of different appearance is present at the base of the coating, which is probably an alumina-based film, as suggested by later analyses.

Figure 4.5 reveals that the coating thickness, determined directly from transmission electron microscopy, increases with immersion time, reaching ~ 93 nm after 600 s. The rate of thickening increases in the initial ~ 60 s, and then progressively decreases with increasing immersion times. The average rate of growth is ~ 0.27 nm s $^{-1}$ up to 300 s and ~ 0.08 nm s $^{-1}$ between 300 and 600 s. Dardona et al [144] reported a growth rate before 300 s of 0.4 nm s $^{-1}$, which is similar to the present value of ~ 0.3 nm s $^{-1}$. A reduced growth rate after 300 s may arise from the impeded oxidation of aluminium due to reduced transport of species across the thickening coating. However, changes in the thickness and composition of the alumina layer at the base of the coating may also occur that reduce the rate of electron tunnelling, and hence the rate of deposition of the coating material.

4.2.3 Coating composition by GDOES, TEM/EDX, RBS and NRA

GDOES elemental depth profiles of the coated aluminium after a TCC treatment for 300 s and the standard post-treatment are shown in Figs. 4.6 (a,b), where the insert profile in Fig 4.6 (a) exhibits the signal of Al. The coating contains chromium, zirconium, oxygen, and carbon and sulphur species. The aluminium/coating interface, determined by the half height of the trailing edge of the oxygen signal, is marked by a dashed line. Whether or not aluminium is present in the film is unclear because of the low intensity aluminium signal in the coating region. A signal from aluminium might also be generated from regions of the coating that contain cracks that expose the substrate. Chromium and zirconium are distributed throughout the coating thickness. The variations in the intensities of the chromium and zirconium signals within the coating may be due to changes in the coating composition and/or of the sputtering rate across the coating thickness. Carbon and sulphur also appear to be present at all regions of the coating, with an enhancement in the optical emissions near the substrate. However, later EDX mapping did not reveal an increase in the concentrations of

these elements, suggesting that the intensity variations arise from changes in the sputtering rate. A peak in the copper signal near the alloy/coating interface indicates an enrichment of the copper impurity in the aluminium substrate immediately beneath the coating. Using the coating thickness from TEM, the sputtering rate of the coating is $\sim 50 \text{ nm s}^{-1}$.

EDX elemental maps of aluminium, oxygen, zirconium, chromium and fluorine in an ultramicrotomed cross-section of the previous specimen that was examined in the TEM are displayed in Fig. 4.7. Most of the coating thickness appears to contain relatively uniform distributions of the elements, although the signal for aluminium is much lower than those of the other elements, indicating the presence of a relatively low concentration. A much thinner, fluorine-rich region, which also contains aluminium and oxygen, is presented adjacent to the aluminium/coating interface.

Figure 4.8 presents the experimental and simulated RBS spectra for the aluminium after a treatment in the TCC bath for 300 s followed by the standard post-treatment and further ageing in laboratory air for 1 week before the analysis. The spectrum for the coated specimen shows peaks for oxygen, fluorine, chromium, zirconium and hafnium in the coating; concerning the last, hafnium is an impurity in the zirconium reagent. Similar spectra were obtained for treatment times of 60 and 120 s apart from reductions in the magnitude of the peaks due to the presence of thinner coatings. The formation of the coating results in a displacement of the aluminium leading edge to a lower energy compared with the non-treated aluminium. The results of fitting of the spectra are given in Table 4.1 for specimens treated for times of 60, 120 and 300 s. The fitting used a two-layer model. The inner layer consisted of aluminium, oxygen and fluorine and the outer layer consisted of oxygen, fluorine, sulphur, chromium and zirconium, in agreement with the elemental distributions indicated by the EDX maps. The Table also includes the results of the analyses of oxygen and carbon by NRA, which show a reasonable agreement with the analysis of oxygen by RBS. Carbon and also hydrogen are too light to be detected by RBS. The coatings contain chromium and zirconium in an atomic ratio of $\sim 0.47 \pm 0.03$ for all treatment times, indicating that the species are added to the coating in relatively constant proportions as the thickness of the coating increases. The detection of sulphur in the coating is probably due to the presence of chromium sulphate in the coating solution. The probable hydrolysis of chromium sulphate in the coating solution is shown in Fig. 4.9, based on the previously proposed hydrolysis of

chromium chloride [139, 140]. The coating compositions, determined by RBS and NRA, and the coating thicknesses, determined by TEM, indicate that the average density of the coatings was $\sim 2.6 \text{ g cm}^{-3}$ (Table 4.2).

4.2.4 Chemical states by XPS and Raman spectroscopy

XPS analyses were carried out for a specimen treated in the TCC bath for 300 s followed by the standard post-treatment. The depth of analysis was $\sim 5 \text{ nm}$. The surface elemental concentrations are presented in Table 4.3. The values in the second row follow correction for the carbonaceous over layer [193]. Figure 4.10 shows the high resolution XPS spectra from (a) the Al 2p and (b) the Zr 3d photoelectron regions. Five peaks were used to fit the Al 2p photoelectron region, including two for Cr 3s species at 77.1 eV and 80.9 eV binding energies that were taken into account for quantification of the aluminium surface elemental concentration. The presence of aluminium oxide, oxyfluoride and fluoride is indicated by peaks at 74.7, 75.3 and 76.2 eV respectively. The Zr 3d region contains two spin orbit split doublets separated by 2.4 eV. With the intensity ratio of the Zr 3d_{5/2} to Zr 3d_{3/2} components fixed at 1.5:1, the peak fitting of Zr 3d_{5/2} peak indicated chemical states consistent with ZrO₂ and ZrF₄, with 95% of the zirconium being in the form of oxide [194].

Figure 4.11 presents the high resolution spectra for (a) the C 1s and (b) the O 1s photoelectron regions. The fitting of the C 1s peak was achieved with a C-H or C-C group at 285 eV, a silicone group at 285.7 eV, a C-O group at 288.5 eV, a Si-O-C group at 287.6 eV, a C=O or O-C-O at 288.6 eV and a COOH group at 589.4 eV. Carbon contamination has previously been regarded to result from contaminants in the deionized water [195, 196]. Five peaks were employed to fit the O 1s photoelectron region, consistent with using the minimum number of peaks to fit the data, but it is certainly more complicated than this. These peaks are expected for oxides, hydroxides and carbonaceous contamination. Biesinger et al. reported peaks at 530.1, 531.6 and 533.2 eV for the oxide, hydroxide and hydrated species of chromium [197]. Oxygen in ZrO₂ and Al₂O₃ is expected to display peaks at 530.5 and 531.5 eV respectively.

The fitting of the Cr 2p_{3/2} peak is shown in Fig. 4.12 (a). The fitting includes the presence of chromium fluoride [191, 192], which has not been considered in previously reported XPS

data [147, 148, 150]. The overall chromium species include $\text{Cr}(\text{OH})_3$ (577.28 eV), $\text{Cr}_2(\text{SO}_4)_3$ (578.49 eV), CrF_3 (580.03 eV) and CrO_3 (579.58 eV) with 59.7, 28.6, 10.4 and 1.3% of the total chromium being associated with the respective species. The amount of chromium present as Cr(VI) is ~ 0.03 atomic % of all the atoms in the analysed region of the coating. Omitting the CrF_3 contribution requires an increase of the amount of chromium present as Cr(VI) to 9.8%, although in the peak fit is then not as good (Fig.4.12(b)).

Table 4.4 compares the atomic concentrations determined by XPS in the outer ~ 5 -10 nm of the coating thickness and by RBS and NRA across the total coating thickness. Less fluorine and aluminium are detected by XPS than by RBS, which is consistent with the fluorine and aluminium being enhanced near the base of the coating. The surface elemental concentration of fluorine determined from the F 2s peak (31.4 eV binding energy) is ~ 10.6 times than that from the F 1s peak (684.9 eV binding energy), indicating enrichment of fluoride in the sub-surface region.

Raman spectra for electropolished aluminium and a TCC coating formed for 1200 s in the SurTec 650 solution under naturally-aerated and de-oxygenated conditions are shown in Fig. 4.13 (a). The results of the Raman analysis apply to the whole thickness of the coating. Analysis of the coatings by RBS indicated that there was no significant difference in the atomic ratio of chromium to zirconium in the coatings. Further, the coatings were of similar thickness. Figure 4.13 (b) shows the fittings of the Raman spectra in the range 700 and 1050 cm^{-1} for TCC coatings formed under the naturally-aerated condition. The specimens were analysed immediately after the 1200 s immersion treatment in the conversion coating bath followed by drying in cool air. The 438, 804 and 945 cm^{-1} peaks in the spectrum of electropolished aluminium are attributed to the air-formed alumina film [78, 157, 198]. The peaks for the coating formed in the naturally-aerated solution reveal the presence of zirconium oxide (ZrO_2 , 233 and 470 cm^{-1}) [199], chromium hydroxide ($\text{Cr}(\text{OH})_3$, 536 cm^{-1}) [159], a mixture of aluminium hydroxide and oxide (438, 804 and 945 cm^{-1}) [157], Cr(VI) oxide (866 cm^{-1}) [159, 200] and the S-O bond in a SO_4^{2-} -containing compound, such as $\text{Cr}_2(\text{SO}_4)_3$ (995, 1050 and 1155 cm^{-1}) [201]. Notably, the peak centred at 866 cm^{-1} , indicative of the presence of Cr(VI) oxide, is consistent in position and shape of a mixed oxide that contains aluminium oxide and Cr(III) oxide in addition to Cr(VI) oxide [78, 157]. Since, the coating was not subject to ageing in air, the Cr(VI) can only have been formed during

formation of the coating. The Cr(VI) was not detected when the solution was deaerated, indicating that the formation of Cr(VI) is associated with reduction of oxygen during the growth of the coating.

4.2.5 Electrochemical impedance spectroscopy

Figures 4.14(a, b, c and d) show the dependence of the impedance on frequency and phase angle-frequency for the aluminium in the non-coated condition and after coating for 60, 300 and 600 s followed by the standard post-treatment of the specimens. The EIS data were obtained in the electrolytes, including (a, b) 0.1 M Na₂SO₄ and (c, d) the mixed solution of 0.1 M NaCl and 0.1 M Na₂SO₄. The measurements commenced after a period of 30 min immersion in the solution to allow the OCP to stabilize. The OCPs of the uncoated aluminium and the coatings formed for 60, 300 and 600 s were similar, with values of ~ -1.2 V vs SCE. The EIS data on the bare and coated Al were fitted using the equivalent circuits of Fig. 4.14 (e, f) respectively. The values obtained for the circuit elements are given in Table 4.5, where the parameters of the EIS data show good consistency in both electrolytes.

The data for the non-coated aluminium were fitted using a simple circuit comprising the solution resistance, i.e. the resistance between the reference electrode and the specimen (R_e), and a parallel combination of a resistance (R_p) representing the charge transfer resistance and a constant phase element (Q_{dl}), with an impedance given by $Z = (j\omega)^{-n}Q^{-1}$. The exponent was close to 1 indicating that the impedance was mainly due to the double layer capacitance. The circuit for the coated specimens included an additional resistance (R_{coat}) and constant phase element (Q_{coat}) that represent the effects of the coating; n has been associated with the heterogeneity of the TCC coating in previous work [165]. Table 4.5 reveals that the charge transfer resistance decreases with increase of the time of the coating treatment, with a relatively large decrease occurring after a treatment of 300 s. The cause of the decrease is possibly associated with the accumulation of fluoride ions at the base of the coating, which thin the alumina film present on the aluminium substrate. In contrast, the coating resistance increases with increase of the treatment time, which may be due to a combination of an increase in the coating thickness and change in the coating morphology, for instance a reduction in pore size. The values of the coating resistance are much lower than those of the charge transfer resistance and are of the order of the solution resistance. The relatively low

resistance of the coating indicates its permeability that allows access of the electrolyte to the substrate through pores and cracks. The most inhomogeneous coating, as indicated by a relatively low value of n , is that formed for 600 s, which is consistent with the earlier findings from SEM of increased cracking of the coating. The effective capacitances of the coatings formed for 60, 300 and 600 s are given by $C_{\text{eff}} = Q^{1/n} R^{(1-n)/n}$, where R represents the ohmic resistance of electrolyte [165, 202, 203]. The maximum effective capacitance of the inner double layer was measured as $\sim 3.55 \mu\text{F}/\text{cm}^2$ for the specimen coated for by a treatment of 600 s; the value is in good agreement with that reported by Guo and Frankel [155].

4.2.6 Effect of air-ageing treatment on Cr(VI)

Three series of specimens were prepared in the same immersion conditions in the trivalent chromium bath for 300 and 1200 seconds and the period of air ageing was selected as 24 and 168 hours, and one type of the freshly-developed specimens was used as the control of the Cr 2p_{3/2} photoelectron regions and the Raman spectra.

Figures 4.15(a and b) show the high resolution photoelectron region of Cr 2p_{3/2} on the surface of the control TCC coatings formed for 300 and 1200 seconds on pure Al without air ageing treatment. Four fitting peaks in the chromium spectra of the Cr 2p_{3/2} peak represented the hydroxide, sulphate and fluoride of chromium (III) and chromium (VI) oxides at 577.4, 578.6, 580.1 and 579.6 eV respectively. XPS analyses of depth of ~ 9 nm were sensitive to the near-surface chemistry, while the area of XPS analysis is of hundreds of micrometres. Thus, the exposed Al substrate in the form of mud cracks after the air ageing cannot avoid in the selected XPS analysis area, possibly influencing the quantitative measurement of Cr (VI) concentration. Support of this fact is that the concentration of aluminium metal (71.8 and 72.2 eV) in the coating control increases from ~ 0.4 at.% (300 s) to ~ 11.3 at.% in the coating formed for 1200 s in Figure 4.16 (a and b) respectively. In addition, the presence of oxyfluoride as the form of AlO_xF at 75.5 eV in the Al 2p photoelectron region displayed a significant concentration increase with the prolonged treatment in the trivalent chromium bath as evidenced by the increasing content from 0.01 at.% at 300 s to 2.64 at.% at 1200 s. This may arise from the replacement reaction between the oxygen and fluoride in the metal oxides by the smaller radius of fluorine atoms [81].

Tables 4.6 (a and b) show the quantified concentration of chromium-containing compounds relative to the total amount of chromium in Cr 2p_{3/2} photoelectron region in TCC coatings formed for 300 and 1200 seconds respectively. The TCC coatings formed for 300 s show a decreased concentration of Cr(VI) oxides of the total chromium from ~7.45% down to ~6.21% after air ageing treatment for 168 h. Accordingly, the concentration of Cr(OH)₃ in the total chromium increased from 31.13% up to 35.07% after such air ageing treatment for 168 h. By contrast, the concentration of Cr(VI) oxides in the total chromium in TCC coatings formed for 1200 s without air ageing and air ageing for 24 and 168 h was measured at ~4.89, 2.54 and 4.91% respectively. The TCC coatings formed for 1200 seconds had the progressive cracks even without air ageing treatment, which led to the surface inhomogeneity to influence the XPS analysis. Thus, the XPS quantification of Cr(VI) in the coatings formed for 1200 s with dependence on the period of air-ageing post-treatments was suggested to be inaccurate. In terms of the decreased Cr(VI) content in the TCC coatings formed for 300 seconds after the prolonged air ageing, the presence of nanosized cracks in the coatings attracts the mobile Cr(VI) anions to self-heal the corrosion of the exposed aluminium substrate. The presence of the nanosized cracks was in good agreement with the early in-situ AFM observation of such coating control.

Raman spectroscopy of analysis dimensions of ~1 micron in depth and in area revealed an effective tool to examine the hexavalent chromium oxides, and further the associated optical microscopy can help locate the coated area to avoid the effect of the exposed substrate on the coating surface. Thus, it was also used in the examination of the air ageing effect on the concentration, represented by the spectrum intensities in Figure 4.17(a-d). The trivalent chromium conversion coatings formed for 1200 seconds with dependence on the air ageing duration and the bare aluminium were detected by the typical Raman spectra ranged from 200 to 2000 cm⁻¹. For the bare aluminium (Fig. 4.17-d), the broad and single peak for the gibbsite (Al(OH)₃) was centred at 804 cm⁻¹ with small narrow peaks around 321 and 1020 cm⁻¹ [198] and the small peak at 1555 cm⁻¹ was assigned to the atmospheric oxygen [78].

The TCC coating control formed for 1200 s without air ageing treatment showed the major, multiple peaks between 400 and 600 cm⁻¹ in Fig. 4.17-a. The fitted shift at 470 cm⁻¹ along the small peak at 233 cm⁻¹ indicated the presence of zirconium oxides [199, 204] and the chromium oxide (Cr(III)-O) was presented around 536 cm⁻¹ [159]. The second major multiple

peaks were fitted with 804 cm^{-1} (aluminium hydroxide) and 860 cm^{-1} that revealed the presence of Cr(VI)-O [78, 159], where the overlap between chromium (VI) oxides (860 cm^{-1}) and aluminium hydroxide (804 cm^{-1}) led to the broader peak between 800 and 900 cm^{-1} . The Raman shift centred at 998 cm^{-1} along the small peak at 1050 and 1155 cm^{-1} was assigned as the sulphate in the coatings, such as the trivalent chromium sulphate [205]. After the air ageing treatment for 24 and 168 h (Fig. 4.17-b and c respectively), the intensity of the distinct Cr(VI)-O Raman peak (860 cm^{-1}) displayed a significant decrease with the increasing period of air ageing treatment and it was even undetectable after air ageing treatment for 168 h. In addition, the occurrence of the broad peaks at 1400 and 1680 cm^{-1} may represent the presence of more aluminium oxide and trivalent chromium oxide respectively. The water loss and coating shrinkage may lead to the intensity decrease of the whole spectra [190].

In addition, the reference Raman spectra of the analytic compounds and the deposits of aqueous solutions are shown in Figure 4.18(a). The evident absence of a Raman peak between 800 to 900 cm^{-1} was observed in the individual spectrum of Cr_2O_3 , CrF_3 and $\text{Cr}_2(\text{SO}_4)_3$. For Cr_2O_3 powders, the primary Raman peaks were revealed at 550 and 610 cm^{-1} along a small shoulder at 525 cm^{-1} . In addition, the 301 , 347 and 1050 cm^{-1} also showed the underlying weak peaks. For CrF_3 powders, the 538 cm^{-1} displayed the characteristic peak, while the broad peaks at 289 and 322 cm^{-1} were also revealed. In terms of the presence of the sulphate component, the reference of Cr(III) sulphate revealed the major Raman peaks at 442 , 488 , 622 and 1027 cm^{-1} along the small shoulder at 1127 cm^{-1} . By contrast, the spectra of sodium and iron (II) sulphates in Figure 4.18 (b) displayed a primary sharp peak at 990 - 993 cm^{-1} , which corresponds to the presence of the free sulphate ions [206]. Furthermore, the possible effect by the aqueous electrolyte on Raman shifts is shown in Fig. 4.18(a), where the deposits on the silicon panel from the $\text{CrF}_3\text{-H}_2\text{O}$ and $\text{Cr}_2(\text{SO}_4)_3\text{-H}_2\text{O}$ solutions were investigated. The strong Raman peak at 520 cm^{-1} was the characteristic shift of the silicon panel. Notably, the presence of water environment decayed the Raman shifts at 400 - 500 cm^{-1} for the Cr(III) sulphate and induced one shoulder peak at 904 cm^{-1} in comparison to the reference powder $\text{Cr}_2(\text{SO}_4)_3$. This is possibly attributed to the hydrolysis of the compound in the aqueous solution. In addition to this influence, the Raman vibrational shifts showed a similar morphology to the situation of the individual powder specimen.

4.2.7 Effect of sodium sulphite on Cr(VI)

The post-treatment immersion in a solution containing the reducing agent of Na_2SO_3 was used. In terms of the selection of the effective reductant solution, the first factor considered is that this reductant and reaction product cannot contaminate the basic composition of TCC coatings to fracture the coating structure. Thus, the reductant sulphite (SO_3^{2-}) salts displays the most promising option and its oxidized product in the form of sulphate (SO_4^{2-}) can form the stable trivalent chromium sulphate and may little influence the corrosion protection by this coating. Thus, the sodium sulphite (Na_2SO_3) was selected and diluted in the deionized water at the concentrations of 10 g/l, 50 g/l and 100 g/l to post-treat the TCC coating for 120 seconds. Specimens were then rinsed by the deionized water and dried in a stream of cool air prior to the examination by Raman spectroscopy and X-ray photoelectron spectroscopy. The period in the air until Raman analyses is as less as 30 min soon after such specimen preparation in order to avoid the effect of the atmospheric oxygen on the transient Cr(VI) formation.

Figure 4.19 show the Raman spectra ranging from 200 to 1200 cm^{-1} of the TCC coatings formed for 1200 s with a post-treatment immersion in the solutions containing 10 and 50 g/l sodium sulphite for 120 s. In comparison with the TCC coating without this post-treatment as reference, the intensity of Cr(VI)-O centred at the 870 cm^{-1} displayed an evident decrease with increasing the concentration of sodium sulphite solution from 10 to 50 g/l. Notably, this fingerprint of hexavalent chromium was not completely removed, indicating the penetration limitation of sodium sulphite into the inner layer of TCC coatings. In addition, the Raman intensity of the sulphate and trivalent chromium oxide (998 and 536 cm^{-1} respectively) increased after post-treatment in a more concentrated sodium sulphite solution. This is in good agreement with the reaction between the sulphite cations and the hexavalent chromium anions as follows.



Furthermore, a 100 g/l Na_2SO_3 solution was also used to examine the reductant effectiveness and possibility of the complete removal of Cr(VI) species in the TCC coatings. A wide scan XPS analysis of the specimen after this post-treatment for 120 s is shown in Figure 4.20(a), where the presence of sodium in the near-surface TCC coating is evident at 1072.2 eV. Figure 4.20(b) shows the high resolution Cr 2p photoelectron region, where the fitting Cr

2p_{3/2} peaks consist of Cr(OH)₃ (577.4 eV), Cr₂(SO₄)₃ (578.5 eV), CrF₃ (581.0 eV) and Cr(VI) oxide (579.7 eV) of ~12.2, 86.5, 1.2 and 0 % of the total chromium as the form of the individual component respectively. The removal of hexavalent chromium oxides by this post-treatment was evident, while the analysis depth of XPS is only ~9 nm. The in-depth examination of Cr(VI) component across the TCC coatings by Raman spectroscopy is shown in Figure 4.21. Because of the influence of concentrated sodium sulphite on the surface chemistry, the Raman peaks of the sulphate in the form of Na₂SO₄ and Cr₂(SO₄)₃ were evident at 626, 945, 998, 1050, 1020 and 1150 cm⁻¹. Notably, three major peaks were presented at 460, 495 and 526 cm⁻¹ where the first two indicated the mixture of sulphate and oxide of zirconium along a small peak at 233 cm⁻¹, and the peak at 526 cm⁻¹ along the shoulder peak at 360 cm⁻¹ correlated with the presence of trivalent chromium oxide. All these peaks are consistent with the early observation in the separate reference compounds in Figure 4.18. In terms of the hexavalent chromium oxides at 859 cm⁻¹, it revealed the presence of Cr(VI) oxides in the TCC coating, consistent with the early observation in Fig.4.19.

4.3 Discussion

4.3.1 Formation and composition of TCC coatings

TCC coating formation is a precipitation process of the zirconium-/chromium- hydroxides due to the interfacial pH increase during the reaction between the acidic bath and aluminium substrate. The initial fall of the open-circuit potential correlates with the thinning process of the pre-existing oxide film on the aluminium surface, which activates the surface by enabling the electron tunnelling for the successive coating formation. The initial decrease in potential 0.35 V_{SCE} indicates thinning of the film that is present on aluminium surface after the electropolishing treatment by about 0.4 nm [71, 84].

In terms of the coating components, the examinations by TEM/EDX, GDOES and RBS/NRA analyses revealed a two-layer coating structure, consisting of a main outer layer of zirconium-/chromium-containing component over an inner alumina layer. For the main part of the TCC coating, a constant atomic ratio of 0.47 Cr/Zr indicates that the species are added to the coating in relatively constant proportions as the thicknesses of the coating increase. By contrast, a TCC coating formed on AA 2024 alloy under the cathodic polarization, using a

different solution composition to that of the present study, was reported to consist of a hydrous oxide of composition $\text{Cr}_2\text{O}_3 \cdot i\text{H}_2\text{O} \cdot x(\text{ZrO}_2 \cdot j\text{H}_2\text{O})$ ($i=2.10 \pm 0.55$, $j=1.60 \pm 0.45$, and $x=0.85 \pm 0.14$) with a Cr/Zr ratio of 2.42 [143]. The composition was attributed to the fast deposition of positively-charged chromium (III) ions on the negatively-charged aluminium surface, while the hydrolysis of ZrF_6^{2-} ions limits the deposition of the zirconium species.

XPS analyses revealed the form of zirconium and chromium species as ZrO_2 , ZrF_4 , $\text{Cr}(\text{OH})_3$, $\text{Cr}_2(\text{SO}_4)_3$, CrF_3 and small amount of transient Cr(VI) oxides in the main coating region. Considering the peak position of hexavalent chromium oxides, it is likely to be a mixture of CrO_3 and CrO_4^{2-} [191]. On the base of the hard-soft acid-base (HSAB) theory, the fluoride of zirconium and chromium is reasonable [59]. Further, the presence of CrF_3 in the Cr 2p_{3/2} photoelectron regions significantly interferes with the concentration of hexavalent chromium oxides, attributed to the overlapping peak energy between them. In addition, the XPS yields an increased concentration of zirconium relative to chromium compared with the ratio determined by RBS, which is possibly related to the difference in the depths of analysis of the two techniques. An increased amount of zirconium at the coating surface may result from zirconium depositing preferentially with the pH increase [116, 143] or from leaching of chromium species from the coating [155].

4.3.2 Growth kinetic mechanism of TCC coatings

In terms of TEM examination of the cross-sectional TCC coatings, the growth kinetics were revealed to depend on the immersion period, consisting of a fast initiation and a slow rate of the further growth after treatment of 300 seconds. This is consistent with the nature of conversion coating formation of a pH-sensitive deposition process, where Li et al have revealed a fast increase of pH up to near 7 and then a general fall back to the pH=4 level [187]. In comparison with the logarithmic growth behaviour of TCC coating examined by in situ spectroscopic ellipsometry, these two distinct linear growth kinetics in our results are possibly attributed to the deterioration of the TCC coating after the prolonged treatment. In this case, the significantly decreased corrosion resistances of TCC coating after the treatment for 300 and 600 s in 0.1 M Na_2SO_4 solution and the mixed solution of 0.1 M Na_2SO_4 and 0.1 M NaCl revealed the transformation to the non-protective type. This supports this fact that this coating has a lot of cracks across the coating as observed by the early SEM. Thus, the

mass-transport control process for a pore blocking mechanism during the coating precipitation is not inconsistent with the fact of the occurrence of lots of cracks [207]. This presence of cracks accelerates the further growth of TCC coatings in the form of linear kinetics instead of the logarithmic initiation of TCC coatings. In terms of the formation of cracks in the TCC coatings after prolonged treatment, the stresses yielded in the coatings would not become fully relieved in the early stage of the coating precipitation and slowly increase as the coating thickens. In addition, the possible incorporation of surface impurities into the TCC coating would lead to the locally enhanced stress to induce the occurrence of cracks [1].

4.3.3 Cr (VI) formation mechanism

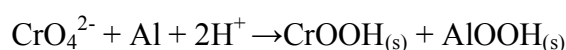
It is suggested that the formation of Cr(VI) species is associated with generation of H_2O_2 by the reduction of dissolved oxygen as $\text{O}_2 + 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}_2$ ($-1.1\text{V}_{\text{SCE}}$). The reduction reaction is proposed to take place at sufficiently thin regions of the alumina layer at the base of the coating, where tunnelling of electrons can occur, or at flaw sites in the layer, associated with the influences on the film composition and morphology of impurities in the aluminium substrate. The H_2O_2 oxidizes the Cr(III) species that have been transported across the permeable outer coating region, forming Cr(VI) species which can then diffuse toward the coating surface, as shown in Fig. 4.22. Cr(VI) species may then be lost to the coating bath.

An accurate value for the amount of Cr(VI) species that remain within the coating cannot be given from the present results. The Raman results are qualitative, while the XPS analyses apply only to the outer ~ 5 to 10 nm of the coating, which has a total thickness of ~ 80 nm after a coating treatment of 300 s. Further, the presence of CrF_3 interferes significantly with the detection of Cr(VI) species. If the CrF_3 is included in the fitting of the Cr 2p peak, the necessity for consideration of Cr(VI) is marginal. If the CrF_3 is excluded from the fitting, an upper limit of ~ 1 wt.% of Cr(VI) in the coating is estimated, since chromium constitutes ~ 9.8 wt% of the coating on the basis of the RBS results of Table 2, while XPS indicates that a maximum on 9.8% of the chromium may be in the form of Cr(VI). Inclusion of CrF_3 suggested an upper limit on the amount of Cr(VI) of ~ 0.1 wt.%. These estimates assume that the Cr(VI) is distributed uniformly through the coating thickness. However, this may not be

the case if Cr(VI) is formed in the inner coating regions and diffuses outward, in which case a greater amount of Cr(VI) would be expected to be present in the coatings.

4.3.4 Effect of air ageing and sodium sulphite on Cr(VI) reduction

The reduction of Cr(VI) species by the prolonged air ageing after conversion treatment is attributed to the role of active aluminium regions that were exposed in the form of cracks. Consequently, the mobile Cr(VI) species are preferentially reduced to form an intact film of the Cr(III)/Al(III) hydroxides on these sites to inhibit the corrosion of aluminium. Thus, the concentration of the hexavalent chromium component by the XPS and Raman spectroscopy was significantly decreased, where the area of Raman examination may contain nano-size cracks that develop beneath the coating surface and were indicated by the AFM observation. Accordingly, the reaction of the self-healing process of Cr(VI) is as follows [64]:



Concerning the effect of sodium sulphite, XPS of analysis depth of ~9 nm revealed a complete removal of Cr(VI) species. By contrast, the fingerprint Raman shift of 840-904 cm⁻¹ for the Cr(VI)-O bond was still observed in the coatings after the post-treatment even in the solution containing 100 g/l Na₂SO₃ addition. This discrepancy revealed the presence of the transient Cr(VI) species on the bottom of TCC coatings where the sulphite cannot penetrate to reduce Cr(VI) species. Further, this seems to provide a potential reservoir of Cr(VI) species in TCC coatings to provide self-healing protection. The near-surface chemistry displayed the absence of the Cr(VI) component to be eco-friendly. Thus, this post-treatment is one promising improvement process.

4.4 Summary

1. The TCC coating formed on the superpure aluminium consists of two main layers. The outer layer, which constitutes most of the coating thickness, consists of AlF₃, Al₂O₃, AlO_xF, Cr(OH)₃, CrF₃, Cr₂(SO₄)₃, ZrO₂ and ZrF₄ species. The inner layer is aluminium-rich, with the presence of oxide and fluoride species.

2. The average rate of coating growth for treatment times of up to 300 s is $\sim 0.27 \text{ nm s}^{-1}$. Thereafter, the growth rate slows significantly, which is due to hindered transport of reactant and product species by the thickening coating layers or changes in the composition and thickness of the inner layer that affect the rate of electron tunnelling.
3. The coatings may partly detach from the aluminium substrate during rinsing with water shortly after their formation. Further, cracks develop in coatings formed after ~ 60 to 300 s. The cracks are probably initiated by stress in the coating related to drying of the coating.
4. Raman spectroscopy revealed qualitatively the presence of Cr(VI) species in the coating and provided evidence of the role of oxygen in Cr(VI) formation. The presence of CrF_3 interferes with the analysis of Cr(VI) species by XPS and with the analysis of Cr(III) oxide by Raman spectroscopy. With the assumption of a uniform distribution of Cr(VI) in the coating, an upper limit of $\sim 1 \text{ wt\%}$ of the coating weight was estimated for the amount of Cr(VI).
5. Raman spectroscopy is an effective tool to examine the presence and the relative concentration change of the hexavalent chromium component across the TCC coatings. Air ageing for more than 24 hours can effectively decrease the hexavalent chromium in the TCC coatings, which preferentially reduce to form the Cr(III) film to protect the oxidation of the exposed aluminium by cracks.
6. The TCC coated Al in 0.1 M Na_2SO_4 and the mixed solution of 0.1 M NaCl and 0.1 M Na_2SO_4 revealed good consistency of the decreased trend of corrosion protection with the prolonged treatment, which is in good agreement with the presence of lots of cracks across coating.
7. The post-treatment in sodium sulphite bath provides an eco-friendly surface chemistry with the absence of the Cr(VI) component by XPS analysis; however, the penetration of sulphite ions into the coating bottom may be limited and the fingerprint Raman evidence of Cr(VI) reservoir was examined.

Figure Captions 4.1-4.22

Figure 4.1 The dependence of the open circuit potential of electropolished aluminium on the time of immersion in a dilute SurTec 650 bath at 40 °C under the usual naturally-aerated condition(named O₂) and under the de-oxygenated condition (named N₂).

Figure 4.2 Scanning electron micrographs (3 kV SE2 signal) of TCC coatings formed on electropolished aluminium in a dilute SurTec 650 bath at 40°C for different times: 15 s; (b) 120 s; (c) and (d) 600 s.

Figure 4.3 Atomic force microscopy topography images of TCC coatings formed on electropolished aluminium in a dilute SurTec 650 bath at 40 °C for different times: (a) the electropolished aluminium; (b)15 s; and (c) and (d) 300 s.

Figure 4.4 Bright field transmission electron micrographs of ultramicrotomed cross-sections of TCC coatings formed on electropolished aluminium in a dilute SurTec 650 bath at 40 °C for different times: (a) 15 s; (b) 60 s; (c) 120 s; and (d) 300 s.

Figure 4.5 Variation of the thickness of TCC coating on aluminium with time of immersion in a dilute SurTec 650 bath at 40°C. The thicknesses of the coatings were determined from TEM of ultramicrotomed sections.

Figure 4.6 GDOES elemental depth profiles of electropolished aluminium following immersion for 300 s in a dilute SurTec 650 bath at 40 °C: (a) Zr, Cr, C, and (b) S, O, Si, Cu. Both are smoothed by 10 neighboured points. The dashed line marks the aluminium/coating interface. The insert shows the Al signal.

Figure 4.7 High angular annular dark field (HAADF) transmission electron micrograph and EDX maps of the coating formed on electropolished aluminium for 300 s in a dilute SurTec 650 bath at 40°C.

Figure 4.8 Experimental and simulated (solid line) RBS spectra for the trivalent chromium coatings formed for 300 s in a dilute SurTec 650 bath at 40°C.

Figure 4.9 Possible hydrolysis mechanism and structure of chromium sulphates.

Figure 4.10 High resolution XPS spectrum for (a) Al 2p and (b) Zr 3d photoelectron regions and curve fitting for the 300 s TCC coated aluminium

Figure 4.11 (a) High resolution XPS spectrum for C 1s and (b) O 1s photoelectron regions and curve fitting for the 300 s TCC coated aluminium

Figure 4.12 High resolution XPS spectrum and curve fitting for the Cr 2p photoelectron region: (a) with CrF_3 ; and (b) without CrF_3 . The aluminium was coated for 300 s.

Figure 4.13 (a) Raman spectra ranging from 200 to 1200 cm^{-1} for (I) electropolished aluminium and the TCC coatings formed after 1200 s of immersion in the SurTec 650 bath at $40\text{ }^\circ\text{C}$ which were under (II) open-air condition and (III) the de-oxygenated conditions. The fresh specimens were analysed immediately after coating formation. All data were smoothed over five neighbouring points. (b) Fittings of Raman spectra ranging from 700 to 1050 cm^{-1} of the fresh TCC coatings formed for 1200 s of immersion in the SurTec 650 bath at $40\text{ }^\circ\text{C}$ which was under naturally-aerated condition.

Figure 4.14 Dependence of the modulus of the impedance on (a, c) frequency and (b, d) phase angle for the bare aluminium in the non-coated condition and following coating for 60, 300 and 600 s. The specimens were post-treated in water at $40\text{ }^\circ\text{C}$. The impedance measurements were carried out in 0.1 M Na_2SO_4 solution (a, b) and in the mixture solution of 0.1 Na_2SO_4 and 0.1 M NaCl (c, d); equivalent circuit models for (e) the bare Al and (f) the coatings formed for 60, 300 and 600 seconds. R_e , R_{coat} and R_p represent the resistances of the electrolyte, coating defects and the charge-transfer process; the constant phase elements Q_{coat} and Q_{dl} represent the region in the coating and coating/substrate interface respectively

Figure 4.15 High resolution of Cr 2p photoelectron region in the TCC coating controls formed for (a) 300 s and (b) 1200 s.

Figure 4.16 High resolution of Al 2p photoelectron region in the TCC coating controls formed for (a) 300 s and (b) 1200 s.

Figure 4.17 Raman spectra ranging from 200 to 2000 cm^{-1} (smoothed by the neighbored 10 points) of the trivalent chromium conversion coatings formed for 1200 seconds: (a) the coating control without air ageing treatment; (b) after the air ageing treatment for 24 h and (c) after air ageing treatment for 168 h.

Figure 4.18 Raman spectra of selected compounds and deposition from the mixture solution: (a) for separate reference compounds of Cr_2O_3 , CrF_3 , $\text{Cr}_2(\text{SO}_4)_3$, $\text{Cr}_2(\text{SO}_4)_3\cdot\text{H}_2\text{O}$ and $\text{CrF}_3\cdot\text{H}_2\text{O}$, (b) Na_2SO_4 and FeSO_4 .

Figure 4.19 Raman spectra ranging from 200 to 1200 cm^{-1} of the TCC coatings formed for 1200 s with post-treatment of immersion in a solution containing sodium sulphite in a concentration of 10 and 50 g/l for 120 s. Specimens used were rinsed in the deionized water and dried in a cool air stream prior to the Raman examination.

Figure 4.20 High resolution of Cr 2p photoelectron region in the TCC coating formed for 1200 s after post-treatment in 100 g/l Na_2SO_3 solution for 120 s.

Figure 4.21 Raman spectra ranging from 200 to 1200 cm^{-1} of the TCC coating formed for 1200 s with post-treatment immersion in 100 g/l Na_2SO_3 solution for 120 s. Specimens used were rinsed in the deionized water and dried in a cool air stream prior to the Raman examination.

Figure 4.22 The schematic drawing of the TCC coating formation and Cr(III) transformation process into Cr(VI) by oxidation of hydrogen peroxides around the cathodic furrows.

Table 4.1 Elemental concentrations ($\times 10^{15}$ atomic/cm²) from RBS and NRA analyses of coatings formed on aluminium for 60, 120 and 300 s.

	Zr	Cr	O _{RBS}	S	F	Al	O _{NRA}	C _{NRA}	Cr/Zr
60 s	7.94	3.70	46.53	0.29	3.97	18.96	45.09	12.61	0.47
120 s	24.98	11.66	122.91	0.96	33.30	33.29	103.40	16.70	0.47
300 s	60.43	26.94	222.23	2.12	76.98	22.15	221.80	25.63	0.47

Table 4.2 Elemental concentrations (g cm⁻³) from RBS and NRA analyses of coatings formed on aluminium for 60, 120 and 300 s.

	Zr	Cr	S	F	Al	O _{NRA}	C _{NRA}	Density
60 s	0.76	0.20	0.01	0.08	0.54	0.76	0.16	2.5
120 s	1.00	0.27	0.01	0.28	0.39	0.72	0.09	2.8
300 s	1.10	0.28	0.01	0.29	0.12	0.71	0.06	2.6

Table 4.3 Surface elemental concentrations (at.%) determined from XPS analyses of a coating formed on aluminium for 120 s, before and following correction for the carbonaceous overlayer.

	Zr 3d	Cr 2p	O 1s	C 1s	Al 2p	S 2p	F 1s
Before correction	9.7	2.3	34.8	42.7	2.1	0.4	4.5
After correction	22.0	5.9	57.1	-	3.1	0.7	8.6

Table 4.4 Comparison of the elemental concentrations (at. %) from RBS, NRA and XPS analyses of a coating formed on aluminium for 120 s.

	O _{NRA}	F	S	Cr	Zr	Al
RBS&NRA	50.9	18.8	0.5	6.6	14.1	9.0
XPS	57.1	8.6	0.7	5.9	22.0	3.1

Table 4.5 Parameters of TCC coatings/Al systems in 0.1 M sodium sulphate solution and the mixture solution of 0.1M NaCl and 0.1 M Na₂SO₄, obtained from EIS data using the equivalent circuits of Figure 4.14 (e) or (f).

0.1 M Na ₂ SO ₄	R _e Ω cm ²	R _{coat} Ω cm ²	R _p ×10 ⁵ Ω cm ²	Q _{coat} (×10 ⁻⁶ s ⁿ /(Ω cm ²))	n _{coat}	Q _{dl} (×10 ⁻⁶ s ⁿ /(Ω cm ²))	n _{dl}	C _{eff-dl} μF/cm ²
Bare Al (e)	38	-	36.8	-	-	3.74	1	3.74
60 s-TCC (f)	25	31	29.4	0.98	0.93	4.25	0.96	3.00
300 s-TCC (f)	25	42	1.80	1.72	0.89	4.55	0.95	2.97
600 s-TCC (f)	25	89	1.05	3.60	0.79	3.55	1	3.55

0.1 M Na ₂ SO ₄ + 0.1 M NaCl	R _e Ω cm ²	R _{coat} Ω cm ²	R _p ×10 ⁵ Ω cm ²	Q _{coat} (×10 ⁻⁶ sn/(Ω cm ²))	n _{coat}	Q _{dl} (×10 ⁻⁶ sn/(Ω cm ²))	ndl	Ceff-dl μF/cm ²
Bare Al (e)	18	-	154	-	-	4.5	0.95	2.7
60 s-TCC (f)	18	42	33.6	1.2	0.93	3.2	0.96	2.1
300 s-TCC (f)	18	76	2.6	2.7	0.86	3.5	0.99	3.2
600 s-TCC (f)	18	53	1	4.8	0.84	3.2	1	3.2

Table 4.6 The quantified concentration (%) of the individual compound relative to the total amount of chromium in Cr 2p3/2 photoelectron region of the TCC coatings formed for (a) 300 and (b) 1200 seconds, where TCC coatings without air ageing treatment were used as coating control and the period of air ageing treatment was selected for 24 and 168 h to investigate the effect of prolonged treatment on the chemical status of chromium-containing compound.

(a)

300 s-TCC	Cr(OH) ₃	Cr ₂ (SO ₄) ₃	Cr(VI) oxides	CrF ₃	Cr5
Coating control	31.13	44.21	7.45	15.39	1.82
Coating after 24 h-air ageing	31.27	45.22	6.85	15.21	1.45
Coating after 168 h-air ageing	35.07	40.12	6.21	16.06	2.53

(b)

1200 s-TCC	Cr(OH) ₃	Cr ₂ (SO ₄) ₃	Cr(VI) oxides	CrF ₃	Cr5
Coating control	34.89	38.92	4.89	19.86	1.45
Coating after 24 h-air ageing	45.76	38.63	2.54	12.77	0.29
Coating after 168 h-air ageing	36.21	39.35	4.91	17.86	1.67

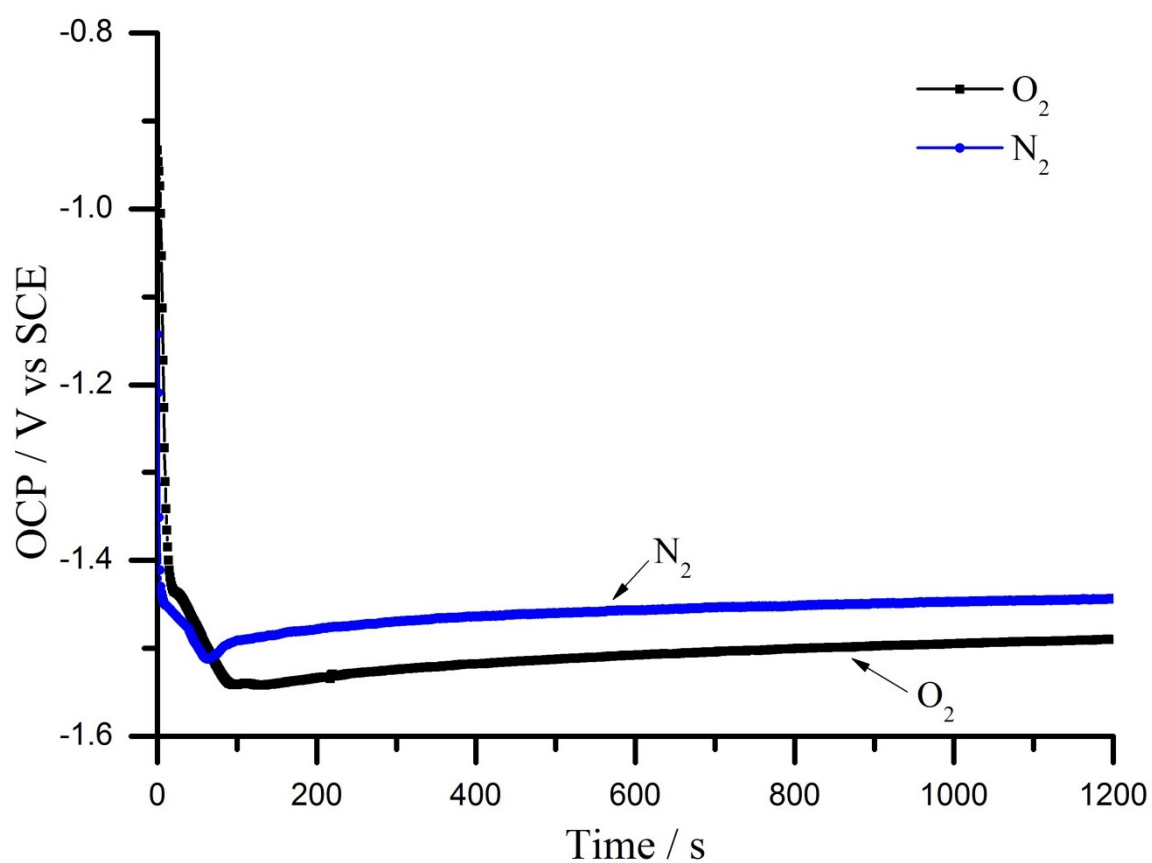


Figure 4. 1 The dependence of the open circuit potential of electropolished aluminium on the time of immersion in a dilute SurTec 650 bath at 40 °C under the usual naturally-aerated condition(named O₂) and under the de-oxygenated condition (named N₂).

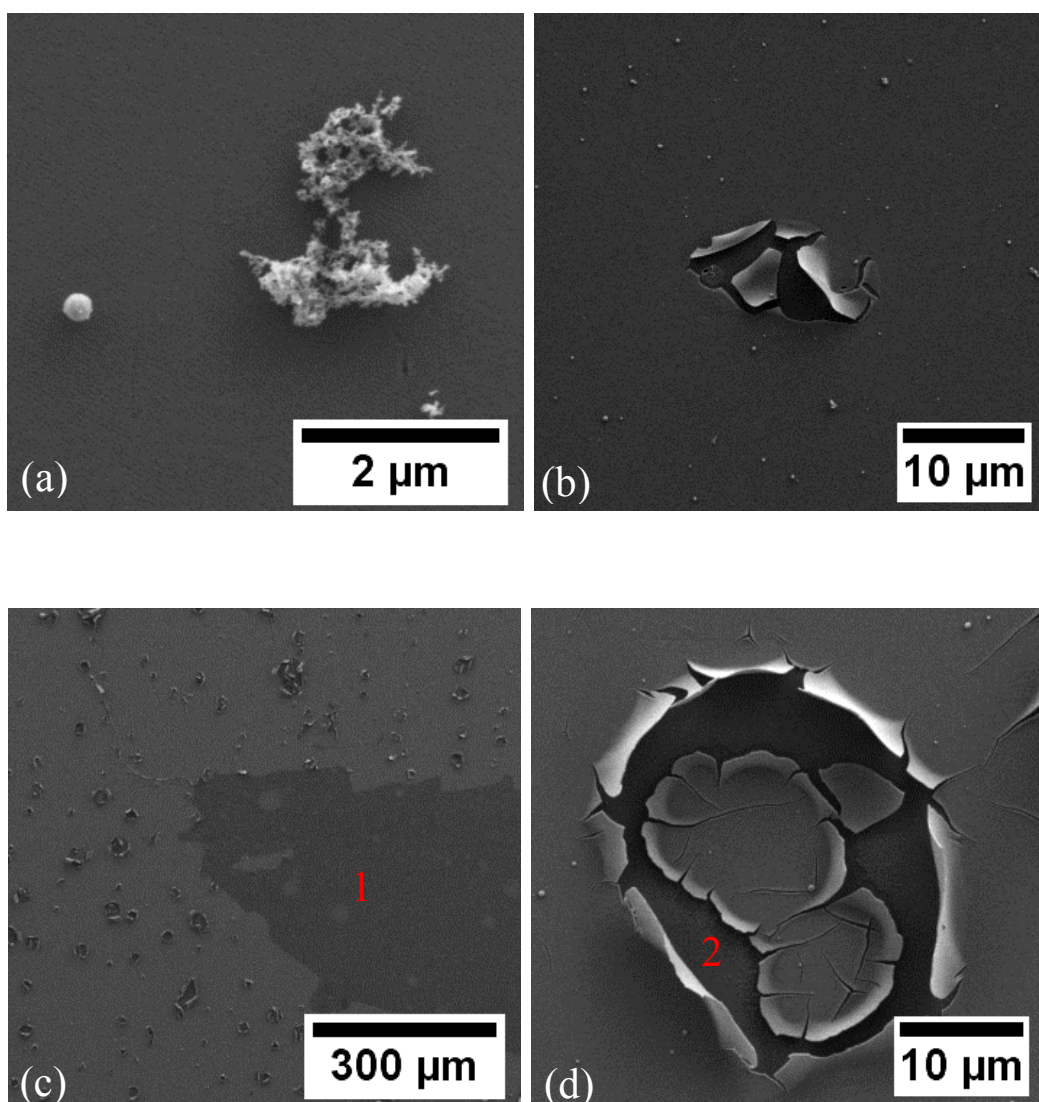


Figure 4. 2 Scanning electron micrographs (3 kV SE2 signal) of TCC coatings formed on electropolished aluminium in a dilute SurTec 650 bath at 40 °C for different times: 15 s; (b) 120 s; (c) and (d) 600 s.

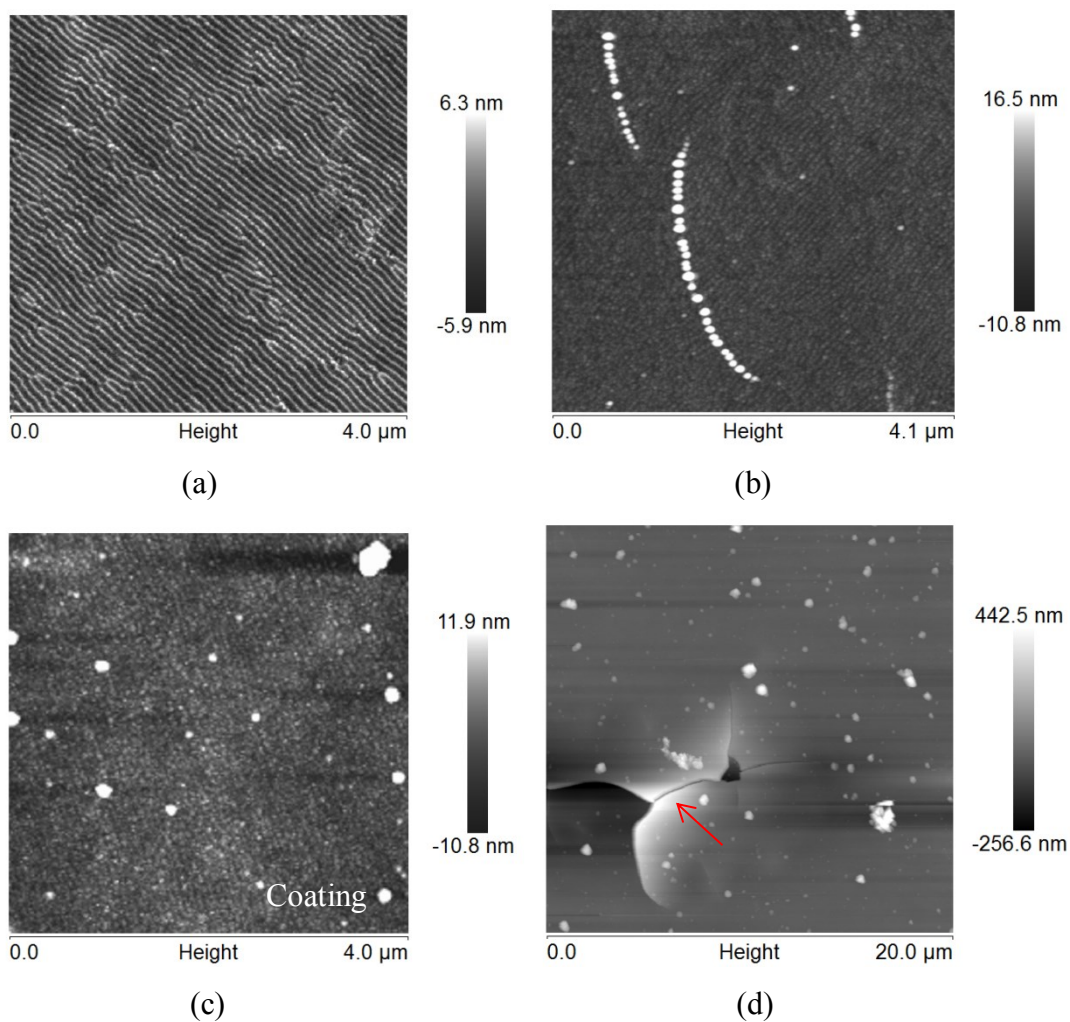


Figure 4. 3 Atomic force microscopy topography images of TCC coatings formed on electropolished aluminium in a dilute SurTec 650 bath at 40 °C for different times: (a) the electropolished aluminium; (b) 15 s; and (c) and (d) 300 s.

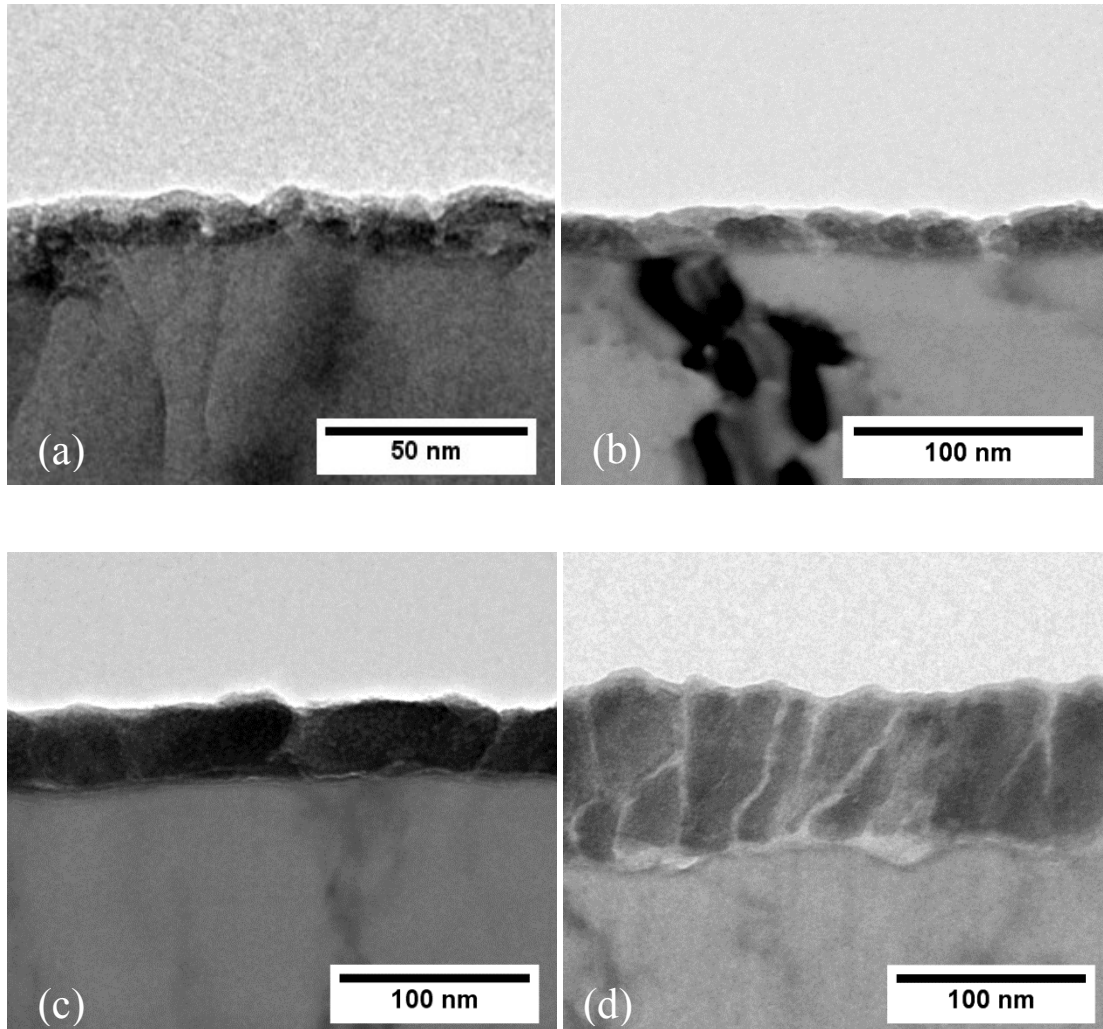


Figure 4. 4 Bright field transmission electron micrographs of ultramicrotomed cross-sections of TCC coatings formed on electropolished aluminium in a dilute SurTec 650 bath at 40 °C for different times: (a) 15 s; (b) 60 s; (c) 120 s; and (d) 300 s.

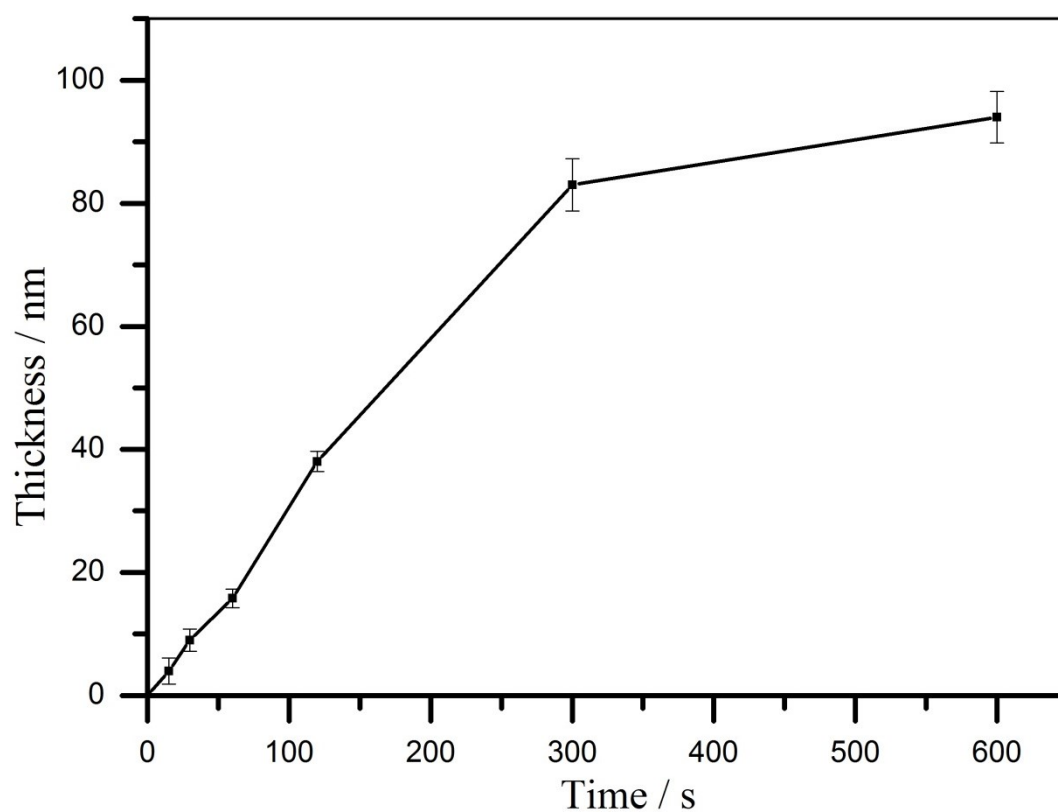
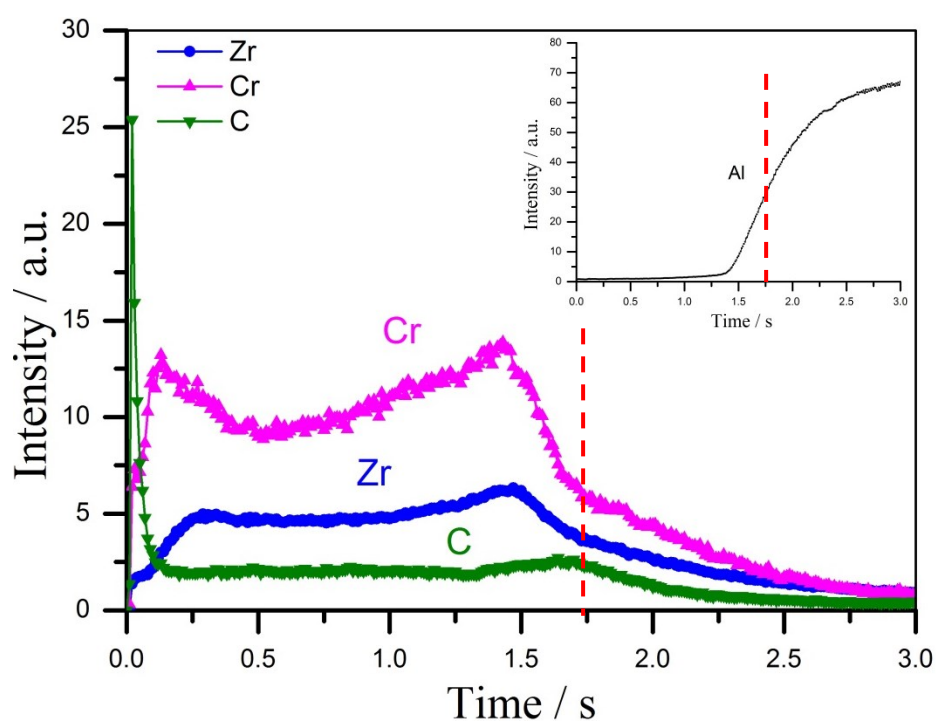


Figure 4. 5 Variation of the thickness of TCC coating on aluminium with time of immersion in a dilute SurTec 650 bath at 40°C. The thicknesses of the coatings were determined from TEM of ultramicrotomed sections.

(a)



(b)

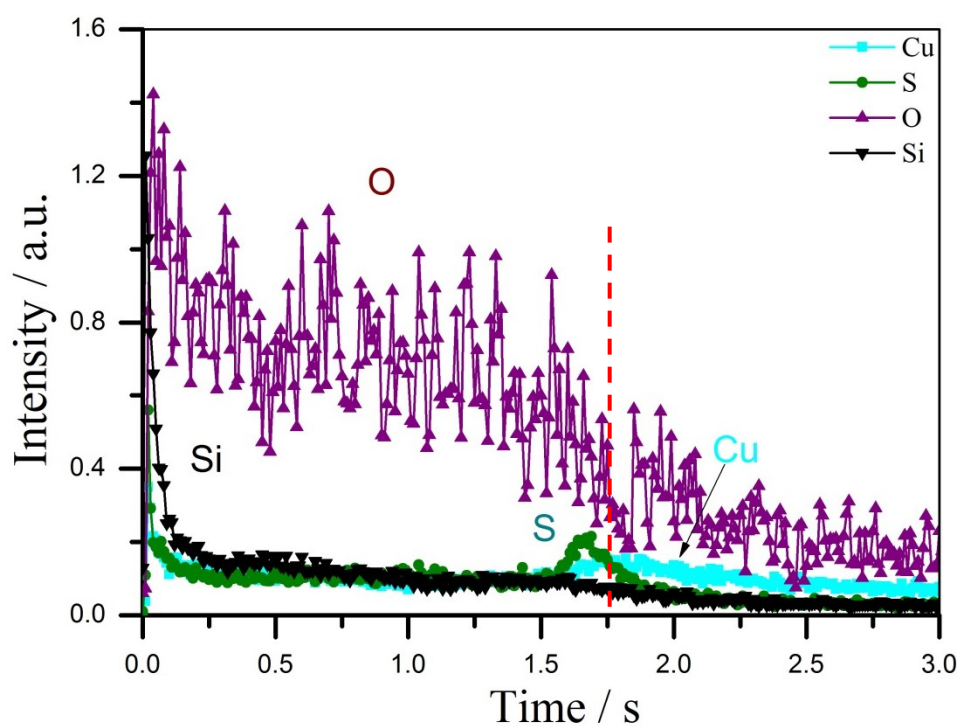


Figure 4. 6 GDOES elemental depth profiles of electropolished aluminium following immersion for 300 s in a dilute SurTec 650 bath at 40 °C: (a) Zr, Cr, C, and (b) S, O, Si, Cu. Both are smoothed by 10 neighboured points. The dashed line marks the aluminium/coating interface. The insert shows the Al signal.

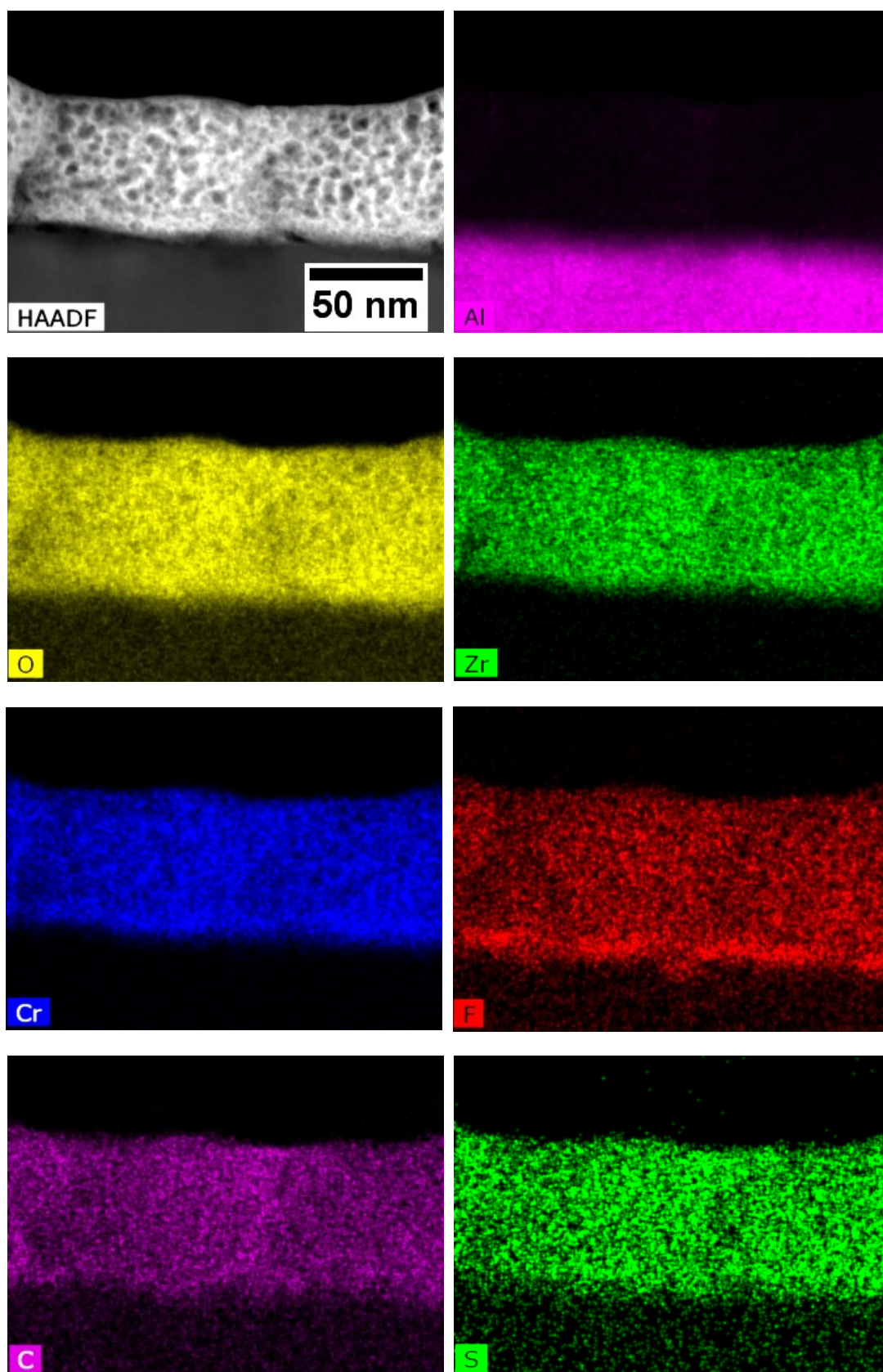


Figure 4. 7 High angular annular dark field (HAADF) transmission electron micrograph and EDX maps of the coating formed on electropolished aluminium for 300 s in a dilute SurTec 650 bath at 40°C.

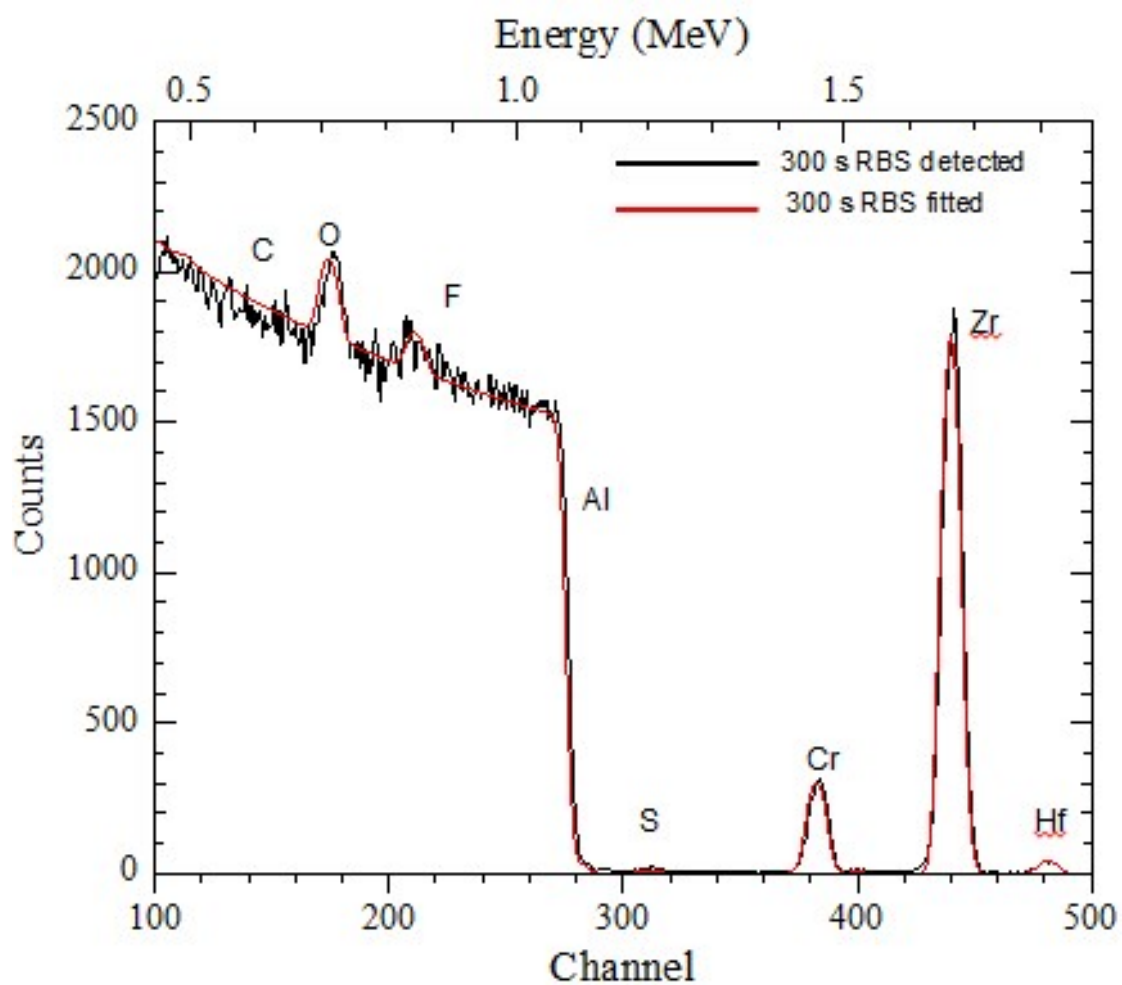


Figure 4. 8 Experimental and simulated (solid line) RBS spectra for the trivalent chromium coatings formed for 300 s in a dilute SurTec 650 bath at 40°C.

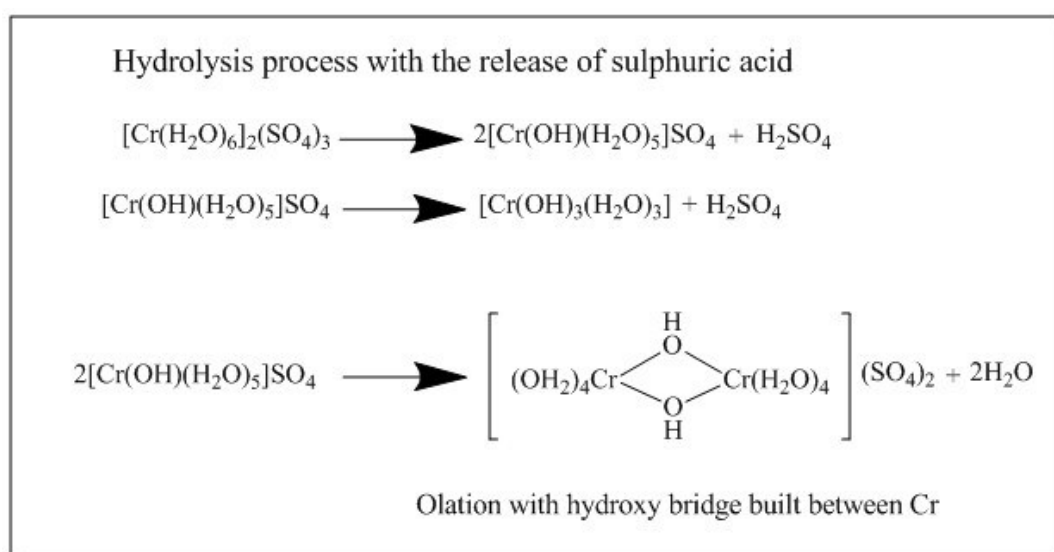


Figure 4. 9 Possible hydrolysis mechanism and structure of chromium sulphates.

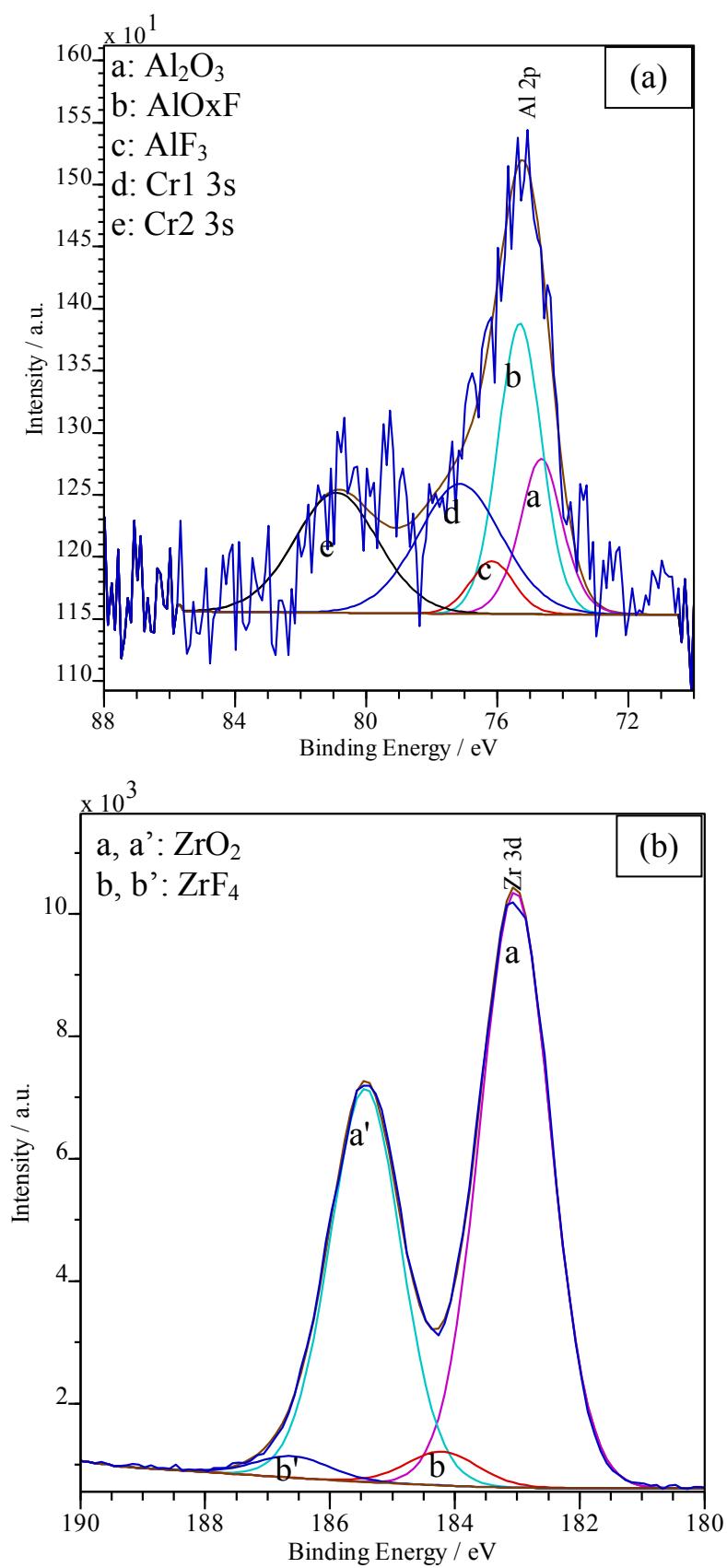


Figure 4. 10 High resolution XPS spectrum for (a) Al 2p and (b) Zr 3d photoelectron regions and curve fitting for the 300 s TCC coated aluminium

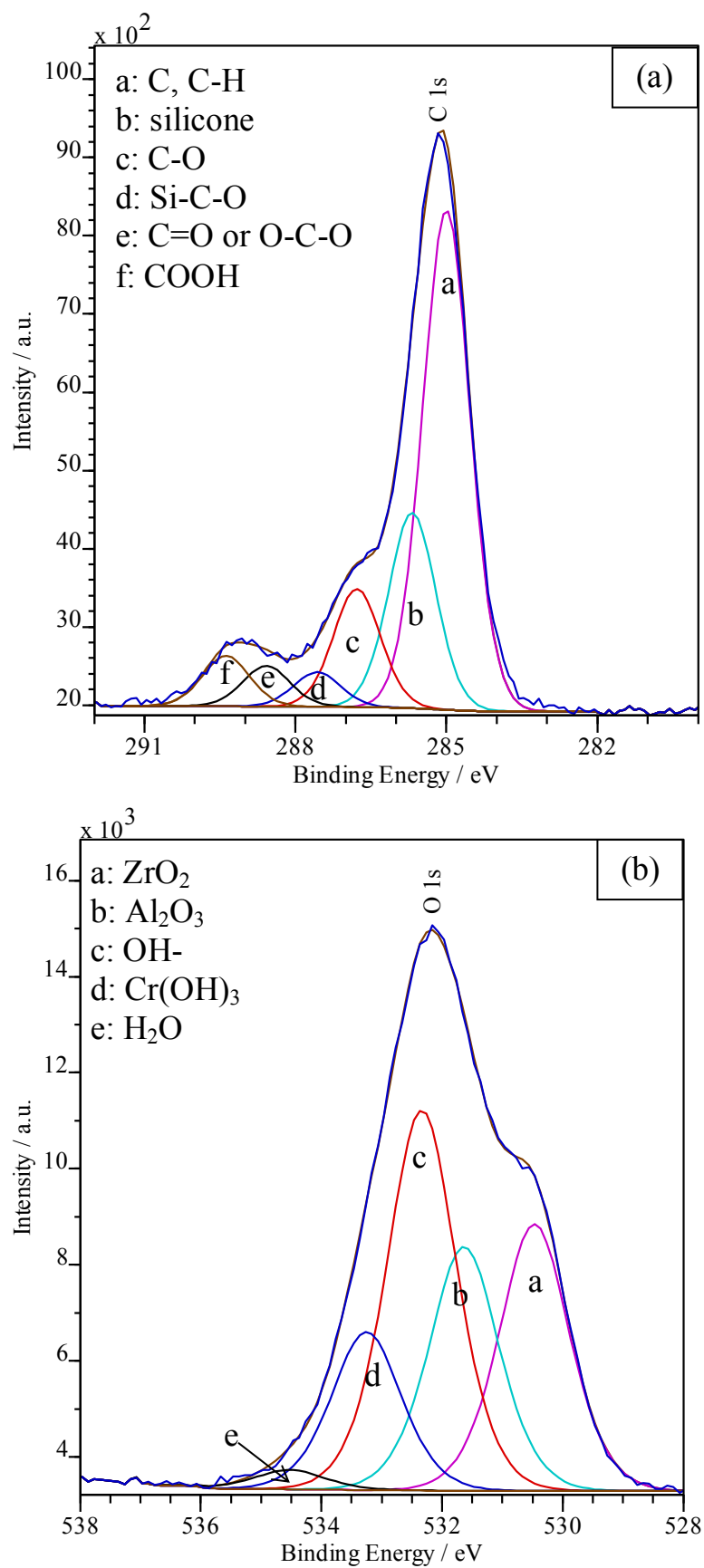


Figure 4. 11 (a) High resolution XPS spectrum for C 1s and (b) O 1s photoelectron regions and curve fitting for the 300 s TCC coated aluminium

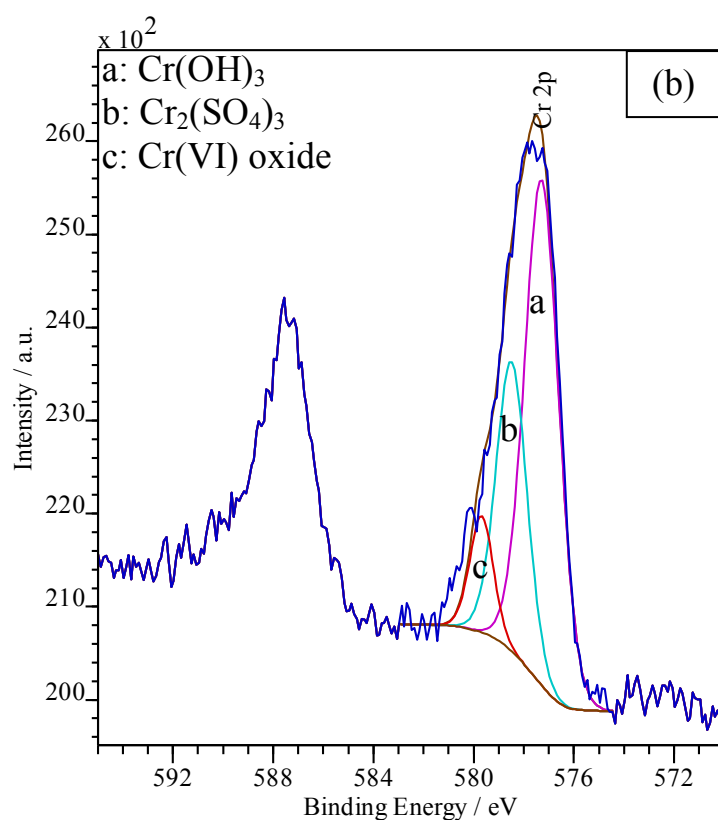
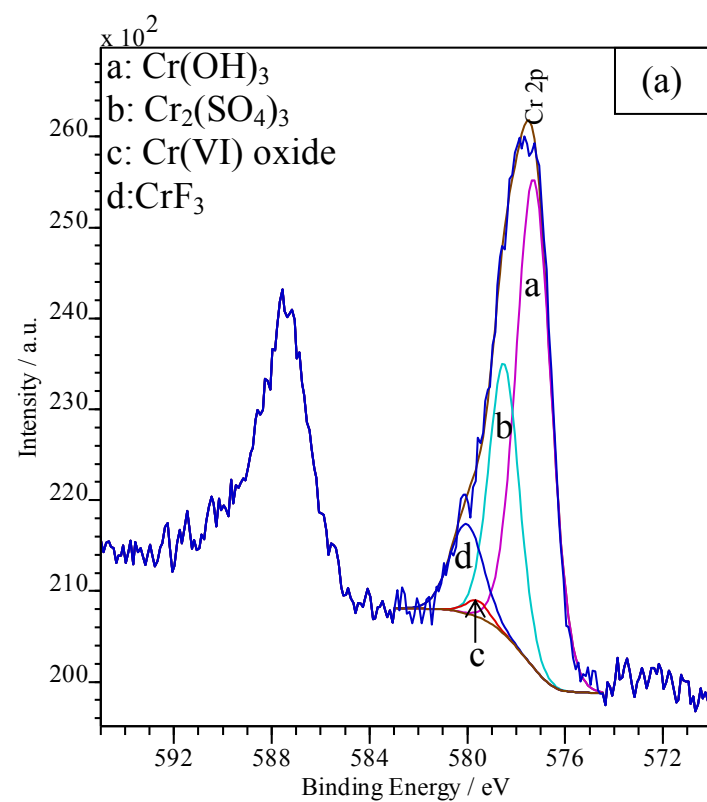


Figure 4. 12 High resolution XPS spectrum and curve fitting for the Cr 2p photoelectron region: (a) with CrF_3 ; and (b) without CrF_3 . The aluminium was coated for 300 s.

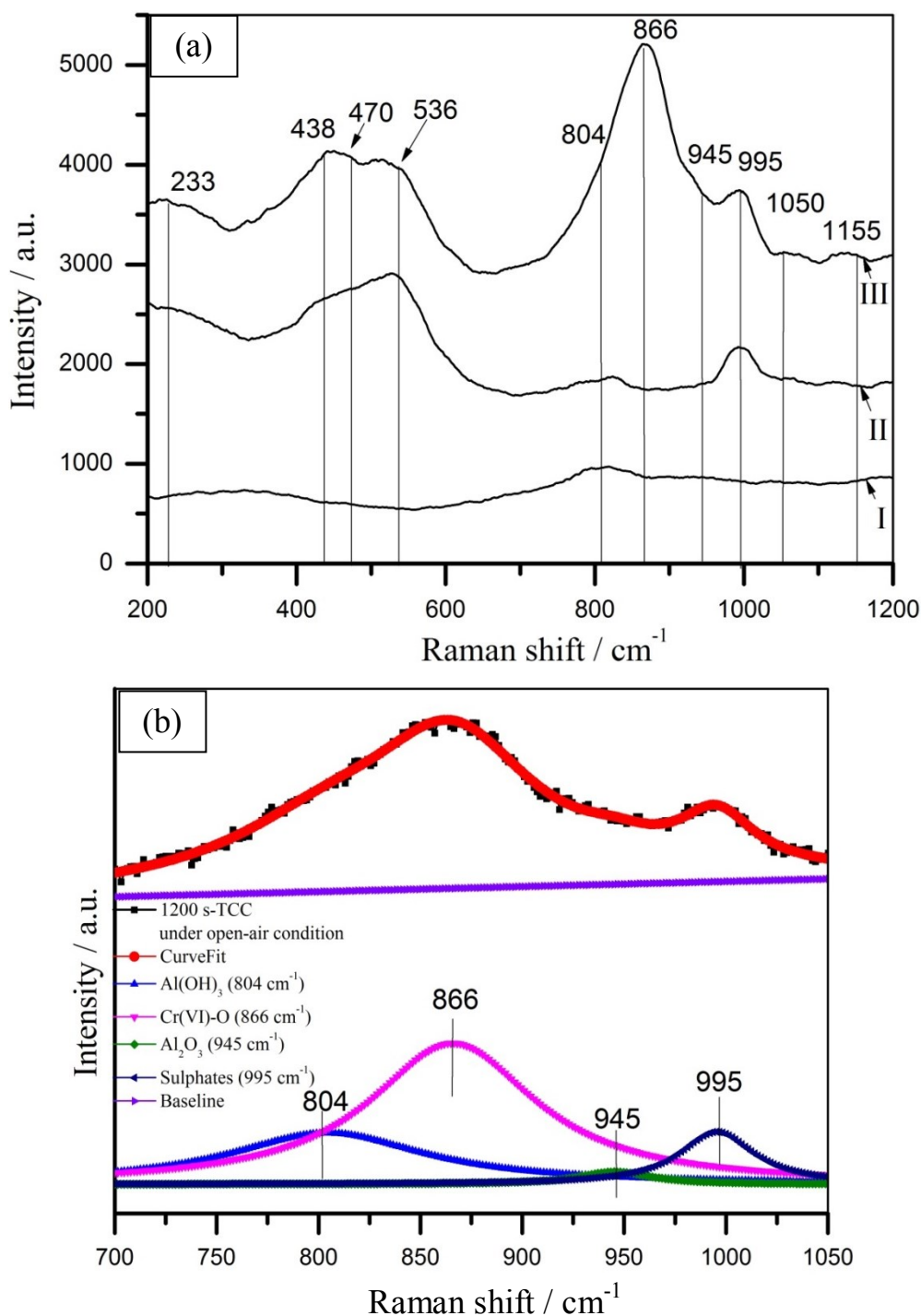


Figure 4. 13 (a) Raman spectra ranging from 200 to 1200 cm^{-1} for (I) electropolished aluminium and the TCC coatings formed after 1200 s of immersion in the SurTec 650 bath at 40 °C which were under (II) open-air condition and (III) the de-oxygenated conditions. The fresh specimens were analysed immediately after coating formation. All data were smoothed over five neighbouring points. (b) Fittings of Raman spectra ranging from 700 to 1050 cm^{-1} of the fresh TCC coatings formed for 1200 s of immersion in the SurTec 650 bath at 40 °C which was under naturally-aerated condition.

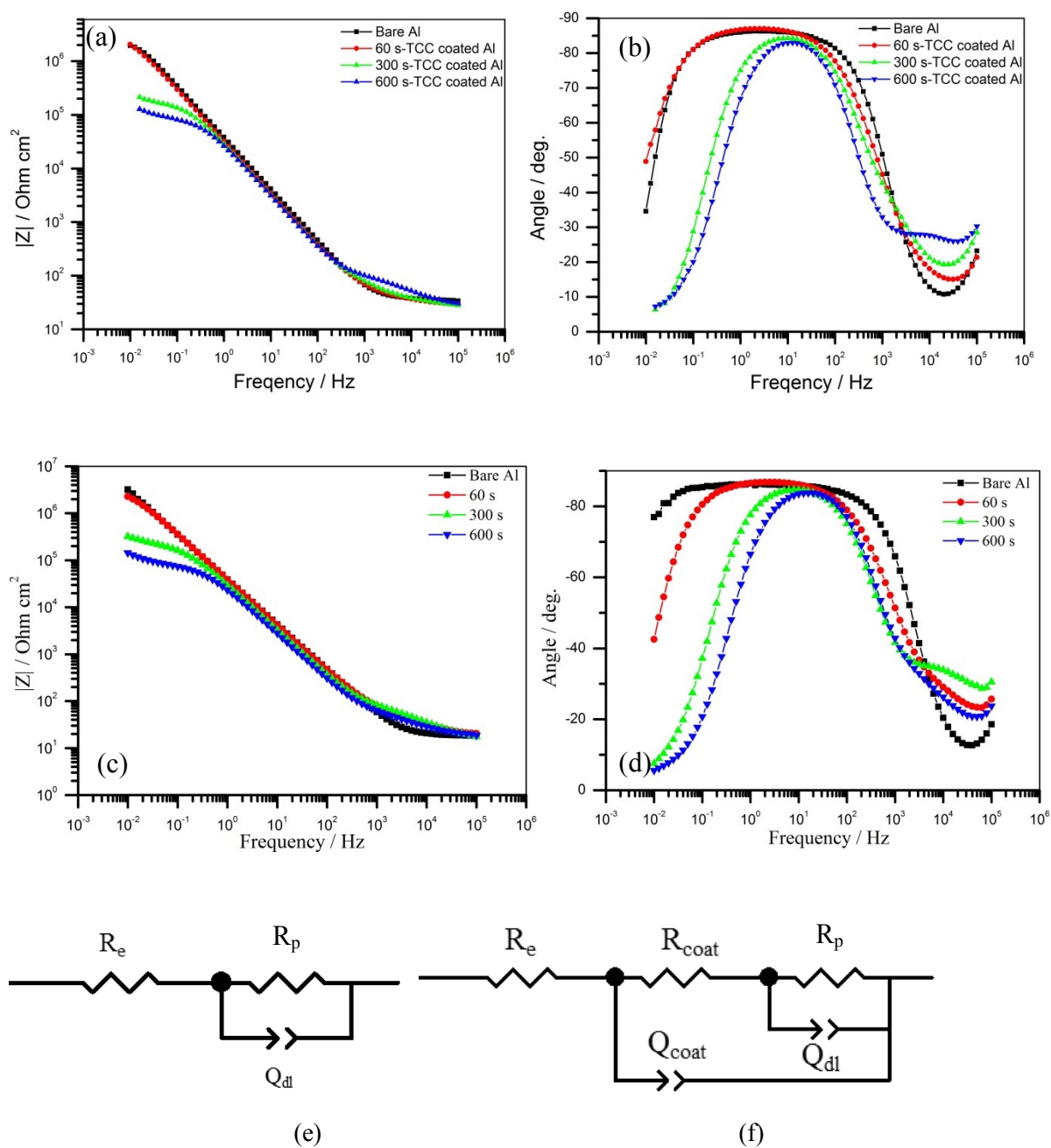


Figure 4. 14 Dependence of the modulus of the impedance on (a, c) frequency and (b, d) phase angle for the bare aluminium in the non-coated condition and following coating for 60, 300 and 600 s. The specimens were post-treated in water at 40 °C. The impedance measurements were carried out in 0.1 M Na_2SO_4 solution (a, b) and in the mixture solution of 0.1 M Na_2SO_4 and 0.1 M NaCl (c, d); equivalent circuit models for (e) the bare Al and (f) the coatings formed for 60, 300 and 600 seconds. R_e , R_{coat} and R_p represent the resistances of the electrolyte, coating defects and the charge-transfer process; the constant phase elements Q_{coat} and Q_{dl} represent the region in the coating and coating/substrate interface respectively.

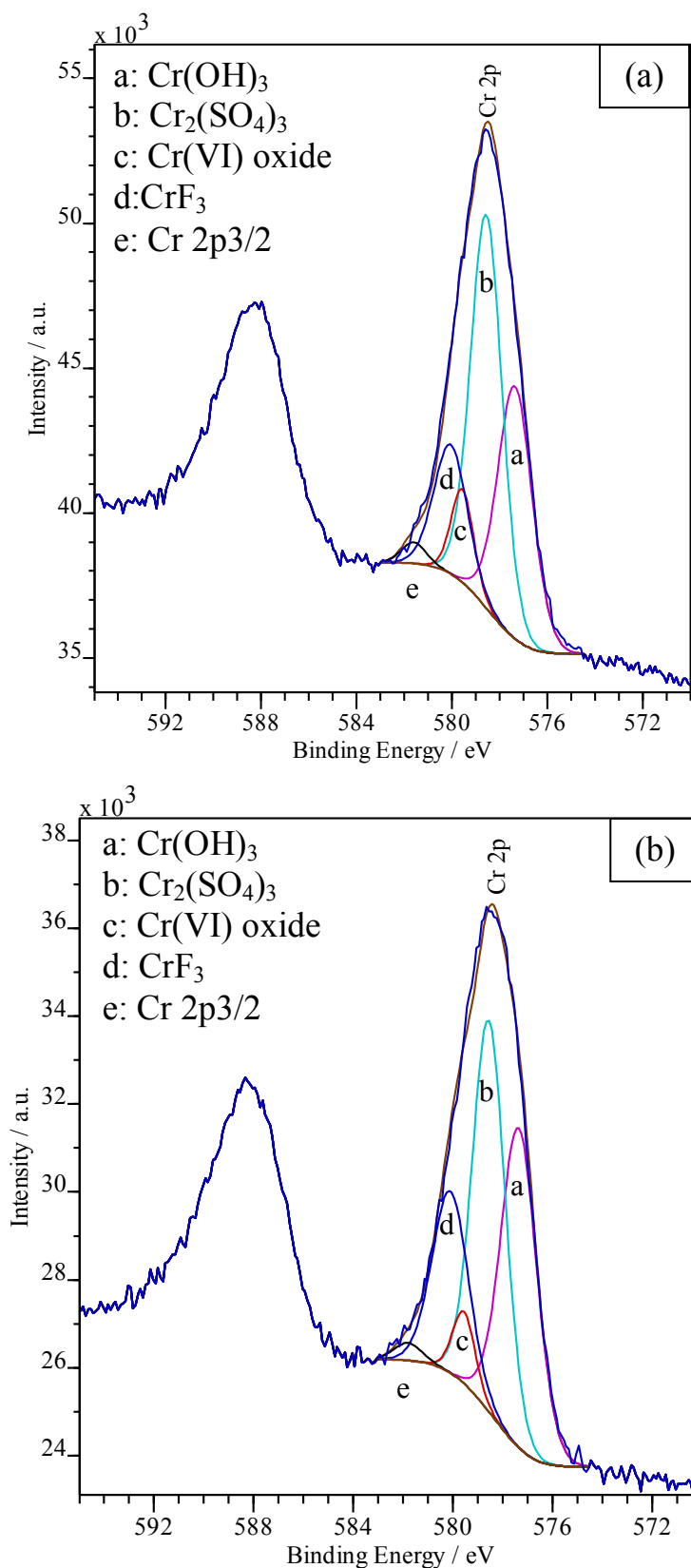


Figure 4. 15 High resolution of Cr 2p photoelectron region in the TCC coating controls formed for (a) 300 s and (b) 1200 s.

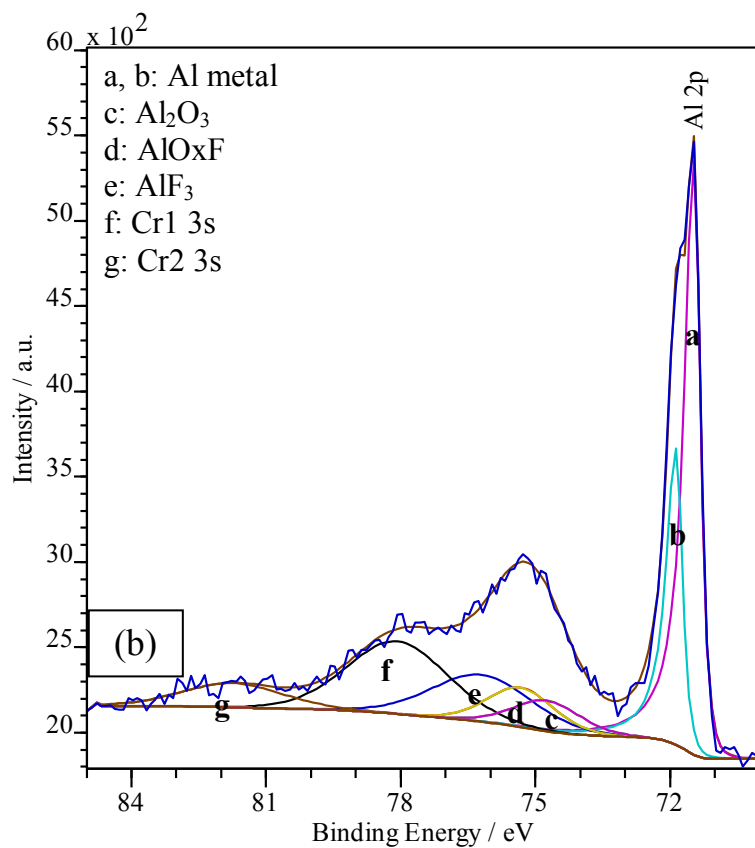
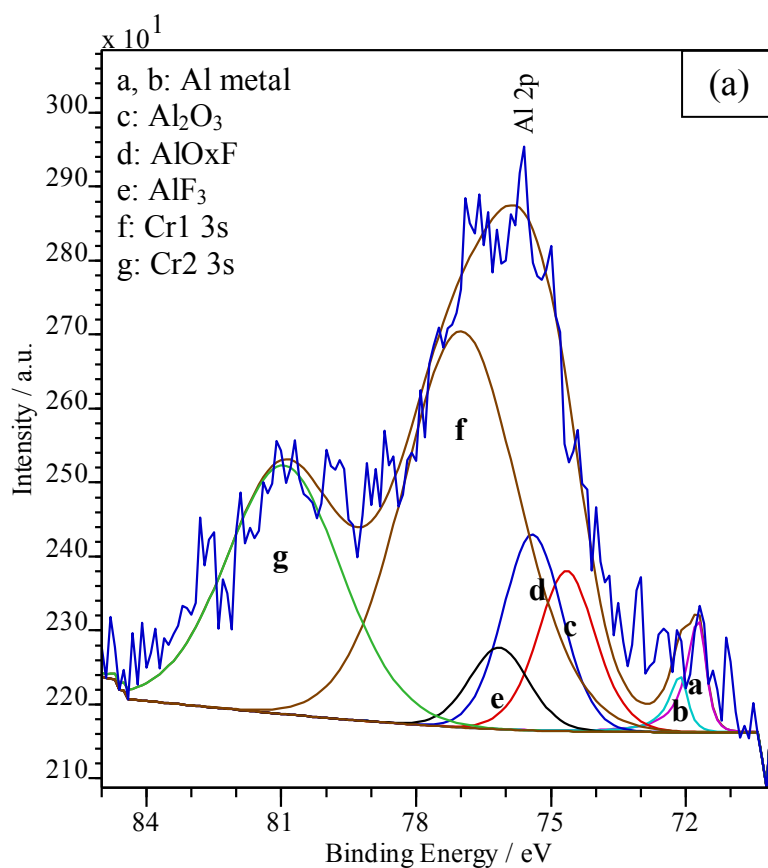


Figure 4. 16 High resolution of Cr 2p photoelectron region in the TCC coating controls formed for (a) 300 s and (b) 1200 s.

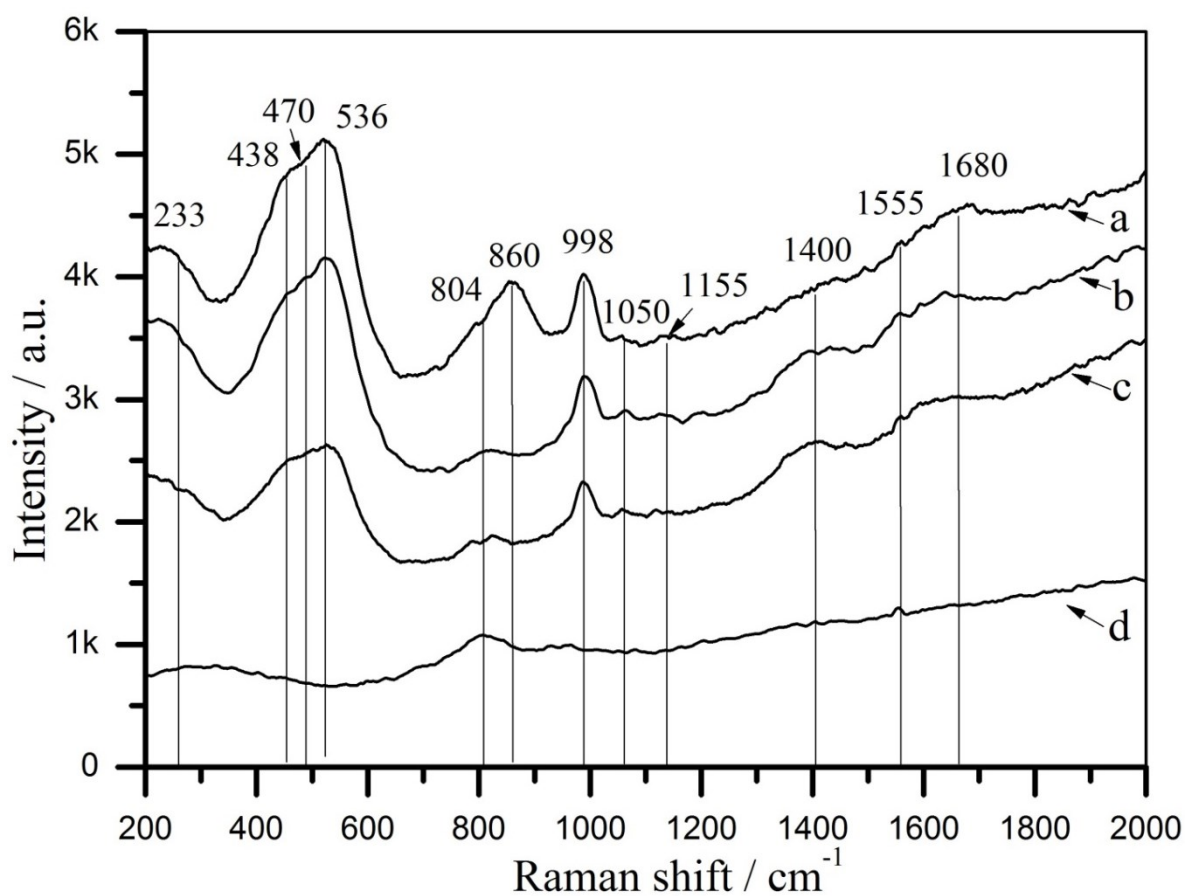


Figure 4. 17 Raman spectra ranging from 200 to 2000 cm^{-1} (smoothed by the neighbored 10 points) of the trivalent chromium conversion coatings formed for 1200 seconds: (a) the coating control without air ageing treatment; (b) after the air ageing treatment for 24 h and (c) after air ageing treatment for 168 h.

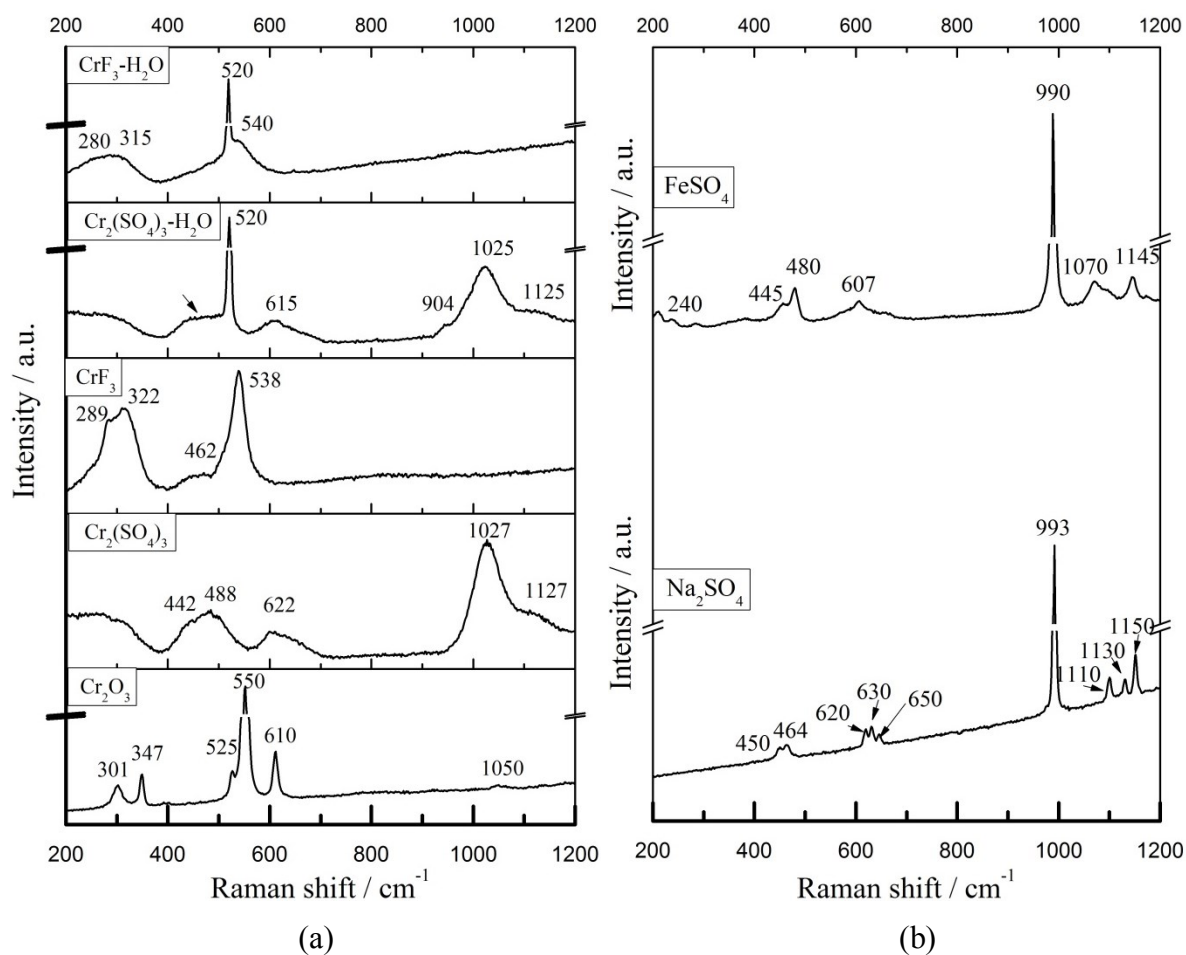


Figure 4. 18 Raman spectra of selected compounds and deposition from the mixture solution: (a) for separate reference compounds of Cr_2O_3 , CrF_3 , $\text{Cr}_2(\text{SO}_4)_3$, $\text{Cr}_2(\text{SO}_4)_3\cdot\text{H}_2\text{O}$ and $\text{CrF}_3\cdot\text{H}_2\text{O}$, (b) Na_2SO_4 and FeSO_4 .

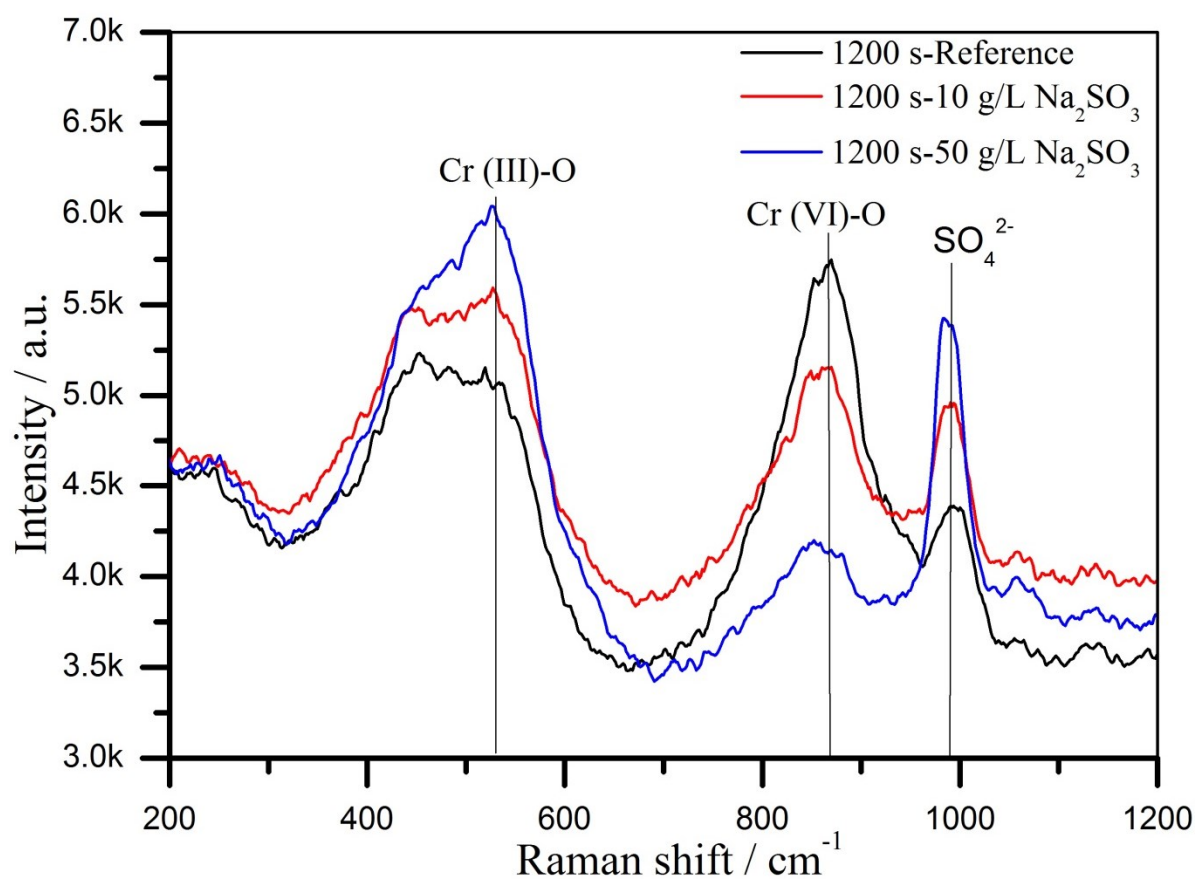


Figure 4. 19 Raman spectra ranging from 200 to 1200 cm⁻¹ of the TCC coatings formed for 1200 s with post-treatment of immersion in a solution containing sodium sulphite in a concentration of 10 and 50 g/l for 120 s. Specimens used were rinsed in the deionized water and dried in a cool air stream prior to the Raman examination.

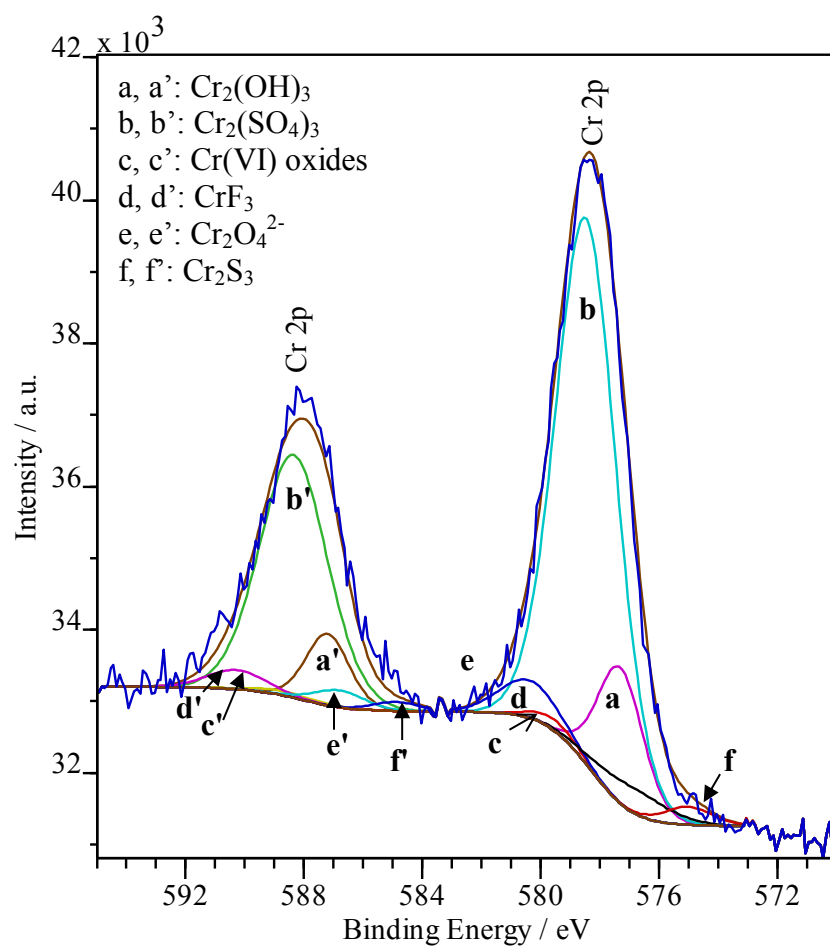


Figure 4. 20 High resolution of Cr 2p photoelectron region in the TCC coating formed for 1200 s after post-treatment in 100 g/l Na_2SO_3 solution for 120 s.

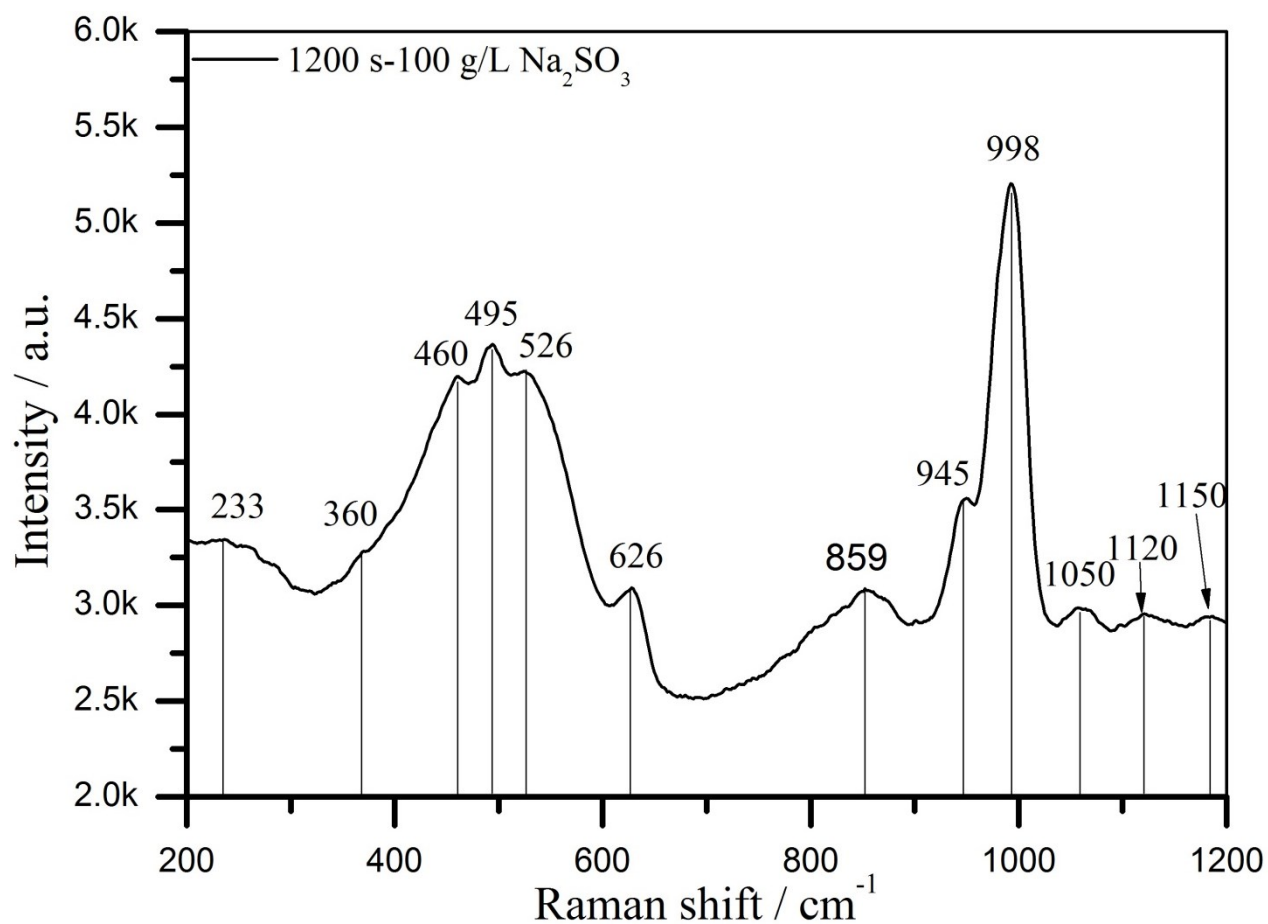


Figure 4. 21 Raman spectra ranging from 200 to 1200 cm⁻¹ of the TCC coating formed for 1200 s with post-treatment immersion in 100 g/l Na₂SO₃ solution for 120 s. Specimens used were rinsed in the deionized water and dried in a cool air stream prior to the Raman examination.

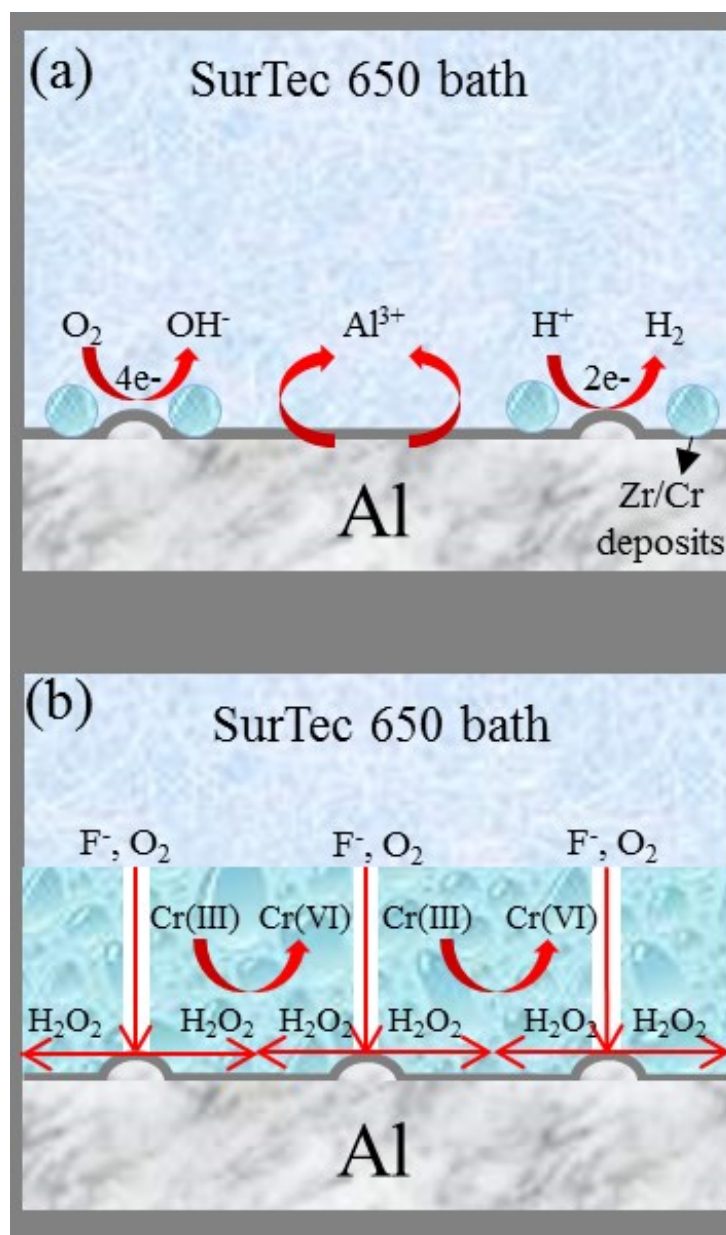


Figure 4. 22 The schematic drawing of the TCC coating formation and Cr(III) transformation process into Cr(VI) by oxidation of hydrogen peroxides around the cathodic furrows.

Chapter 5 TRIVALENT CHROMIUM CONVERSION COATINGS ON AA2024-T351 ALLOYS

This chapter consists of an introduction, results and discussion, and finally the summary of the findings. The results include (i) alloying components on the surface and in 3-D space, (ii) the coating initiation on the second phase particles, (iii) the coating morphology and growth kinetics, (iv) the coating composition by TEM/EDX, (v) the quantitative composition by RBS and NRA, (vi) the chemical states of coatings by XPS, and (vii) the electrochemical behaviour.

Accordingly, the discussion includes (i) the coating formation, (ii) the influence of the second phase particles, (iii) the coating composition on alloys, (iv) the Cr(VI) formation mechanism and (v) the electrochemical behaviour. The comparison with coatings on superpure Al is also fully discussed here.

5.1 Introduction

AA2024-T3 aluminium alloys are widely used in aerospace applications due to their high strength to weight ratio and damage tolerance [2]. However, the presence of copper as a primary alloying element leads to an increased susceptibility to localized corrosion, especially pitting corrosion [42, 43, 51]. Hence, the alloy requires protective treatments to provide the necessary corrosion resistance. Such treatments have involved the application of chromate (Cr (VI)) conversion coatings (CCC). However, the toxicity and high disposal costs of Cr(VI) wastes necessitate eco-friendly alternatives.[64]. One promising candidate treatment uses a trivalent chromium bath [95], generally consisting of zirconium hexafluoride and trivalent chromium salts [143-145, 147, 148, 150, 187].

In terms of the relationship with alloy microstructure, the alkaline-etching and acidic-pickling pre-treatment generates copper-enriched layer on alloy surface [35], which promote the deposition of pH-driven species and further lead to the poor adhesiveness and coating detachment with prolonged treatment.[87, 208] This loss of coating material on copper-rich particles is associated with the critical enrichment of copper beneath and the possible

incorporation of copper nanoparticles into the coating then disrupts the interfacial bonding due to either the presence of particles or the hydrogen evolution.[88, 89, 209] Further, the accumulation of copper oxides in the coating was proposed to potentially inhibit Al^{3+} ion transport to give rise to the impeded deposition kinetics of zirconium species [210], although the outward mobility of copper species was revealed to proceed at a faster rate than aluminium (III) cations. [211] Concerning Cr(VI) in TCC coatings, the presence of copper-rich particles has been proposed to promote the formation of H_2O_2 generated by reduction of the dissolved oxygen and then H_2O_2 oxidizes the Cr (III) to Cr(VI).[159]

In the present study, AA2024-T351 alloy panels of ~1.5 mm thickness, supplied by Airbus Corp., were used, with the nominal composition shown in Table 2.2 (Chapter 2) [2]. Specimens, of dimensions of 30×24 mm and 30×12 mm, were cut from the panels, and cleaned with acetone, ethanol and deionized water. In terms of the reference control, the alloy was mechanically polished to a fine finish of ~0.25 μm . In addition, the other specimens were also ground to a 4000 SiC grit finish, followed by etching in 5 wt.% NaOH for 60 s at 60 °C and desmutting in 50 v/v% HNO_3 for 30 s at ambient temperature. All treatments were followed by a deionized water rinse and drying in a cool air stream. These alloys used in the following experiments were respectively named as the polished and pre-treated alloys.

For the formation of the TCC coating, a 20 vol.% SurTec 650 solution (SurTec Corp.) was used. The pre-treated specimens were immersed in the SurTec 650 bath at 40 °C for 15, 30, 60, 120, 300, and 600 s. For the polished alloys, the immersion period of alloys in SurTec solution was selected as 15, 60, 120 and 750 seconds. All specimens were post-treated by immersion in deionized water for 120 s and then rinsed in deionized water for 5 s, dried in a cool-air stream and then aged for 24 h in laboratory air before characterization. The water immersion may improve the elemental distribution in the coating to stabilize the interfacial bonding of the coating with the alloy substrate.

5.2 Results

5.2.1 Alloying component on surface and in 3-D space

Figure 5.1 reveals the backscattering electron micrographs of AA2024-T351 alloy after mechanically polishing to a 0.25 μm finish, where the clustering of Al_2CuMg and Al_2Cu phase particles was evident. The former S phase particles were relatively grey compared with the bright θ phase particles in Fig. 5.1(a), attributed to the effect of the copper component. Further, α phase particle of $\sim 10\ \mu\text{m}$ in diameter and an irregular panel shape is shown Fig. 5.1(b). The corresponding SEM/EDX analyses in Fig. 5.1 (c and d) revealed the underlying composition of these particles, where the presence of nanosized dispersoids on the matrix lead to the examination of 0.3 at.% manganese in the total components. In terms of the particle distribution in space, the GATAN 3View System in a Quanta 250 FEG-ESEM instrument along with in-SEM ultramicrotomy was used to observe serial micrographs of the sectioned block and all data were analysed by the Microanalysis Software (Bruker, UK) as shown in Figure 5.2. The variance of the greyscale of second phase particles was used to distinguish the form of second phase particles by the early work of our research group [212, 213] in which the average greyscales of Al_2Cu , Al_2CuMg , $\text{Al}_{20}(\text{FeMn})_3\text{Cu}_2$ and Al were ~ 240 , 190, 160 and 20 respectively. Evidently, the dark space represents the aluminium block and the greyscale in this present study increased along the colour from dark, blue, green, yellow to red at the level of 255 in the color-coded image. Thus, the inhomogeneous distribution of particles in space can be revealed with a large cluster in the centre as the form of Al_2Cu (red part) and Al_2CuMg (yellow part). This clustering of S-/ θ -phase particles in space is in good agreement with such clustering on the surface in Fig. 5.2(a). Furthermore, the effective diameter (named by D_d) and nearest neighbour distance (named by D_{NN}) of particles were fitted by the mathematic simulation of these data and the results are shown in Fig. 5.2(b), where the ideal relationship of D_d/D_{NN} was linear at the slope angle of 45° (the blue line). It is evident that most of the fitted data were concentrated beneath this ideal line and the fitted values of D_d and D_{NN} were ~ 0.713 and $1.286\ \mu\text{m}$ respectively. This further revealed the clustered distribution of alloying particles in space.

5.2.2 Coating initiation on the second-phase particles

The scanning electron micrographs of the TCC coating after 5 s immersion in the trivalent chromium bath revealed the evidence of coating initiation on the clusters of θ and S phase particles with the corresponding EDX line scans as shown in Figures 5.3 (a and b). For the θ phase particle (named I), a featureless and intact morphology indicated the absence of coating

initiation. By contrast, the S phase particles (named II) were relatively active over this short duration of immersion as evidenced by the surrounding crevices and the nodule deposits along the particle/matrix boundary. The following EDX line scans over the S phase particle revealed that the initial deposits comprised zirconium oxides, especially at the boundary as outlined by the red spot, while the chromium signal was relatively undetectable. Figures 5.4 (a and b) show the scanning electron micrographs of α phase particles (named III), where the higher magnification for the selected area was outlined by the white square. An intact particle was evident after the short immersion in the trivalent chromium solution, which was similar to the situation of the cathodic θ phase particles in Figs. 5.3. Notably, Fig. 5.4(b) highlighted the copper-rich particles of nanometre dimensions associated with the effect of the mechanical polishing, and the relatively porous matrix was attributed to the acidic attack to thin the air-formed oxides.

Figures 5.5 (a and b) show the scanning electron micrographs and the EDX point analyses of TCC coatings after treatment for 15 seconds around the cluster of θ and S phase particles. For such SEM/EDX analyses, the high accelerating voltage of 15 keV led to the strong background Al signal, and, in order to decrease the influence of the variance of background signal between analyses, the SEM/EDX spectra were all normalized with respect to the maximum Al content [208]. Thus, the relative count of ZrL β signal (2.1 keV) in the inert image roughly represented the coating thickness, while the chromium signal is too weak to represent the coating thickness. Compared to the intact θ phase particle (named I), the dealloying crevices and nodule deposits developed around the S phase particles (named II). In addition, some solution deposits in the form of the spherical nodules were also observed on the matrix as outlined by the yellow arrow. In terms of the SEM/EDX point analyses (Fig. 5.5 (b)), zirconium, chromium, oxygen and fluorine indicated the presence of coating precipitation on particles. Notably, the more concentrated zirconium was detected on the S phase particles (spectra 1 and 2) compared to the situation of the θ phase particle (spectrum 3), revealing the preferential coating initiation on these S phase particles. For these S phase particles, both the active and cathodic behaviours were revealed in the hexavalent chromium conversion coating [19], and similar evidence was also investigated in this situation of the TCC coating in Figure 5.6. Compared to the evident coating deposits over the active type of the right particle, the left particles appeared relatively noble with fewer deposits. The brighter area in SEM/EDX maps represented the locally concentrated elements, and hence, a

relatively concentrated copper and fewer zirconium deposits were indicated on this cathodic type of S phase particle in comparison to the situation of the active particles. This revealed that some S phase particles became ennobled because of the copper enrichment by the initial dealloying reaction. Compared with the active S phase, the coating deposition kinetics on the cathodic type of S phase particles displayed at a decreased rate, which was similar to the situation of the situation of the cathodic θ phase particle (Fig. 5.5 (a)).

After the coating initiation, the coating further developed over the whole surface as evidenced by the presence of $ZrL\beta$ signal at 2.1 keV on the matrix after treatment of 30 and 60 seconds as shown in Figures 5.7. Considering the effect of second-phase particles on the coating thickness represented by the relative counts of zirconium, the SEM/EDX spectra in the coating formed for both periods revealed that a thicker coating probably formed on the second-phase particles, especially for the active S phase particles. This indicated that the coating was inhomogeneous on the particles and matrix with the prolonged treatment, possibly leading to the occurrence of cracks in the TCC coatings.

5.2.3 Coating morphology and growth kinetics

Figure 5.8 shows the open-circuit potentials (OCP) during the treatments of the etched and mechanically-polished specimens for 1200 s in the SurTec 650 bath at 40 °C. The potentials initially decreased to the minimum values of ~ -1.0 and -1.3 V (SCE) respectively, followed by the increases up to ~ -0.82 and -0.95 V (SCE) after ~ 600 s, with little change thereafter. The latter potentials are ~ 400 mV greater than that of relatively pure aluminium treated under the similar conditions [71, 84].

The surface appearance of the matrix of the bare alloy after alkaline and nitric acidic pre-treatment is shown in Figs. 5.9 by scanning Kelvin probe force and scanning electron microscopy. For the SKFM result, the brighter particles with heights ranging up to 60 nm (Fig. 5.9(a)) correspond to the cathodic sites, i.e. the brighter areas visible in the potential map of Fig. 5.9(b). This was also consistent with the Mn- and Cu-rich particles (named 1, Fig. 5.9 (c and d)) by SEM/EDX analyses at ~ 1.1 and 5.7 wt.% respectively. For the matrix (named 2, Fig. 5.9(a) and (c)), the nanosized particles with the cathodic nature by the potential map were also indicated in both diameter and height ranging between tens of

nanometres, which are enriched in copper of ~ 4.6 wt.% on the matrix (Fig. 5.9(d)). In addition, the dark region in Fig. 5.9 (b) near the cathodic particle is related to the anodic microstructure of the periphery phase. This microstructure was reported by Hughes et al to play the role of the galvanic coupling with the particles to lead this zone to occur the trenching corrosion near the second-phase particles.[6, 11]

Bright field transmission electron micrographs of ultramicrotomed cross-sections of the coating above the matrix of the pre-treated alloys immersed for 15, 60, 120 and 300 s are shown in Figures 5.10 (a, b, c and d) respectively. The sections reveal a main coating layer overlying a thin lighter layer next to the alloy and a dark band, ~ 2 nm thickness, which was a region of the alloy enriched in copper, as shown by later RBS. Along the alloy/coating interface, few regions of locally enhanced oxidation of the alloy were evident. Bubble-like features, of size up to ~ 32 nm, occurred in the coating at these locations. These features were also observed in Fig. 5.10 (d) when an ethanol-based polishing solution was used instead of water for ultramicrotomy to avoid corrosion during collection of the sections in the diamond knife [18, 28]. There appeared to be patches of the light material at the surface of the coatings, which seemed to form an almost continuous, though poorly adherent, layer on the coating formed for 300 s (Fig. 5.10(e)). Treatments were also carried out on a mechanically-polished alloy. The resulting coatings formed for 750 seconds were similar to those presented in Fig. 5.10(f), except the regions of locally enhanced oxidation were not detectable. Thus, it appears that these features were related to the etching and de-smutting of the alloy. It is possible that residues of copper remained on the surface after the pre-treatment that acted as cathodic sites during the formation of the conversion coating, leading to localized corrosion of the alloy.

Figure 5.11 reveals the kinetics of coating growth on the matrix of the pre-treated alloys for times up to 600 s, when the thickness had reached ~ 50 nm. [150] The growth up to 120 s occurs at an approximately constant rate of ~ 0.23 nm s⁻¹, which then slows significantly to an average of ~ 0.04 nm s⁻¹ between 120 and 600 s. The kinetics were similar for an alloy that had been mechanically polished with similar growth rates of ~ 0.3 nm s⁻¹ and 0.04 nm s⁻¹ before and after ~ 100 seconds. The reduced rate of coating growth with prolonged treatment time has been related to the slowing of mass transport through the coating and the reduced alkalization associated with the cathodic reaction [214]. Notably, the coating thickness

achieved on the alloy matrix following a treatment of 600 s is about 50% of that achieved on the superpure aluminium.

The ultramicrotomy is hard to readily apply to the determination of the thickness of coatings on the Al-Cu-Mg (S) and Al-Cu (θ) phase that are relatively smaller in size present in the alloy and with the hard and brittle nature of the phases. One distinct example of the TCC coatings formed for 60 seconds on the mechanically polished alloys, including α phases, is shown in Fig. 5.12. The coating thickness was ~ 28 nm on the particle, compared with ~ 35 and 20 nm at adjacent and remote regions of the matrix. The normalized zirconium signals from EDX analyses of the coatings formed above θ , S and α particles for 15 and 300 s are shown in Figs. 5.13 (a and b) respectively, revealing the thicker coating above the second phases compared with the matrix and the preferential formation of the coating above the S phase in the early stages of coating formation. Figures 5.13 (c and d) show an S phase particle coated for 15 s and an α phase particle coated for 300 s, with the latter coating displaying cracks. Evidently, the growth rate is significantly higher on these phases than on the matrix, which is associated with the increased local pH of the bath due to the active reactions at these sites [43].

5.2.4 Coating composition by TEM/EDX

Figure 5.14 shows high-resolution TEM/EDX maps of aluminium, oxygen, zirconium, chromium, fluorine, carbon, sulphur and copper in a cross-section of the pre-treated alloy following an immersion treatment for 60 s. It discloses two aluminium-rich layers, one at the coating surface and the other next to the alloy. These layers are separated by a zirconium- and chromium-rich layer. Oxygen, fluorine, sulphur and carbon are present throughout the coating. The last three elements appear to be present in greater concentrations in the inner part of the coating. Carbon is possibly from the contamination of deionized water.[195] Copper is enriched in a thin layer of the alloy beneath the coating. The results for coatings formed for 30, 90, 120 and 300 s were similar to those of Fig. 5.14, but did not reveal an outer aluminium-rich layer. From the evidence of Fig. 5.10(e), this layer appears to be weakly attached to the coating surface and is probably detached easily during ultramicrotomy. EDX maps around the regions of locally increased pre-treated alloy oxidation for the coating formed for 300 s are shown in Figures 5.15(a and b). Fluorine is enriched at these locations

(Fig. 5.15(a), outlined by the arrows). The enriched copper region in the alloy is less evident than elsewhere along the alloy/coating interface. Evidently, the penetration of fluoride into the substrate around the intact copper particles is highlighted by arrows in Fig. 5.15(b). This indicates that the locally enhanced oxidation by the chemical attack of enriched fluorine leads these nano-sized copper-rich particles to dissolve.

5.2.5 Quantitative composition by RBS and NRA

Figure 5.16 shows the experimental and simulated RBS data for two specimens, one in the etched and de-smutted condition and the other following coating for 300 s. The former displays a peak due to the enrichment of copper in the alloy that is generated by the pre-treatment process. This peak is displaced to a slightly lower energy for the coated specimen, since the enrichment now lies beneath the coating. The presence of the coating is indicated by peaks from zirconium and chromium. The main aluminium leading edge is accordingly displaced to a lower energy due to the presence of the coating. However, a small yield is evident from aluminium in the coating. The coating also generated a small signal from sulphur. The sulphur possibly originates from the use of $\text{Cr}_2(\text{SO}_4)_3$ in the SurTec 650 formulation. Hafnium is also detected, which is an impurity presented in zirconium.

The results of RBS examination of the coatings formed for 60, 120 and 300 s of treatment are recorded in Table 5.1. A two-layer model for the coatings formed for 120 and 300 s was sufficient to fit the data. The specimen treated for 60 s revealed an additional aluminium-rich layer at the coating surface, suggesting a mixture of aluminium hydroxide and oxides. Carbon and oxygen were determined by NRA, which provides a more accurate analysis of light elements than the RBS. Chromium and zirconium occur in an atomic ratio of $\sim 0.47 \pm 0.03$ for all times of treatment. The copper contents of the coatings were ~ 0.78 , 0.90 and 0.92 at.% following treatments for 60, 120 and 300 s respectively. The enrichment of copper in the alloy following etching and desmutting of the alloy was $\sim 7.3 \times 10^{15}$ copper atoms cm^{-2} . The values following treatments for 60, 120 and 300 s were 5.5×10^{15} , 6.4×10^{15} and 4.6×10^{15} copper atoms cm^{-2} . The apparent reduction in the copper enrichment may be associated with the localized oxidation of the alloy at the base of the coating, which increased roughness of the alloy/coating interface, particularly after 300 s. Such roughening can lead to an underestimate of the enrichment due to it being spread over an increasing range of depths

beneath the surface of the coating. The localized oxidation possibly caused the copper of the enriched layer to be released and incorporated into the overlying coating material as similar as the situation of the anodic film growth on Al-Cu alloy [209]. The coating thicknesses from TEM and the analyses by RBS and NRA indicated coating densities of 4.45, 3.67 to 3.03 g/cm³ for treatment times of 60, 120 and 300 s respectively.

5.2.6 Chemical states by XPS

The results of XPS analyses of coatings on the pre-treated alloys formed for 300 s are given in Table 5.2, revealing the presence of aluminium, chromium, zirconium, copper, oxygen, fluorine and sulphur. The Table also gives the analyses following correction for carbonaceous contamination on the basis of Seah's method [193]. Figures 5.17 show the high resolution spectra from (a) the Zr 3d and (b) the Al 2p photoelectron regions for a coating formed for 300 s. Two spin orbit split doublets were separated by 3.1 eV in the Zr 3d photoelectron region (Fig. 5.17(a)), where the intensity ratio of the Zr 3d_{5/2} to Zr 3d_{3/2} component was fixed at 1.5:1. Thus, zirconium components consist of ZrO₂ and ZrF₄ with ~97% of the total zirconium being in the form of oxide. Ten peaks were used to fit the Al 2p region in Fig. 5.10(b), which include a peak for Cr 3s components at 80.4 eV and five peaks for Cu 3p species at 75.3, 76.4, 77.7, 78.8 and 85.0 eV as respectively named as d, e, g, h and j symbols. The aluminium metal, oxide and fluoride were revealed by the respective peaks at 72.2 ('a'), 72.6 ('b'), 75.1 ('c') and 76.9 ('f') eV.

Peak fittings of Cu 2p photoelectron region in Figure 5.18 for the specimen treated for 300 s reveals four forms of the chemical states, namely Cu metal, Cu₂O, CuO and Cu(OH)₂. The presence of Cu₂O is possibly attributed to the reduction of Cu(II) by XPS irradiation [209]. The high resolution spectrum of the Cr 2p region for the coating formed for 300 s is shown in Figure 5.19. The spectrum was fitted by Cr(OH)₃ (577.3 eV), Cr₂(SO₄)₃ (578.5 eV), CrF₃ (580.1 eV) and CrO₃ (579.6 eV) [191, 192], with 58, 32, 8 and 2% of the chromium being the associated respective species. The fitting does not provide conclusive evidence of Cr(VI) species, since the Cr(VI) peak is not clearly resolved. If CrF₃ was not considered (Fig. 5.19 (b)), fitting was achieved with ~7% of the chromium as Cr(VI). However, RBS showed that fluorine species were present in the coating.

The percentages of the total amounts of zirconium, aluminium, chromium and copper in the analysed regions of the coating that can be assigned to the various components used to fit the XPS data are shown in Tables 5.3 -5.6. A large discrepancy in the amount of carbon present across the samples, expected to be present as a contamination over layer, makes it difficult to compare the elemental concentrations for each sample. Thus, the data corrected for the carbonaceous contamination are used [193]. The amount of zirconium assigned to ZrO_2 was ~20 to 30 times that assigned to ZrF_4 , with no clear relationship with the treatment time (Table 5.3). In contrast, the aluminium metal component fell to a low value after a treatment of 60 s, due to the thickening of the coating and detection of less aluminium from the alloy substrate, while the amount of aluminium assigned to fluoride relative to oxide tended to increase with time (Table 5.4). The chromium was assigned mainly to $Cr(OH)_3$ and $Cr_2(SO_4)_3$, with the chromium assigned to the former species being between 2 to 8 times that assigned to the latter (Table 5.5). A low percentage, between 2 to 5% of the total chromium was assigned to CrF_3 . Further, between 2 to 9% of the chromium was assigned to CrO_3 . Copper metal, Cu_2O and CuO were detected for all times of treatment (Table 5.6). No consistent trend with treatment time was revealed by any of the copper species. The interpretation of the copper data is also affected by the possible reduction of $Cu(II)$ during XPS analysis.[209]

If a uniform distribution of $Cr(VI)$ is assumed through the coating thickness, the weight percentage of $Cr(VI)$ can be estimated for the results of the XPS and RBS analyses in Table 5.1 and 5.5. The estimated amounts are ~0.6, 0.2 and 0.2 wt.% after treatments for 60 120 and 300 s respectively. $Cr(VI)$ formation in a TCC coating after air ageing for at least 1 h was supposed to arise from oxidation of $Cr(III)$ by H_2O_2 formed during oxygen reduction at copper-rich particles[159], where the alloying elements such as Cu and Mn may play a catalytic role in $Cr(VI)$ formation [54, 215]. And then $Cr(VI)$ diffused through the coating towards the coating surface to provide the active self-healing protection [141, 154, 159]. However, the prolonged air ageing has been suggested to reduce the amount of $Cr(VI)$ in the active aluminium region covered by chromate conversion coatings [80], which may also occur in the present TCC conversion coatings.

5.2.7 Electrochemical behaviour

Figure 5.20 shows the potentiodynamic polarization curves of the bare AA2024-T351 alloy after etching and desmutting and the coated alloys after immersion in the trivalent chromium bath for 300 s. The open-circuit potentials prior to the polarization scan were ~ -0.5 and -0.6 V vs SCE respectively. The corrosion potentials (~ -0.5 V_{SCE}) and the corrosion current densities of these specimens were measured by the Tafel regions of the anodic and cathodic polarization curves. The coatings showed an excellent corrosion protection as evidenced by the significantly decreased $\times 10$ corrosion current density of $\sim 1.4 \times 10^{-7}$ A/cm² in comparison to the situation of the bare alloy ($\sim 1.5 \times 10^{-6}$ A/cm²). Furthermore, the cathodic polarization curves indicated that the TCC coating played a barrier role in effectively impeding the oxygen reduction reaction. By contrast, the limitation of the anodic inhibition was attributed to the presence of cracks on the protruded second-phase particles produced by the pre-treatment. For example, the current densities at -0.6 and $+0.2$ V_{SCE} in the TCC coated specimens were $\sim 4.5 \times 10^{-7}$ and 2.0×10^{-3} A/cm², while the current densities of $\sim 3.0 \times 10^{-6}$ and 2.8×10^{-3} A/cm² was observed in the bare alloys respectively.

For the long-term corrosion protection exposition of TCC coatings, the electrochemical noise analyses (ENA) were used. The fast Fourier transform (FFT) of the time domain data calculated the noise data by the in-house developed software to provide the evidence of frequency domain during the corrosion process [185, 186, 216]. Figure 5.21 shows the real-life corrosion on the bare alloy after etching and desmutting pre-treatment and the TCC coatings formed for 60, 120 and 300 seconds during the long-term immersion in 3.5 wt.% NaCl solution.

The calculation of the electrochemical noise data at 0.005 Hz in the form of time-evolution impedance modulus and noise resistance are shown in Figures 5.22 (a and b) respectively. On the bare alloy control specimen, the evident corrosion was observed and the noise resistance immediately increased from $\sim 2 \times 10^3$ to 1.5×10^4 Ω cm² in the initial period of 10 h. This is in good agreement with the evident corrosion in the real-life macrographs and is consistent with the corrosion propagation on the aluminium alloy [185]. By contrast, the coated alloys after conversion treatment for 60, 120 and 300 s show the larger resistances of $\sim 3 \times$, $4 \times$ and 10×10^4 Ω cm² respectively after the first period of 10 h in the NaCl solution. Furthermore, the corrosion macrographs on the TCC coatings occurred since the immersion in sodium chloride

solution of ~20, 40 and 60 h in Fig. 5.23. It indicated the good corrosion protection by the TCC coatings formed on the pre-treated alloys after conversion treatment for 300 seconds.

The impedance modulus of the coating formed for 300 s initially shows a stable level at $1 \times 10^5 \Omega \text{ cm}^2$ up to the immersion time of 8 h, following a fast decrease down to $\sim 4 \times 10^4 \Omega \text{ cm}^2$. It was possibly attributed to the initiation of a few pits at the crack defects either at the particles or on the matrix. After the stabilization of such pits, a plateau impedance modulus of $1 \times 10^5 \Omega \text{ cm}^2$ met a general decrease to $7 \times 10^4 \Omega \text{ cm}^2$ between the immersion time of 20 and 30 h; and then, the visible corrosion macrograph was also observed after 40 h. This may relate to the consumption of TCC coatings such as the dissolution and mobility of the active chromium species to self-heal the pitting corrosion in this corrosive electrolyte [155]. Finally, the low frequency impedance modulus displayed an impedance of $\sim 2 \times 10^5 \Omega \text{ cm}^2$ until 60 h immersion test. In comparison, the TCC coatings formed for 60 and 120 s show the visible corrosion on the coating surface after the immersion of 20 h, in particular for the coating formed for 60 seconds with the evidence of the general corrosion on the surface. This is attributed to the thinner coatings to ineffectively impede the corrosive mass transport through the coating.

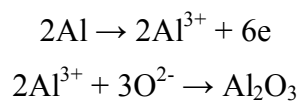
Considering the zero meter application and potential-/current density-time evolution, this measured noise resistance can also be calculated by the Faraday function. In the case of the coating formed for 300 s, the potential difference between the two identical electrodes was ~25 mV with an average current density of $0.9 \mu\text{A cm}^{-2}$ in Figure 5.23 (a). The resultant noise resistance is $\sim 3 \times 10^4 \Omega \text{ cm}^2$. Notably, the peak current densities ($\sim 1 \mu\text{A cm}^{-2}$) and the valley potentials were observed in the specimens after immersion for ~27 and 51 h. This corresponded with the corrosion occurrence on the coated substrate in the form of pits. In addition, the impedance spectroscopy measurements were also recorded and the test procedure proceeds as follows: (i) 30 min OCP measurement and (ii) EIS measurement from 10^5 to 10^{-2} Hz at the OCP level, using a sinusoidal waveform in a scale of 10 mV above the OCP. The reproducible EIS data of three-time measurements are shown in Figure 5.23(b) and were processed with an equivalent circuit model. The corrosion resistance by this coating was calculated to be $\sim 4 \times 10^4 \Omega \text{ cm}^2$, which is in good agreement with the noise resistances of $\sim 3 \times 10^4 \Omega \text{ cm}^2$.

The morphologies of the TCC coating formed for 60 s after 138 h of immersion in 3.5 wt.% NaCl solution were examined by the high-resolution TEM/EDX maps as shown in Figures 5.24 (a and b). The copper signal was visible along the substrate and in the outer layer of the coating region, indicating its release from the surface and incorporation into the main layer of the coating. Further, no significant corrosion defects were observed in the coating, however, the coating possibly swollen up to ~30 nm which is thicker than the coating of 18 nm thick before corrosion test.

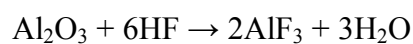
5.3 Discussion

5.3.1 Coating formation

The formation of the zirconium- and chromium-rich coating layer occurs in response to an increase in pH due to the reduction of oxygen and hydrogen evolution. The pH change is enhanced at the second phase particles, which provide preferred cathodic sites, resulting in an increased rate of coating formation at these locations. At the matrix, thinning of the air-formed oxide on the macroscopic alloy surface, due to the presence of fluoride ions [118], and consequent electron tunnelling across the film enable the oxidation and reduction reactions to take place [71]. The main oxidation process at the matrix region of the alloy is the oxidation of aluminium ions leading to formation of amorphous anodic alumina according to the reactions:



The continuation of the process requires the migration of Al^{3+} and/or O^{2-} ions across the alumina layer. In amorphous alumina, the transport numbers of Al^{3+} and O^{2-} ions are typically ~0.4 and 0.6 respectively.[217, 218] The Al^{3+} ions are ejected to the electrolyte under low pH conditions. The alumina is dissolved at the outer region according to the reaction:



The growth of amorphous alumina films on Al-Cu alloys results in an enrichment of copper in the alloy immediately beneath the oxide film [219-223]. In the case of the etched and desmuted alloy, enrichment is initially generated as a result of etching. The level of copper enrichment depends upon the amount of copper in solid-solution. Once the enriched layer is established, the aluminium and copper are incorporated into the alumina in proportion to the concentrations of their in the matrix. During the formation of the alumina layer at the base of the present coating, the enrichment created during etching is expected to be sustained by the continuing formation of the alumina layer at the base of the coating. In the case of the mechanically polished alloy, the enrichment of copper is initially negligible and the enrichment builds as the conversion coating is formed. Since similar coating thicknesses are achieved on the etched and desmuted alloy and on the mechanically-polished alloy, the reduced thickness of the coating on the alloy does not appear to be related to the copper enrichment. The copper is possibly incorporated into the coating as nanoparticles of copper metal at the relatively low potential of the alloy in the SurTec 650 solution, as shown in Fig. 5.25. Once isolated from the substrate, the nanoparticles can be oxidized. The initial generation of the particles may locally enhance the cathodic activity

The compositions of the main layer of the coating formed on the alloy and on aluminium are very similar, although the rate of coating growth above the alloy matrix is slower than on the aluminium. Further, the open-circuit potential is ~400 mV higher during coating formation of the alloy, which can increase the thickness of the alumina film by ~0.4 nm. A consequent reduction in the electron tunnelling may then explain the reduced rate of coating formation of the alloy in comparison with aluminium.

5.3.2 Influence of the second phase particles

In terms of 2-/3-dimension SEM examination of the alloys, the main second-phase particles contains S, θ and α phase particles and the clustered S-/ θ -phase particles were revealed in AA2024-T351 alloys. This presence of clustered particles and the galvanic coupling with aluminium matrix influences surface chemistry to influence the coating homogeneity. For the θ -/ α -phase particles, the cathodic components of copper, iron and manganese relative to the active aluminium matrix lead to the preferential cathodic reaction of oxygen reduction/hydrogen evolution, coupled by the anodic aluminium dissolution of the adjacent matrix. By

contrast, the S phase particles of Al_2CuMg component are relatively anodic. The dealloying reaction of this type particle was observed in a short period of 5 seconds as evidenced by the morphology of cavities and deposits. Notably, some S phase particles become noble and display featureless after a longer period of 15 seconds, similar to the situation in the cathodic θ -/ α -phase particles. This reveals a dual role of the S phase particles in TCC coating initiation. In order to avoid the influence of background generated by the SEM/EDX analysis of $\sim 1\text{ }\mu\text{m}$ in depth, the normalized counts of zirconium relative to the matrix aluminium was used to represent the coating thickness. Thus, the coating thickness appeared a subsequent order as follows, anodic S-phase > cathodic S-/ θ -/ α -phase > aluminium matrix.

The preferential coating deposition over the particles impedes the aluminium dissolution and the growth kinetics were then reduced, following by the lateral growth on the surrounding surface. Consequently, the relative counts of zirconium on the cathodic θ -/ α -phase particles are close to those on the anodic S-phase particles by the SEM/EDX analyses of TCC coatings formed for 300 s. Notably, the coating on the matrix is still the thinnest as determined by the lowest count of zirconium signal. Thus, the improvement of the coating homogeneity on alloys depends on the clean surface chemistry in the absence of second-phase particles.

5.3.3 Compositions of TCC coatings on alloys

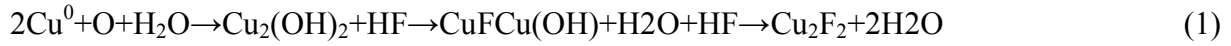
The TCC coating on alloys is a two-layer structure, consisting of a Zr-/Cr-rich outer main layer over a thin alumina layer, where aluminium component in the alumina layer concentrated near substrate. RBS/NRA analysis revealed a constant atomic ratio of chromium relative to zirconium at 0.47 ± 0.03 . The ratio is similar to that determined for treatment of relatively pure aluminium in the same coating bath [224]. Further, the decreased density of TCC coating with prolonged treatment correlates with the interfacial chemistry change, especially the copper release from the substrate. Once isolated from the substrate, the nanoparticles may incorporate into the coating region to impede the mass transport as evidenced by the decreased concentration of aluminium and oxygen that primarily enrich in the inner layer. For coating growth kinetics, the alloys show a similar initiation rate to the superpure Al; after initiation, the relatively intact coatings on alloys ($\sim 3.8\text{ g/cm}^3$) impede the mass transport and lead to a decreased $\times 2$ rates of the coating growth in comparison to the situation of aluminium ($\sim 2.6\text{ g/cm}^3$).

The form of copper component in the coating surface consists of copper metal and copper oxides (Cu_2O , CuO and $\text{Cu}(\text{OH})_2$) by XPS examination. The TEM/EDX maps revealed the locally enhanced oxidation of substrate once the copper-rich particle was isolated from the substrate. In terms of oxidation mechanism, the presence of fluorine and dissolved oxygen has been revealed to promote copper dissolution on the copper surface by a syngeneic effect and the oxidation rate was the first-order kinetic of the individual concentration of fluorine and oxygen [54, 55]. Further, Liu et al have revealed a critical concentration of copper enrichment at 40 at.% to lead to the detachment of the chromate conversion coating, attributed to either the copper nanoparticles incorporation into the coating or gas evolution beneath such coating [89]. For the hydrated TCC coating, the mass transport was suggested to correlate with the presence of channels that were sealed after air ageing treatment to improve corrosion protection [153]. Concerning copper incorporation in the coating region, these nanoparticles may obstruct the hydrated channels to impede the outward egress of aluminium cations, while fluorine ingress was little influenced as revealed in the zirconium-based conversion coating on Al-Cu alloys [210]. Thus, a local acidic environment consisting of fluorine-rich component is highly aggressive to aluminium and copper to enhance the local oxidation. The TEM/EDX maps revealed the evidence of the fluorine enrichment beneath the coating, especially at the locally enhanced oxidation sites.

5.3.4 Cr(VI) formation mechanism

The Cr(VI) oxides in TCC coatings after 24 air ageing were revealed by XPS analysis, with the presence of either CrO_3 or CrO_4^{2-} . Guo et al [155] revealed the presence of chromium in the sodium chloride solution after corrosion testing of the TCC coatings and suggested that the mobile hexavalent chromate may be produced in the corrosive environment. Further, Li et al [150, 159] used Raman spectroscopy to reveal the fingerprint evidence of the Cr(VI)-O band in the coating after at least 1 hour or after the corrosion test. They further revealed the effectiveness of hydrogen peroxide on the oxidation of trivalent chromium conversion coatings. One reasonable hypothesis is that the dissolved oxygen was reduced to hydrogen peroxides around cathodic copper-rich particle and then H_2O_2 oxidized Cr(III) to Cr(VI) species. In our case, the trivalent chromium bath is naturally-aerated and the transient formation of H_2O_2 was reasonable to explain the formation of Cr(VI) species. In terms of the

chemistry environment of H_2O_2 formation, aluminium dissolution provides sufficient electrons on the substrate and copper particles may play a catalytic role under the fluorine environment as follows [54].



Considering these factors, the transformation mechanism by oxidation of H_2O_2 is more reasonable.

5.3.5 Electrochemical behaviour

The TCC coatings as a pH-deposited film mainly play a role of the cathodic barrier against corrosion as evidenced by the relatively significant inhibition of the cathodic polarization behaviour. A reduced factor of 10 of corrosion current densities was revealed in comparison to the situation of the bare alloy. This is in a good agreement with the report by Guo et al, who suggested that TCC coating limited the availability of oxygen into the coating and consequently suppressed its reduction reaction on alloys [148].

The improved corrosion protection by the TCC coatings formed for 300 seconds has been revealed by the electrochemical impedance spectroscopy (EIS) in 0.5 M NaCl solution and the electrochemical noise analysis (ENA) in 3.5 wt.% NaCl solution. The best process on the alloys after alkaline etching and nitric acid desmutting is the coating formed for 300 seconds, followed by immersion in deionized water for 120 seconds. The EIS results are in excellent agreement with the low-frequency impedance modulus by the ENA examination, where the impedance modulus represents the corrosion resistance of coatings [183, 185]. Further, the level of corrosion resistance of $\sim 10^5 \Omega \text{ cm}^2$ is acceptable for protection by conversion coating of nanometre thickness [167]. Notably, the real-life macrographs of the TCC coatings provide the direct evidence of corrosion, where the absence of corrosion was observed in the coating formed for 300 s after a long-term immersion up to 60 hours. Concerning the effect of the

corrosive solution on the coated substrate, the TEM/EDX maps of the TCC coating formed for 60 s reveal that it is swollen with the presence of corrosion products. Notably, the release of copper particles from the substrate and incorporation into the coating region indicate corrosion occurrence and this thin coating cannot provide an effective barrier against corrosion.

5.4 Summary

1. TCC coating preferentially initiates around the second-phase particles and the S-phase particles play a dual role, one type being anodic dealloying with the fast coating formation and the other type with an intact morphology as similar as that on cathodic θ -/ α -phase particles.
2. The coating formed on AA2024-T351 alloy in a SurTec 650 bath usually consists of two layers, comprising a main layer containing chromium and zirconium species, with an atomic ratio of chromium to zirconium of $\sim 0.47 \pm 0.03$, and a thinner, underlying aluminium-rich layer. A thin layer of hydrated alumina may also form at the coating surface.
3. The coating growth on the alloy occurs at an average rate of ~ 0.23 nm/s during the first 120 s of treatment, and then decreases to ~ 0.04 nm/s. The coating thickness reaches ~ 50 nm following a treatment of 600 s, which is roughly 50% of that achieved on aluminium in the same time.
4. Hydroxide, oxide, fluoride and sulphate species are present in the coating. Zirconium is mainly present as oxide, while chromium is present mainly as hydroxide. Small amounts of fluoride are associated with both metals, while sulphate is associated with chromium.
5. The enhanced local corrosion with the feature of substrate recession along the copper-rich layer in the coatings formed for 120 s correlates with the fluorine enrichment and the chemical attack promotes the local dissolution of aluminium and copper.

6. XPS data indicated the presence of Cr(VI) species in the coating. Using RBS data, the total amount of Cr(VI) was estimated to be ~0.1 to 1% of the coating weight. The formation of the Cr(VI) is associated with the generation of H_2O_2 by reduction of oxygen.

7. TCC coating primarily provides the cathodic barrier against corrosion and the long-term corrosion protection by the TCC coatings formed for 300 s was revealed by the electrochemical noise analyses to be as long as ~60 hour in 3.5 wt.% NaCl solution.

Figure Captions 5.1-5.25

Figure 5.1 Scanning electron micrographs of the AA2024-T351 alloy after the mechanical polishing to 0.25 μm finish. (a) Clustering for S phase (grey particles; red arrow) and θ phase (bright particles; yellow arrow), (b) α phase particles of $\sim 10\text{ }\mu\text{m}$ in size, (c and d) the corresponding EDX analyses of the second-phase particles.

Figure 5.2 (a) Particle distribution in space by 3D-SEM examination in a dimension of $42.5 \times 47.3 \times 25\text{ }\mu\text{m}$, where the histogram value ranges from 0 to 255; (b) the nearest neighbour distribution of particles was simulated as 1.29 μm (red line), revealing the clustered distribution of particles in space.

Figure 5.3 Scanning electron micrographs of the TCC coatings formed for 5 s at the Al-Cu (name I) and Al-Cu-Mg (named II) phase particles at 3 kV and the following EDX line scan corresponds to the yellow line across the Al-Cu-Mg particle along 3 μm dimension.

Figure 5.4 Scanning electron micrographs of the TCC coatings formed for 5 s at the α phase particle (named III) at 3 kV and the square area was examined in higher magnification on the right, where the yellow arrows marked the copper-enriched particle on the surface and the relative porous matrix indicated the acidic etching effect during immersion in the SurTec 650 solution.

Figure 5.5 (a) Scanning electron micrographs of the TCC coatings formed for 15 s at the Al-Cu (name I) and Al-Cu-Mg (named II) phase particles at 3 kV, where the yellow arrow marks the spherical deposits from solution and (b) EDX point analyses corresponded to the red points named as 1, 2 and 3 and the inert spectra is highlighted with the amount of zirconium relative to the count of aluminium.

Figure 5.6 Scanning electron micrographs of the TCC coatings formed for 15 s at the S phase particles (named II) at 15 kV by the secondary electron (SE2) and backscattering electron (ASB) signals, and the following EDX map analyses revealed the variance of TCC coatings on these form of particles as evidenced by the zirconium maps.

Figure 5.7 SEM/EDX analyses of the count of zirconium relative to the count of aluminium, which revealed a proportional correlation with the coating thickness and the variance on the particles and matrix in the TCC coatings formed for (a) 30 s and (b) 60 s.

Figure 5.8 Time-dependent evolution of the open circuit potential of the polished and pre-treated AA 2024-T3 alloys after during immersion in a dilute SurTec 650 bath at 40 °C

Figure 5.9 (a and b) The topographic maps of height and potential of the bare AA2024-T3 alloy after pre-treatment with alkaline etching and nitric acid desmutting by the examination of scanning Kelvin probe force spectroscopy; (c and d) the SEM/EDX analyses of the pre-treated alloy surface with the presence of Mn-/Cu-rich particles and matrix, named 1 and 2 respectively.

Figure 5.10 Transmission electron micrographs of ultramicrotomed cross-sections of the TCC coatings on pre-treated AA2024-T3 alloy formed for different times: (a) 15 s; (b) 60 s; (c) and (d) 120 s; (e) 300 s and (f) 750 s on the mechanically polished alloys in a dilute SurTec 650 bath at 40 °C. The TEM sample of figure (d) was collected in ethanol-based solution.

Figure 5.11 The time-dependent evolution of the average thickness of TCC coatings formed on the matrix of pre-treated alloy in the dilute SurTec 650 bath at 40°C. The coating grows linearly over the first 120 seconds of treatment at a rate of ~ 0.23 nm/s, which is followed by a reduced growth rate of ~ 0.04 nm/s.

Figure 5.12 Transmission electron micrographs of ultramicrotomed cross-sections of the TCC coatings on the polished alloy matrix after TCC coating treatment of 60 seconds: (a) and (b) Al-Cu-Fe-Mn-Si phase particle; (c) the matrix far away the particles.

Figure 5.13 The normalized amount of the elemental components relative to the count of aluminium by SEM/EDX analyses of the TCC coatings formed on the pre-treated alloys: (a) 15 s; (b) 300 s; (c) the matrix and (d) S phase particles.

Figure 5.14 The high angular annular dark field (HAADF) transmission electron micrograph and EDX elemental maps of a coating formed on pre-treated AA 2024-T3 alloy for 60 s in a dilute SurTec 650 bath at 40°C.

Figure 5.15 High angular annular dark field (HAADF) transmission electron micrograph and EDX elemental maps of a coating formed on pre-treated AA 2024-T3 alloy for 300 s in a dilute SurTec 650 bath at 40°C for two different samples (a and b).

Figure 5.16 Experimental and simulated (solid line) RBS spectra for the AA2024-T3 alloy in the etched and de-smutted condition and following coating for 300 s in a dilute SurTec 650 bath at 40°C.

Figure 5.17 High resolution XPS spectra for: (a) Al 2p; and (b) Zr 3d photoelectron regions and curve fitting for the pre-treated AA 2024-T3 alloy following coating for 300 s in a dilute SurTec 650 bath at 40°C.

Figure 5.18 High resolution XPS spectrum for the Cr 2p photoelectron regions and curve fitting for the pre-treated AA 2024-T3 alloy following coating for 300 s in a dilute SurTec 650 bath at 40°C.

Figure 5.19 High resolution XPS spectrum for Cu 2p photoelectron regions and curve fitting for the pre-treated AA 2024-T3 alloy following coating for 300 s in a dilute SurTec 650 bath at 40 °C

Figure 5.20 The potentiodynamic polarization curves of the bare AA2024-T351 alloy after alkaline etching and nitric acid desmutting and the coated alloys after immersion in the trivalent chromium bath for 300 s with the standard post-treatment. The open-circuit potentials prior to the polarization scan are ~ -0.5 and -0.6 V vs SCE respectively and both of the corrosion potentials were measured at ~ -0.5 V_{SCE}.

Figure 5.21 The real-time images with corrosion evolutions up to 60 h for the bare alloy reference and the TCC coating formed for 60, 120 and 300 s in the 3.5 wt.% NaCl electrolyte.

Figure 5.22 The time evolution of the impedance modulus (left) and noise resistance (right) at 0.005 Hz by the electrochemical noise analysis for the bare alloy reference and TCC coating formed for 60, 120 and 300 s in the 3.5 wt.% NaCl electrolyte.

Figure 5.23 The time evolution of current density and potential at 0.005 Hz (left) by the electrochemical noise analysis in the 3.5 wt.% NaCl electrolyte and the electrochemical impedance spectroscopy analysis (right) for the TCC coating formed for 300 s in the 0.05 M NaCl solution.

Figure 5.24 The high-resolution transmission electron micrographs and EDX maps of TCC coating formed for 60 after the long-term ENA test for 138 h in the 3.5 wt.% NaCl electrolyte for two positions (a) and (b).

Figure 5.25 The schematic diagram displaying the trivalent chromium conversion coating formation process with copper evolution into the coating on the pre-treated alloys, where the free copper islands incorporation into the TCC coating by proceeding HF attack, leading to substrate recession features.

Table 5.1 RBS and NRA analyses ($\times 10^{15}$ atomic/cm²) of TCC coatings formed for different times on pre-treated alloys.

	Zr	Cr	Hf	S	F	Al	Cu	O _{NRA}	C _{NRA}	Cr/Zr
60 s	15.32	7.15	0.10	0.82	34.61	21.04	1.73	124.47	13.31	0.47
120 s	23.50	10.97	0.16	1.25	54.75	38.99	2.73	143.61	23.34	0.47
300 s	28.36	13.23	0.19	1.51	68.74	30.07	2.92	141.81	30.82	0.47

Table 5.2 Results of XPS analyses (at.%) of coatings on pre-treated alloys with treatment for 300 s before and following correction for the carbonaceous overlayer.

Element	Before	After
Zr	8.5	19.7
Cr	2.3	6.2
O	31.6	51.8
Al	5.9	8.7
S	0.6	0.9
F	5.1	9.9
Cu	0.5	2.9
C	45.6	-

Table 5.3 The relative concentration (%) for Zr component in the Zr 3d photoelectron region for coatings formed on pre-treated alloys with treatment times of 15, 30, 60, 120, 300 and 600 s after carbonaceous correction.

	ZrO ₂	ZrF ₄	ZrO ₂ /ZrF ₄
15 s	95.31	4.69	20.3
30 s	96.98	3.02	32.1
60 s	96.16	3.84	25.0
120 s	97.12	2.88	33.7
300 s	96.87	3.13	30.7
600 s	96.47	3.53	29.0

Table 5.4 The relative concentration (%) for Al component in aluminium species of Al 2p photoelectron region for coatings formed on pre-treated alloys with treatment times of 15, 30, 60, 120, 300 and 600 s after carbonaceous correction. The sum concentration of Al(3+) comes from the addition of those in Al₂O₃ and AlF₃.

	Al(0)	Al ₂ O ₃	AlF ₃	Al(3+)	Al(0)/Al(3+)
15 s	10.2	86.7	3.1	89.8	0.11
30 s	13.5	80.7	5.8	86.5	0.16
60 s	3.6	93.3	3.1	96.4	0.04
120 s	4.0	72.3	23.6	96.0	0.04
300 s	0	37.8	62.2	100	0
600 s	3.9	50.2	45.9	96.1	0.04

Table 5.5 The relative concentration (%) for Cr component in the Cr 2p photoelectron region for coatings formed on pre-treated alloys with treatment times of 15, 30, 60, 120, 300 and 600 s after carbonaceous correction.

	Cr	Cr(OH) ₃	Cr ₂ (SO ₄) ₃	CrF ₃	CrO ₃	Cr(VI)/Cr(III)
15 s		70.1	23.2	3.2	2.6	0.027
30 s		70.9	23.9	2.7	2.5	0.026
60 s		59.2	25.5	6.2	9.1	0.100
120 s		59.4	31.9	7.5	2.4	0.026
300s		58.2	31.9	7.5	2.4	0.025
600 s		63.9	28.1	2.4	4.8	0.050

Table 5.6 The relative concentration (%) for Cr component in the Cr 2p photoelectron region for coatings formed on pre-treated alloys with treatment times of 15, 30, 60, 120, 300 and 600 s after carbonaceous correction. The sum concentration of Cu(I) and Cu(II) is calculated by the individual concentration of Cu₂O and CuO.

	Cu	Cu metal	Cu ₂ O	CuO	Cu(I)+Cu(II)
15 s		23.5	25.7	50.8	76.5
30 s		43.2	56.1	0.8	56.8
60 s		74.9	9.1	16.1	25.1
120 s		12.2	13.3	74.5	87.8
300s		15.5	17.6	66.9	84.5
600 s		23	29.3	47.7	77

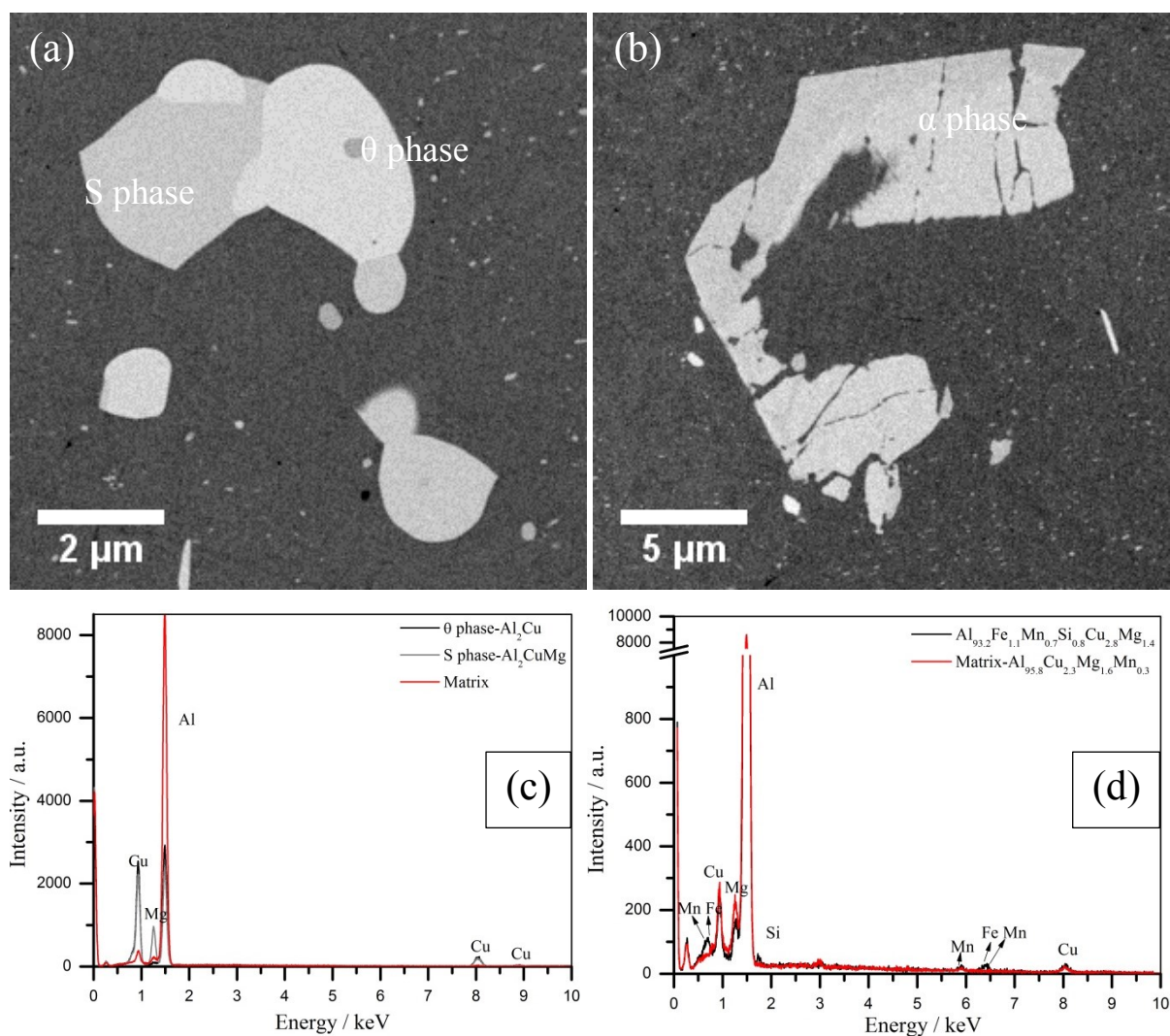


Figure 5. 1 Scanning electron micrographs of the AA2024-T351 alloy after the mechanical polishing to 0.25 μm finish. (a) Clustering for S phase (grey particles; red arrow) and θ phase (bright particles; yellow arrow), (b) α phase particles of ~10 μm in size, (c and d) the corresponding EDX analyses of the second-phase particles.

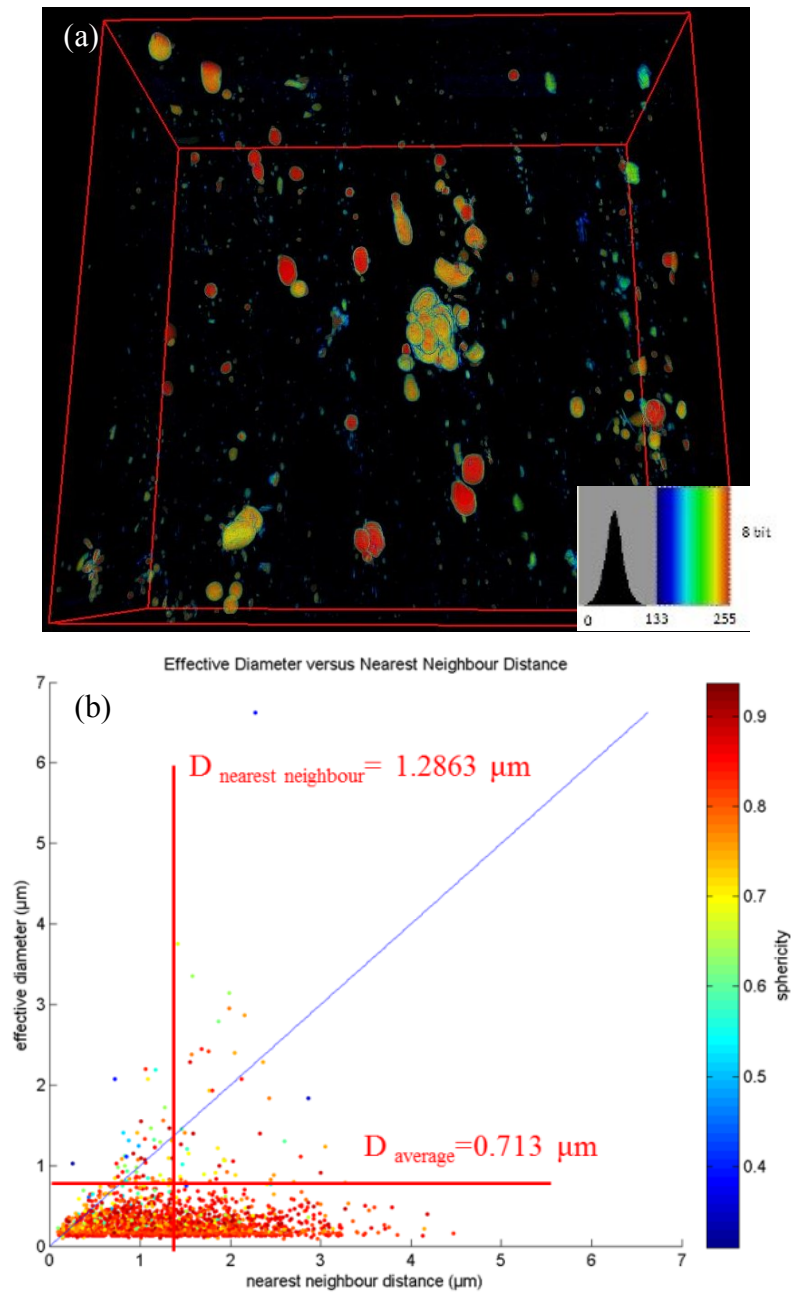


Figure 5. 2 (a) Particle distribution in space by 3D-SEM examination in a dimension of $42.5 \times 47.3 \times 25 \mu\text{m}$, where the histogram value ranges from 0 to 255; (b) the nearest neighbour distribution of particles was simulated as $1.29 \mu\text{m}$ (red line), revealing the clustered distribution of particles in space.

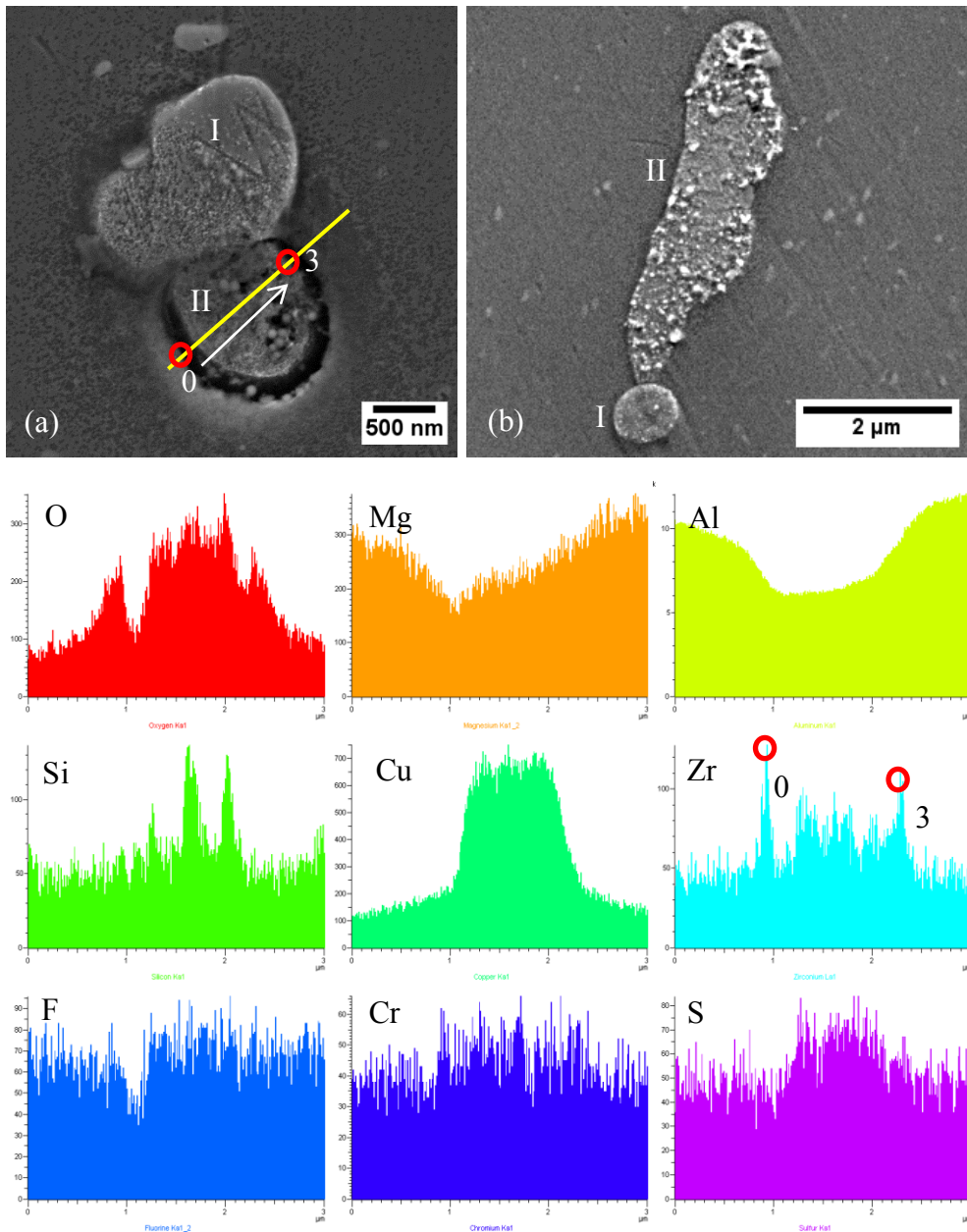


Figure 5. 3 Scanning electron micrographs of the TCC coatings formed for 5 s at the Al-Cu (name I) and Al-Cu-Mg (named II) phase particles at 3 kV and the following EDX line scan corresponds to the yellow line across the Al-Cu-Mg particle along 3 μm dimension.

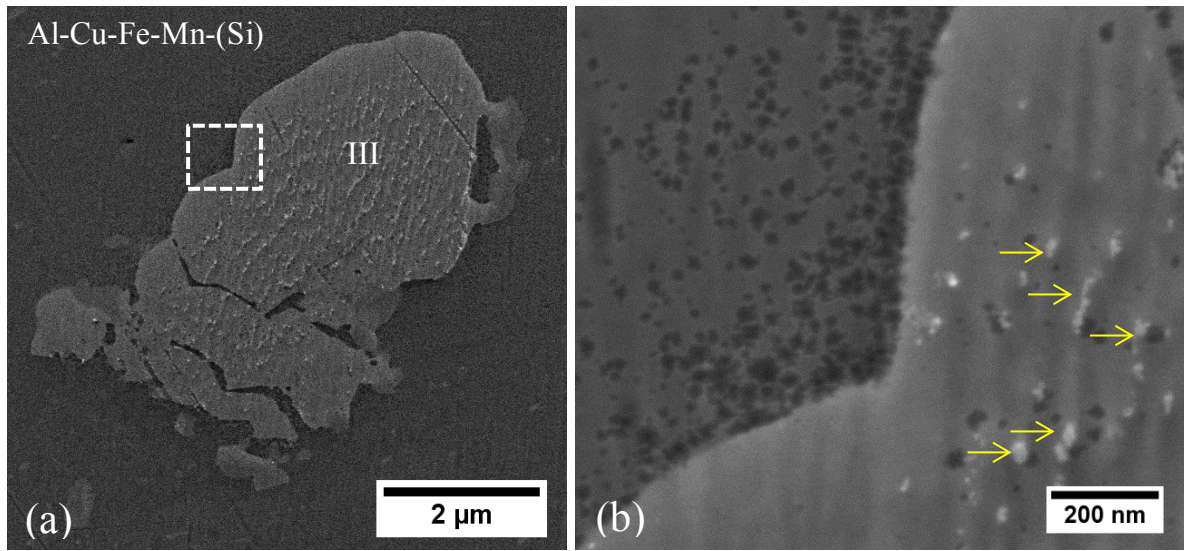


Figure 5. 4 Scanning electron micrographs of the TCC coatings formed for 5 s at the α phase particle (named III) at 3 kV and the square area was examined in higher magnification on the right, where the yellow arrows marked the copper-enriched particle on the surface and the relative porous matrix indicated the acidic etching effect during immersion in the SurTec 650 solution.

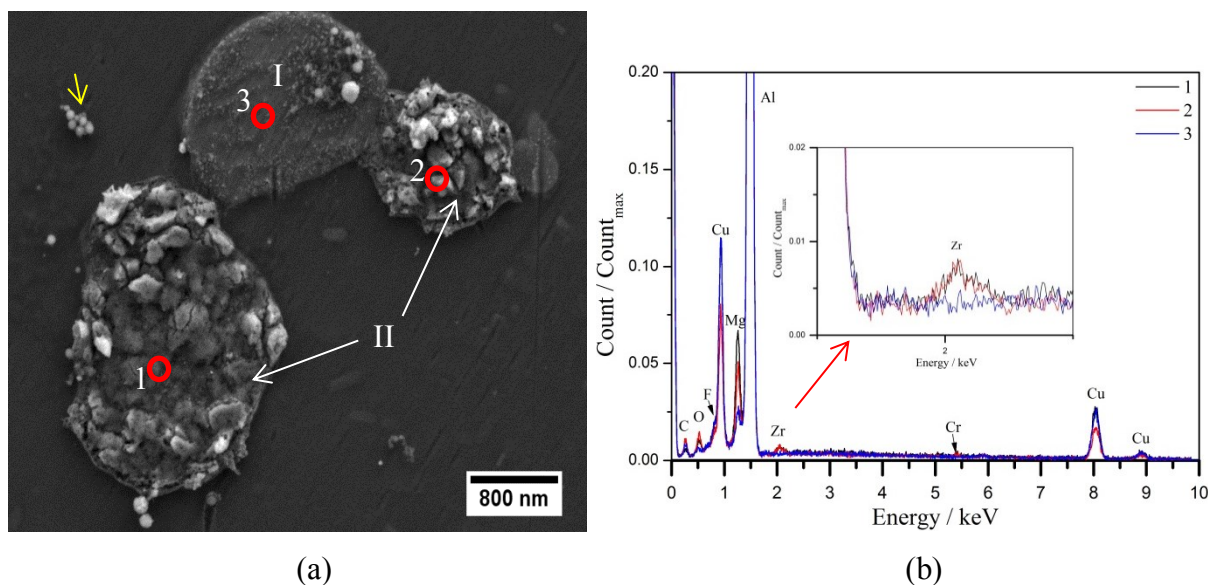


Figure 5. 5 (a) Scanning electron micrographs of the TCC coatings formed for 15 s at the at the Al-Cu (name I) and Al-Cu-Mg (named II) phase particles at 3 kV, where the yellow arrow marks the spherical deposits from solution and (b) EDX point analyses corresponded to the red points named as 1, 2 and 3 and the inert spectra is highlighted with the amount of zirconium relative to the count of aluminium.

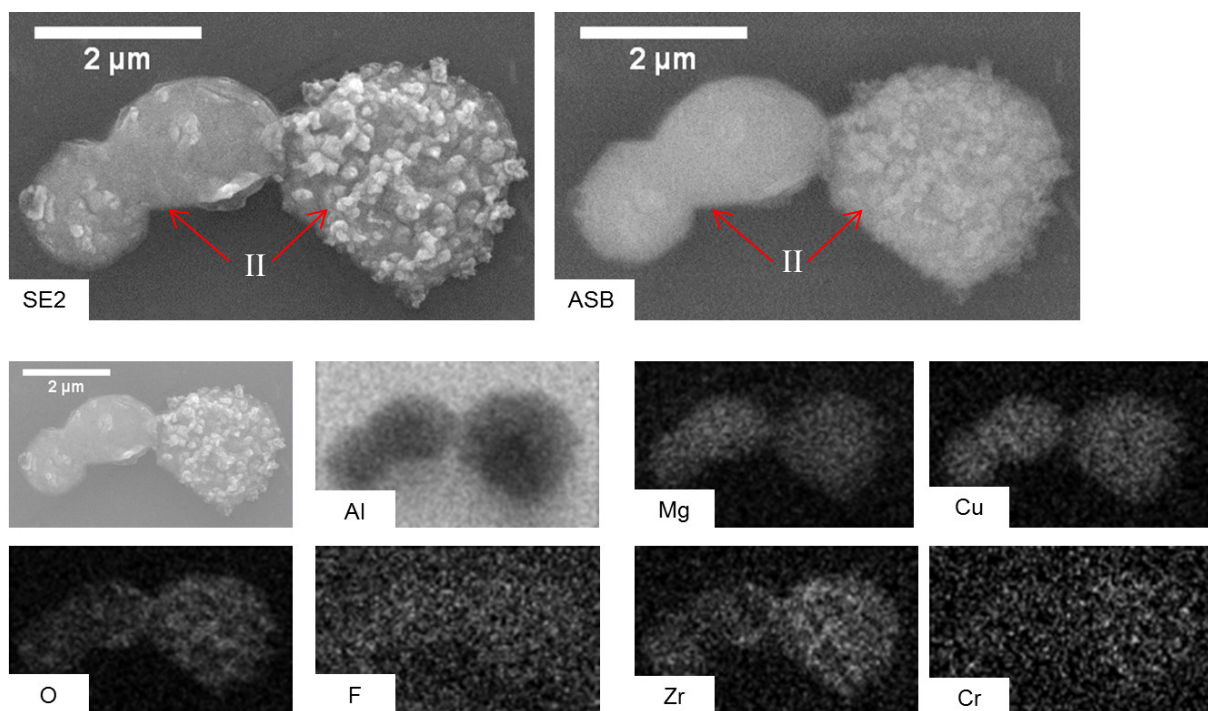


Figure 5. 6 Scanning electron micrographs of the TCC coatings formed for 15 s at the at S phase particles (named II) at 15 kV by the secondary electron (SE2) and backscattering electron (ASB) signals, and the following EDX map analyses revealed the variance of TCC coatings on these form of particles as evidenced by the zirconium maps.

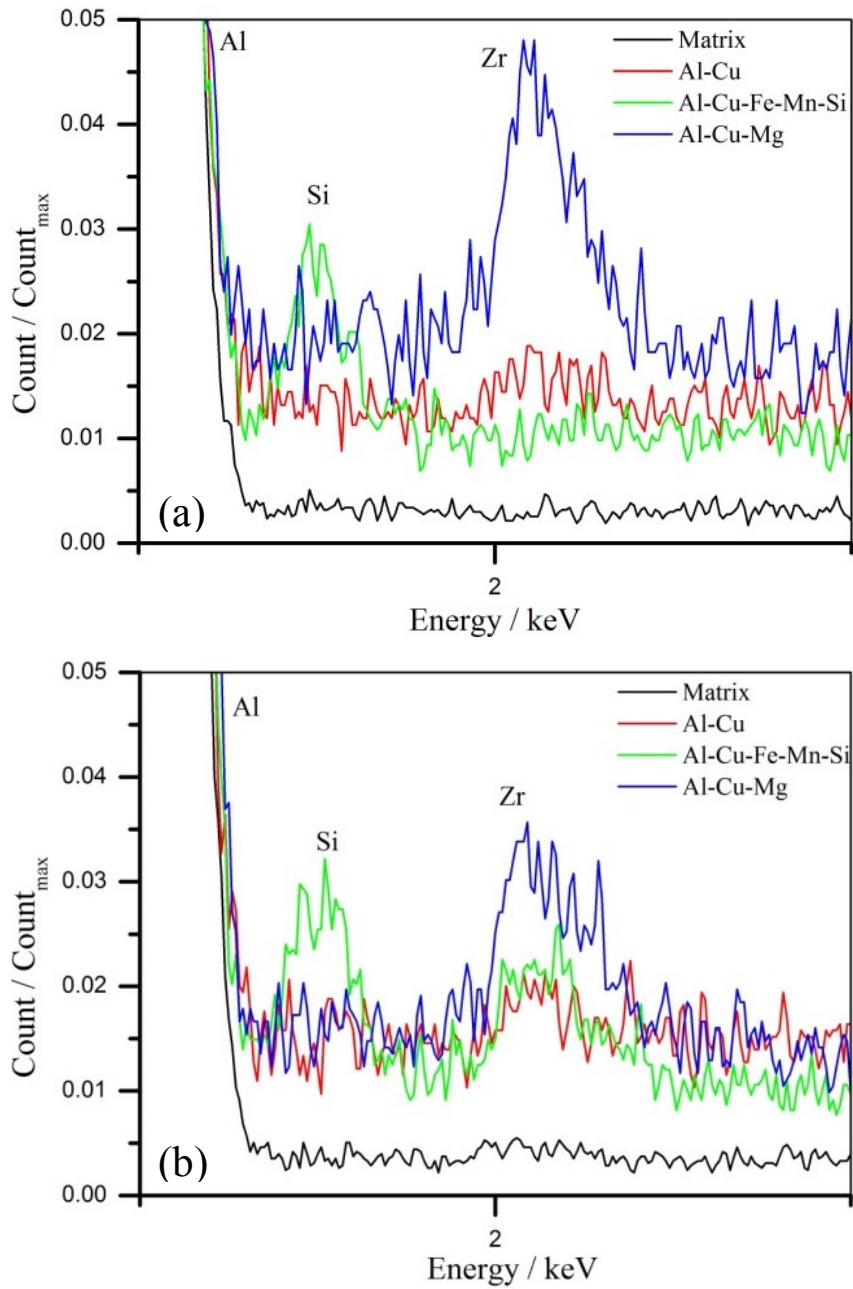


Figure 5. 7 SEM/EDX analyses of the count of zirconium relative to the count of aluminium, which revealed a proportional correlation with the coating thickness and the variance on the particles and matrix in the TCC coatings formed for (a) 30 s and (b) 60 s.

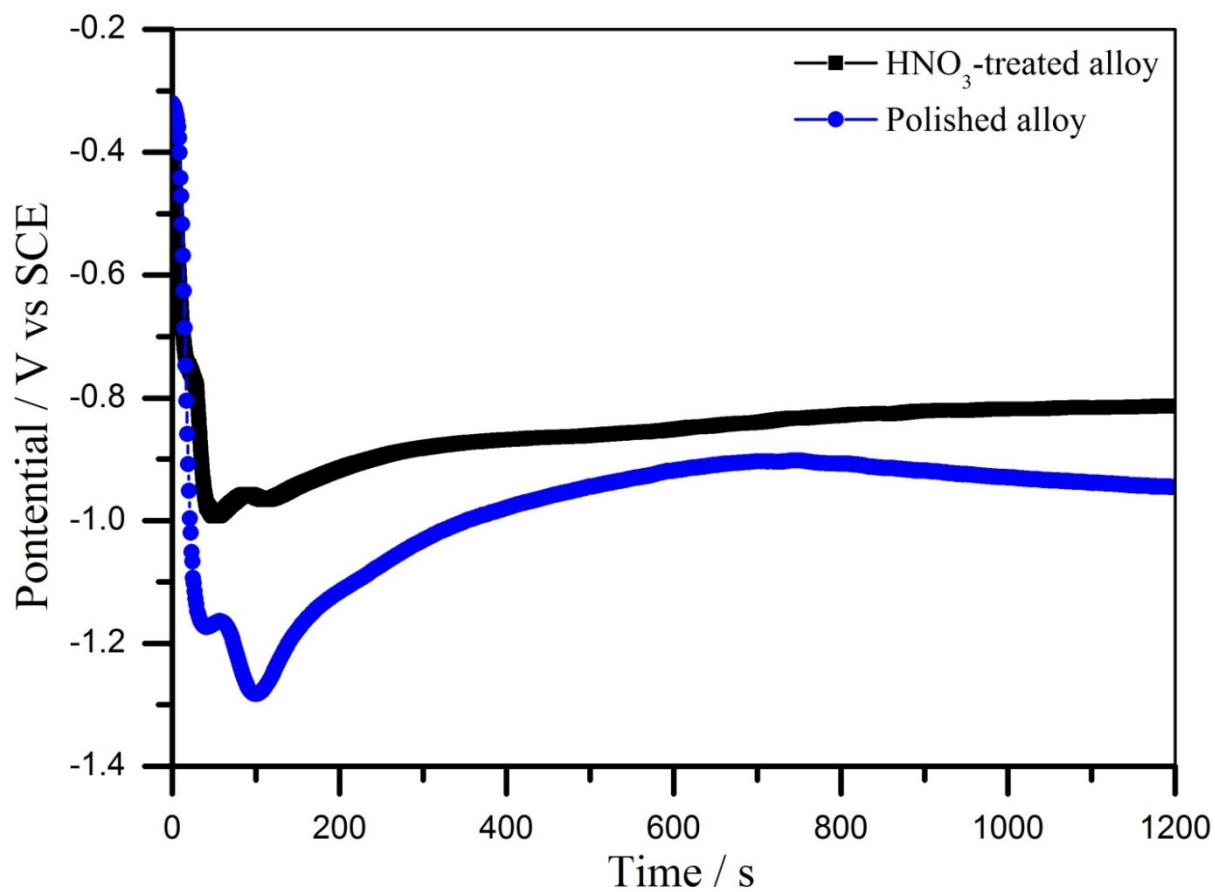


Figure 5. 8 Time-dependent evolution of the open circuit potential of the polished and pre-treated AA 2024-T3 alloys after during immersion in a dilute SurTec 650 bath at 40 °C

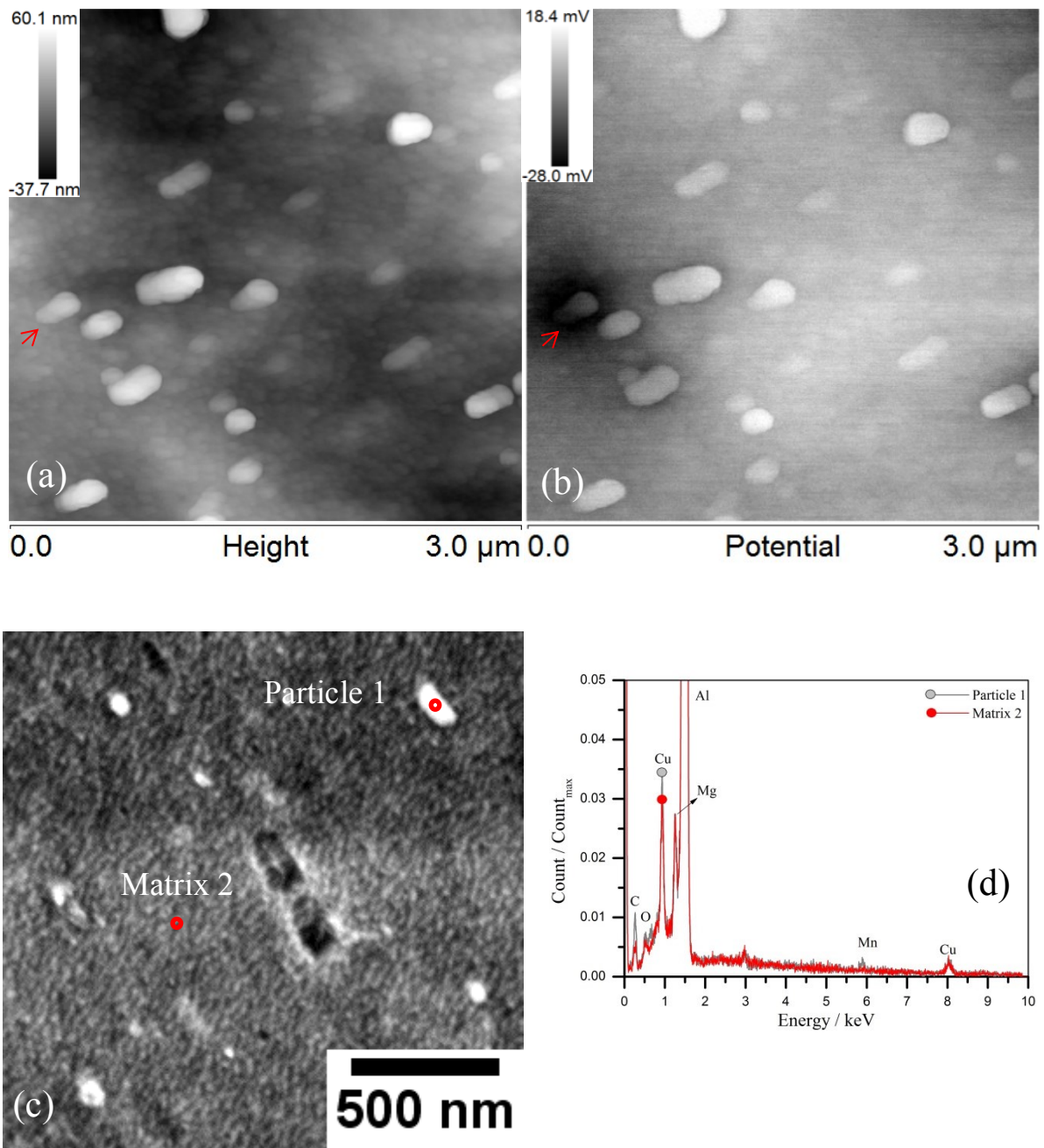


Figure 5. 9 (a and b) The topographic maps of height and potential of the bare AA2024-T3 alloy after pre-treatment with alkaline etching and nitric acid desmutting by the examination of scanning Kelvin probe force spectroscopy; (c and d) the SEM/EDX analyses of the pre-treated alloy surface with the presence of Mn-/Cu-rich particles and matrix, named 1 and 2 respectively.

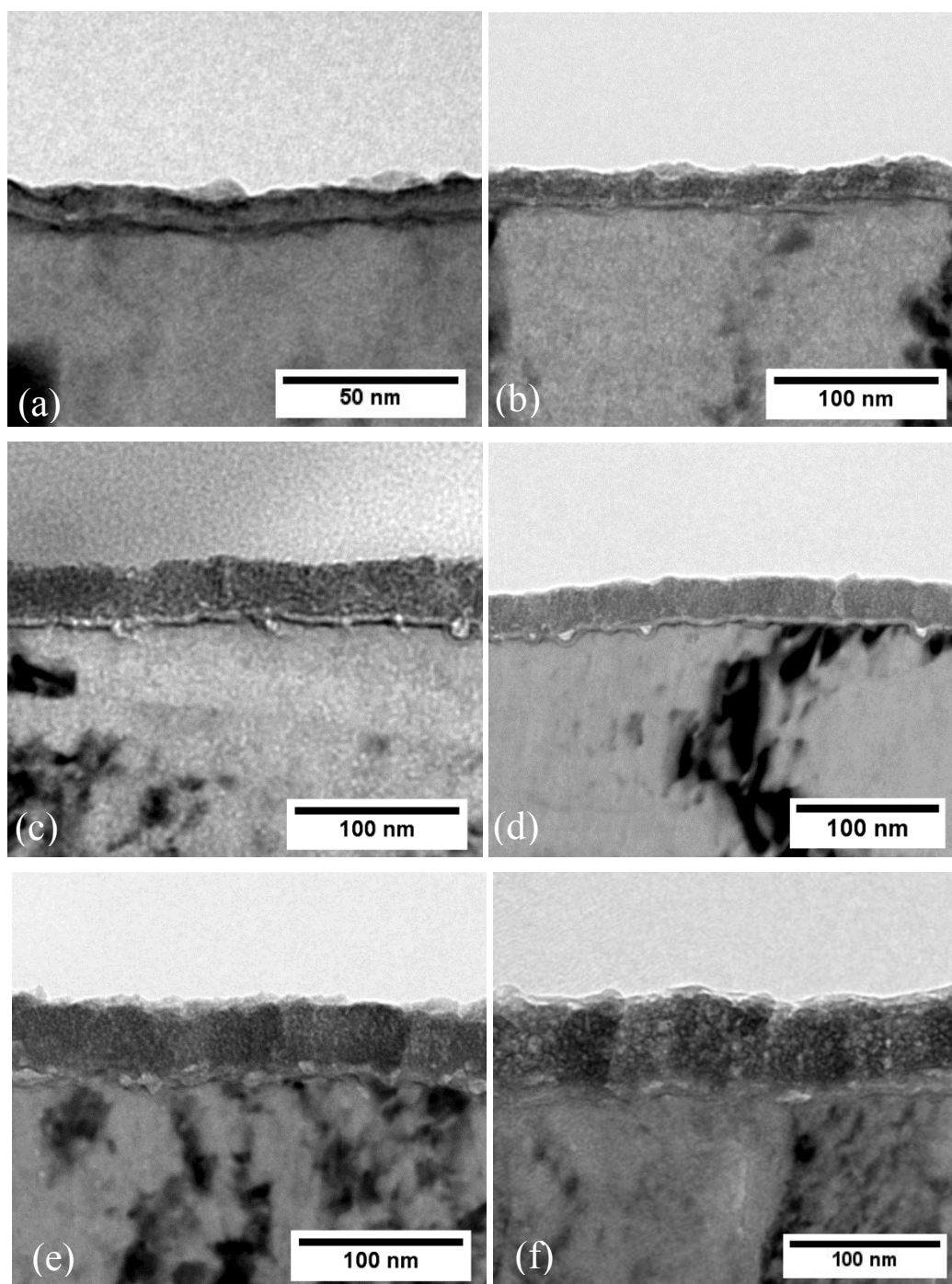


Figure 5. 10 Transmission electron micrographs of ultramicrotomed cross-sections of the TCC coatings on pre-treated AA2024-T3 alloy formed for different times: (a) 15 s; (b) 60 s; (c) and (d) 120 s; (e) 300 s and (f) 750 s on the mechanically polished alloys in a dilute SurTec 650 bath at 40 °C. The TEM sample of figure (d) was collected in ethanol-based solution.

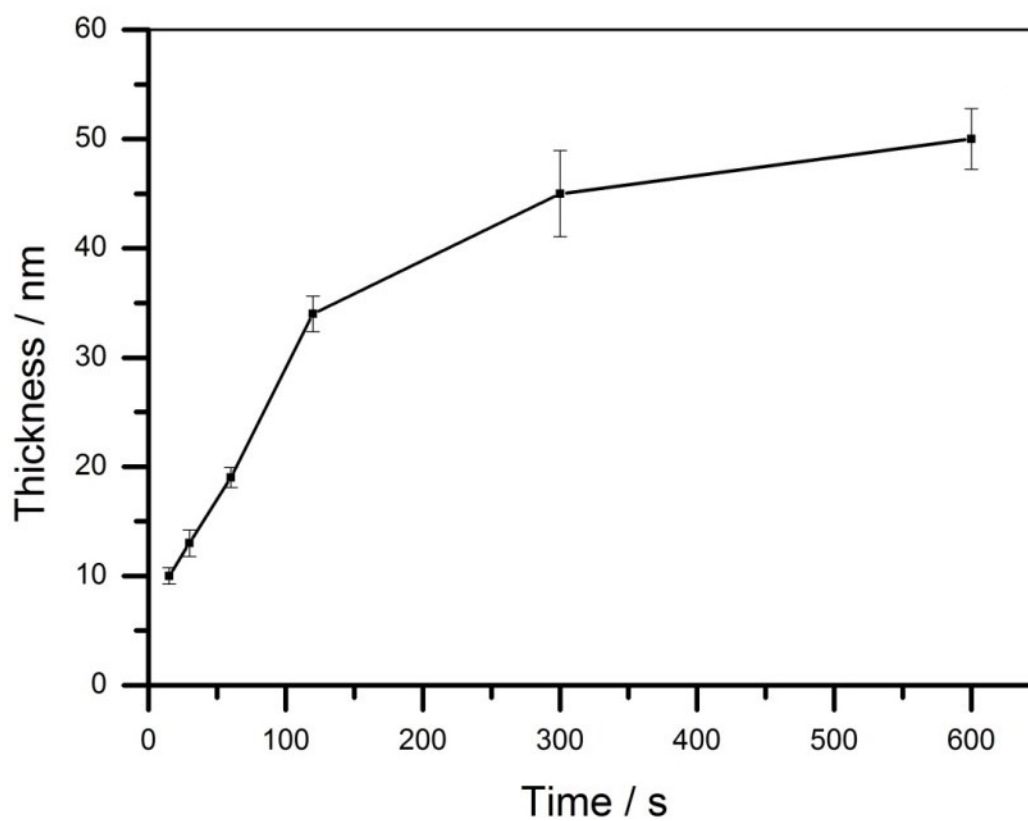


Figure 5. 11 The time-dependent evolution of the average thickness of TCC coatings formed on the matrix of pre-treated alloy in the dilute SurTec 650 bath at 40 °C. The coating grows linearly over the first 120 seconds of treatment at a rate of ~ 0.23 nm/s, which is followed by a reduced growth rate of ~ 0.04 nm/s.

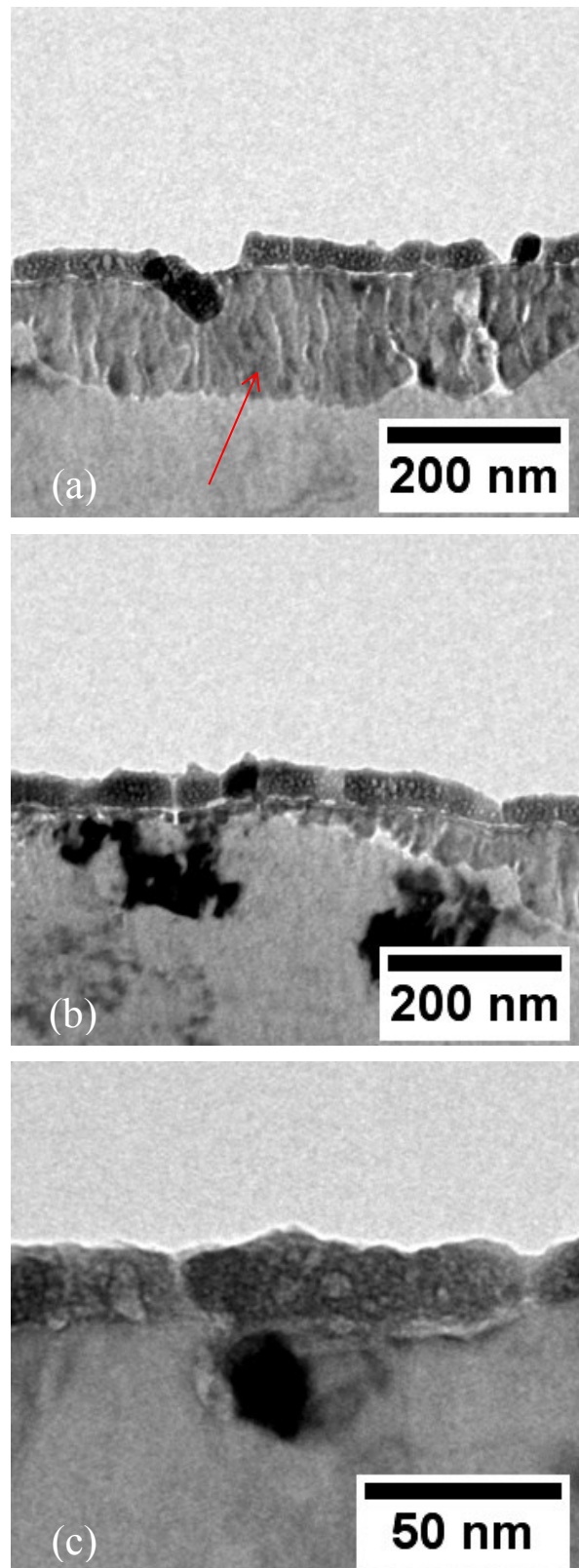


Figure 5. 12 Transmission electron micrographs of ultramicrotomed cross-sections of the TCC coatings on the polished alloy matrix after TCC coating treatment of 60 seconds: (a) and (b) Al-Cu-Fe-Mn-Si phase particle; (c) the matrix far away the particles.

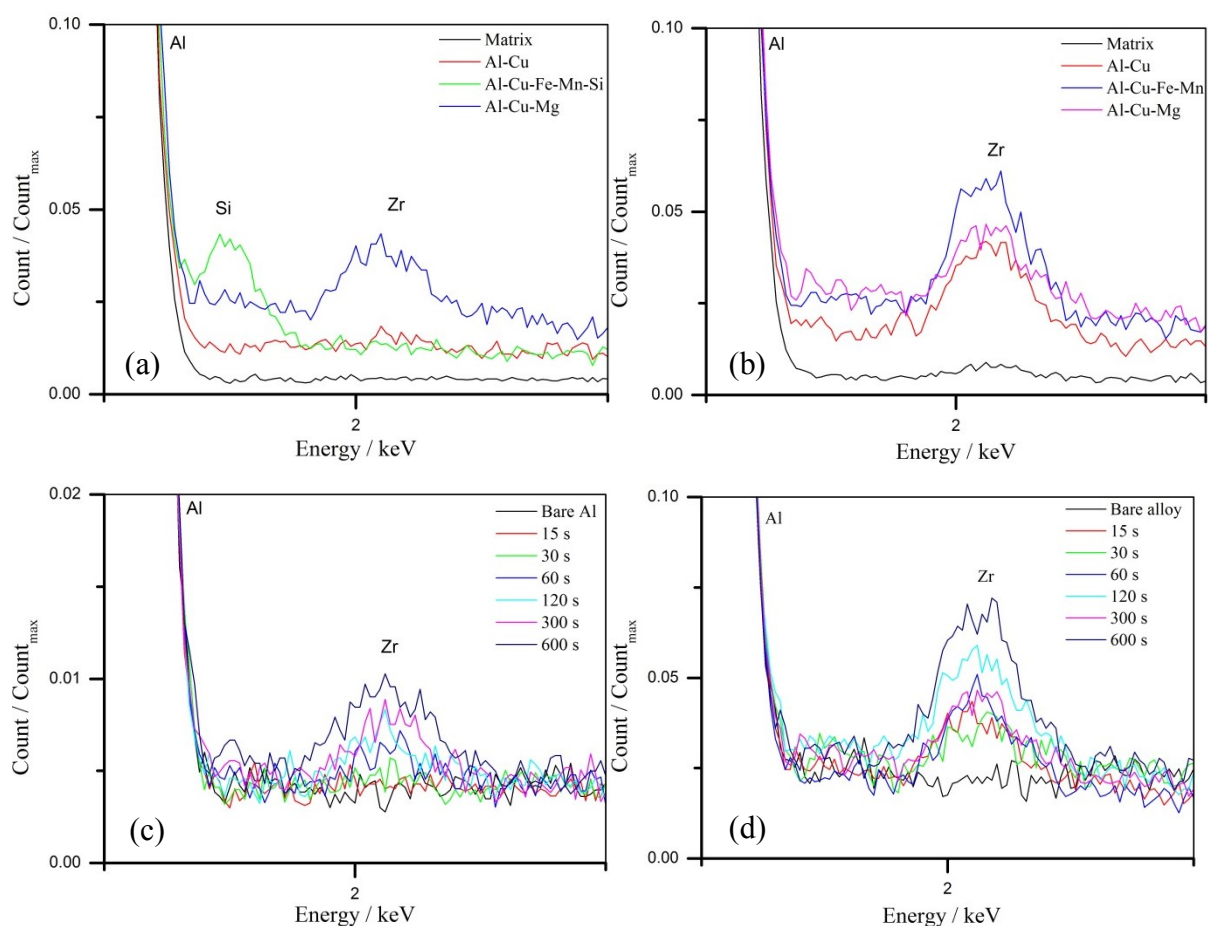


Figure 5. 13 The normalized amount of the elemental components relative to the count of aluminium by SEM/EDX analyses of the TCC coatings formed on the pre-treated alloys: (a) 15 s; (b) 300 s; (c) the matrix and (d) S phase particles.

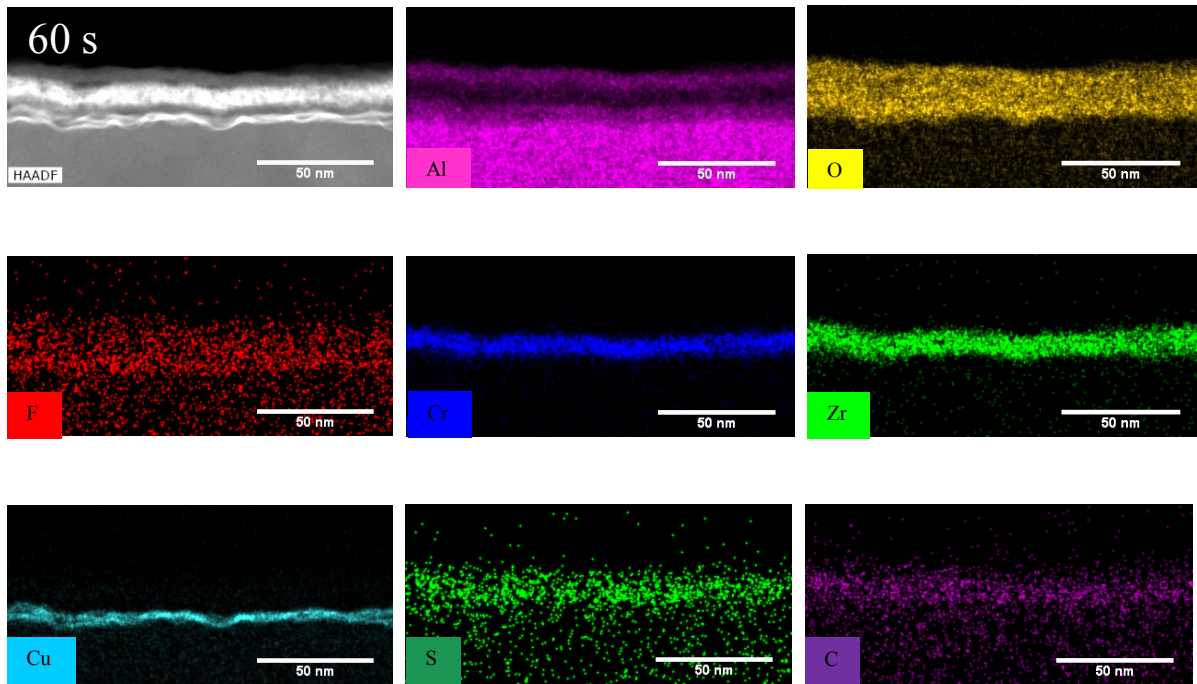


Figure 5. 14 The high angular annular dark field (HAADF) transmission electron micrograph and EDX elemental maps of a coating formed on pre-treated AA 2024-T3 alloy for 60 s in a dilute SurTec 650 bath at 40 °C.

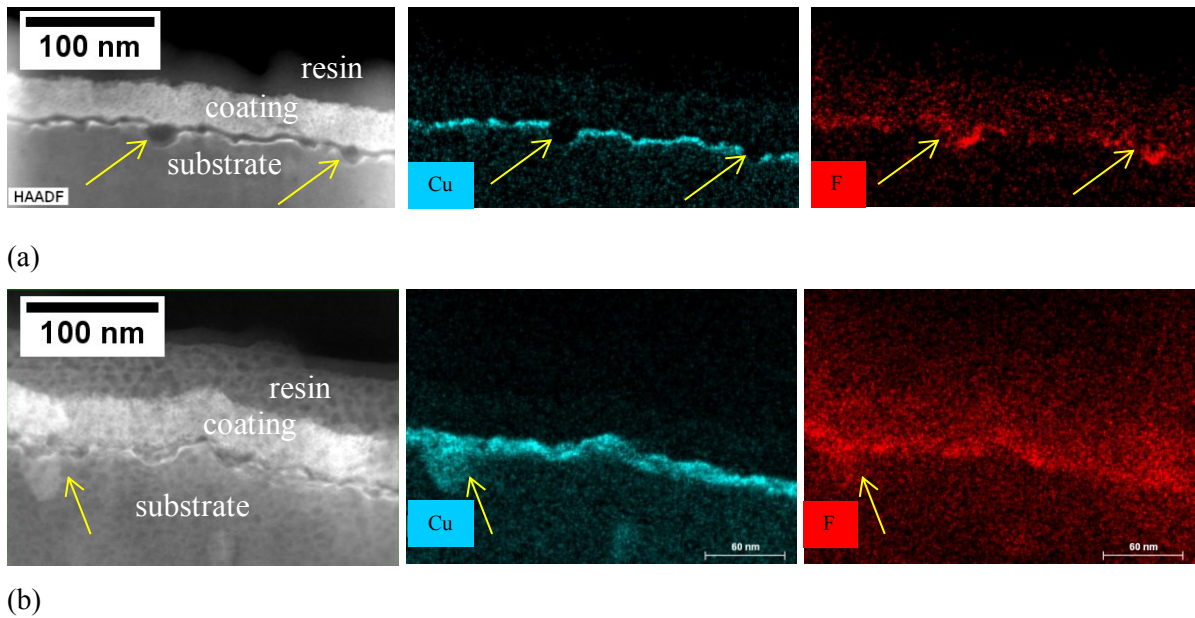


Figure 5. 15 High angular annular dark field (HAADF) transmission electron micrograph and EDX elemental maps of a coating formed on pre-treated AA 2024-T3 alloy for 300 s in a dilute SurTec 650 bath at 40 °C for two different samples (a and b).

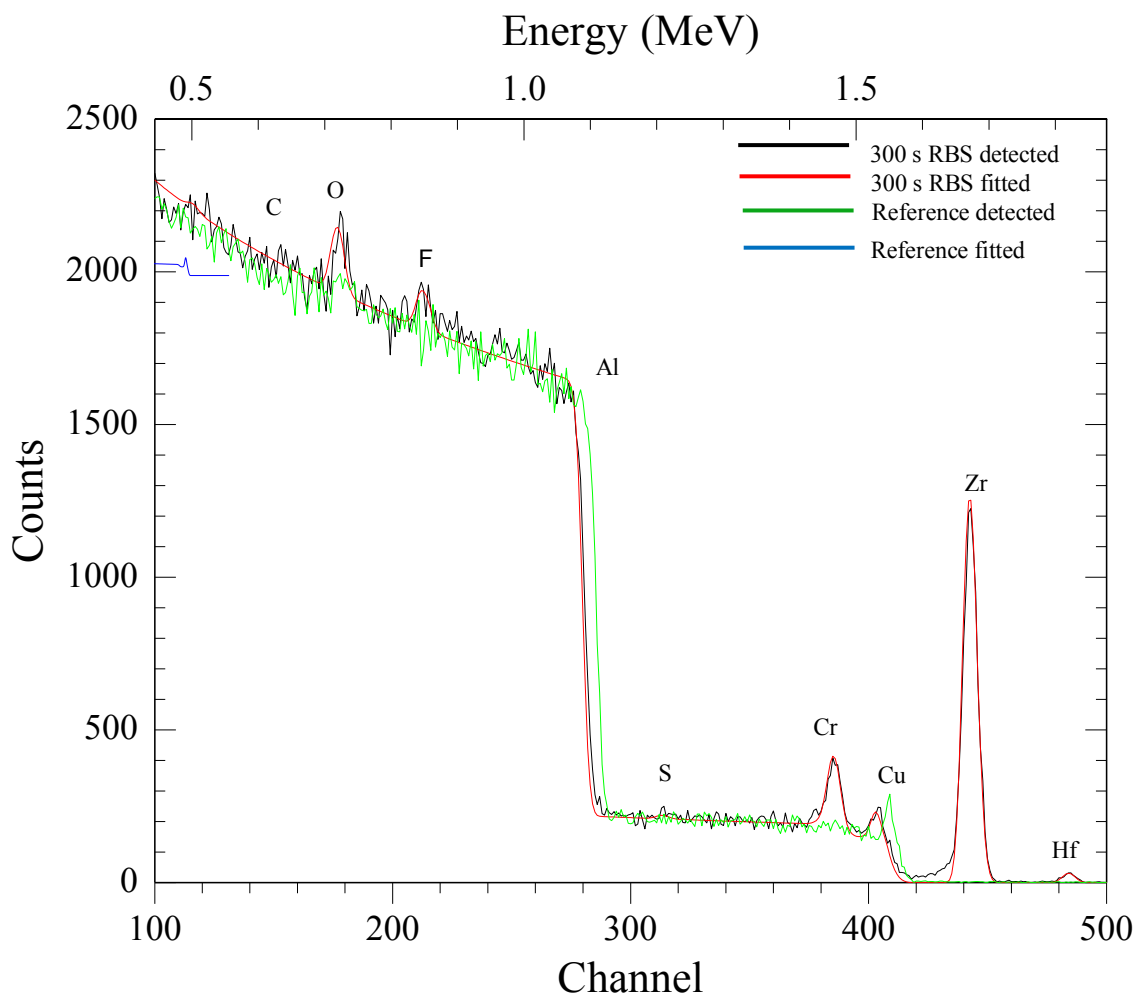


Figure 5. 16 Experimental and simulated (solid line) RBS spectra for the AA2024-T3 alloy in the etched and de-smutted condition and following coating for 300 s in a dilute SurTec 650 bath at 40 °C.

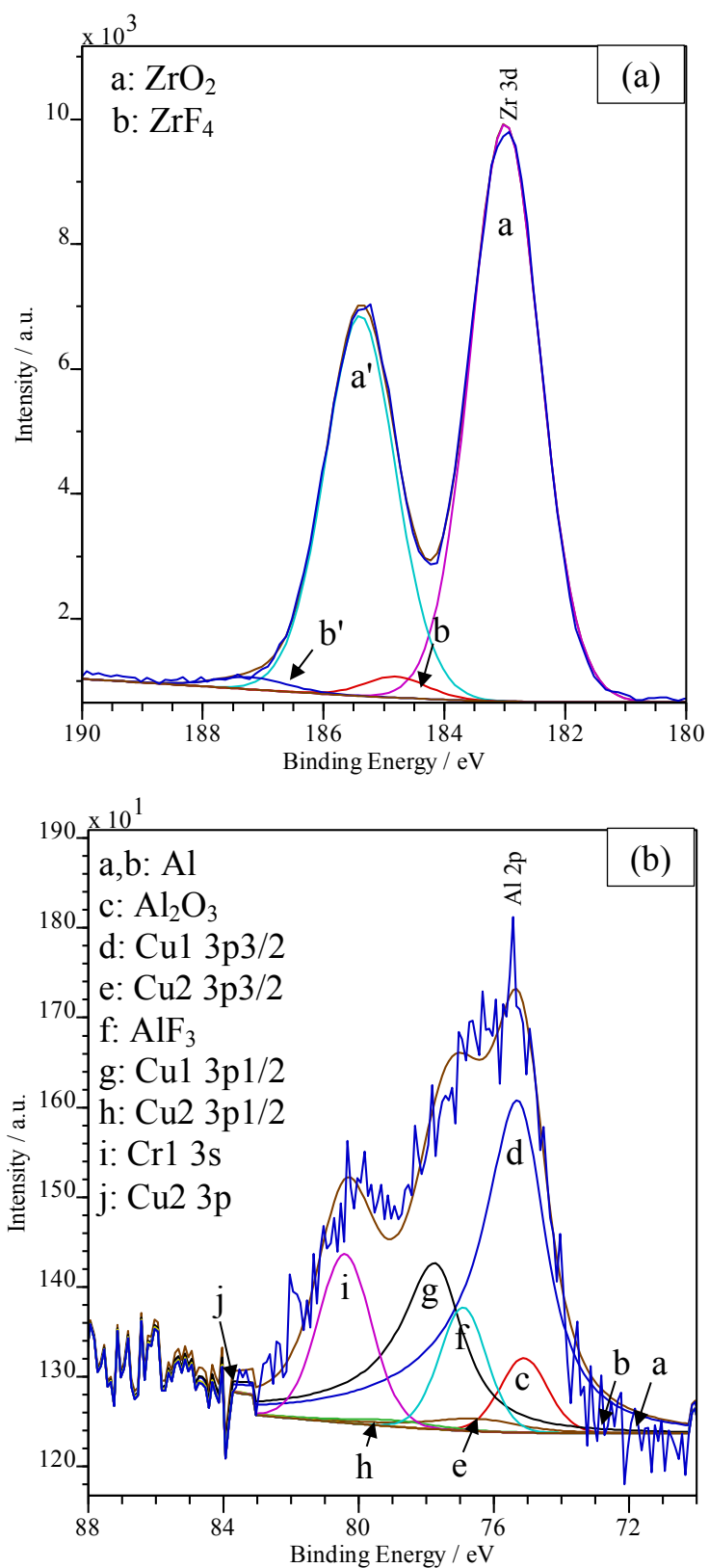


Figure 5. 17 High resolution XPS spectra for: (a) Al 2p; and (b) Zr 3d photoelectron regions and curve fitting for the pre-treated AA 2024-T3 alloy following coating for 300 s in a dilute SurTec 650 bath at 40 °C.

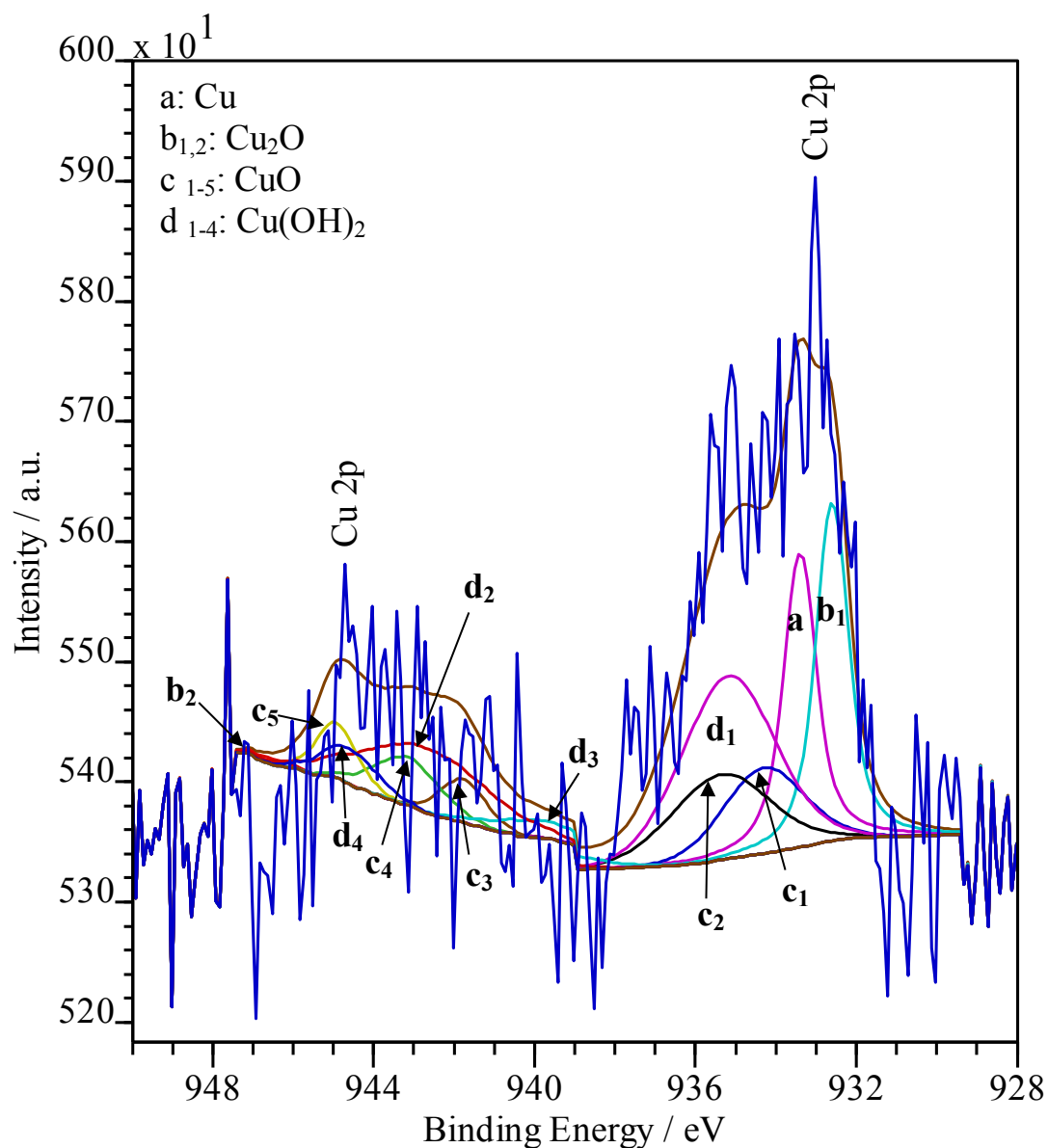


Figure 5. 18 High resolution XPS spectrum for the Cr 2p photoelectron regions and curve fitting for the pre-treated AA 2024-T3 alloy following coating for 300 s in a dilute SurTec 650 bath at 40 °C.

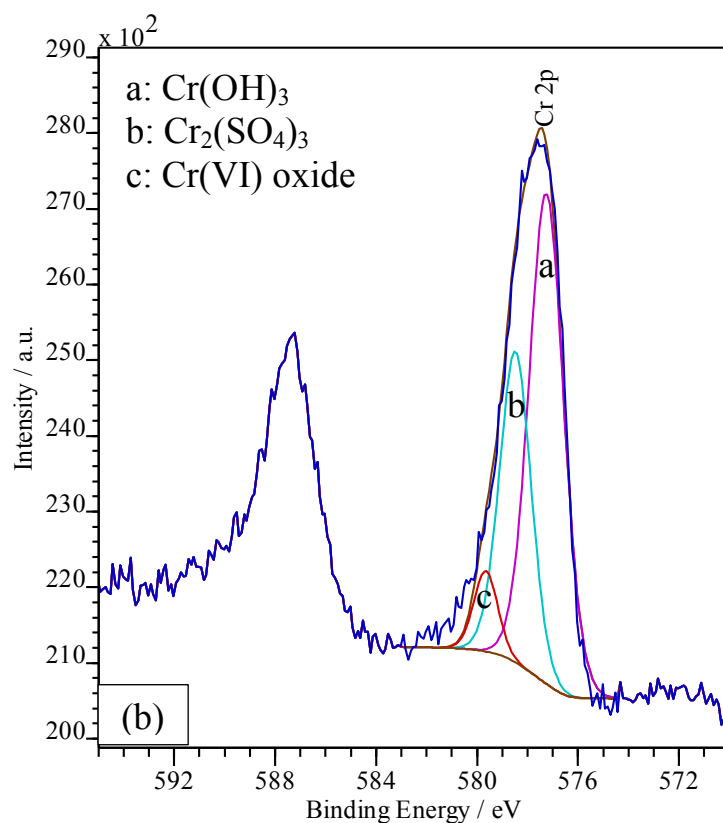
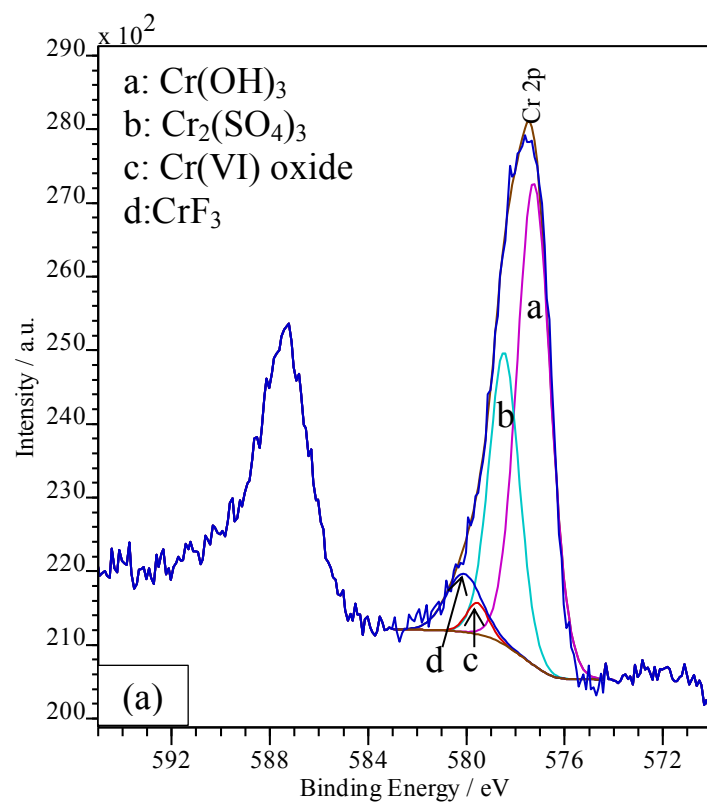


Figure 5. 19 High resolution XPS spectrum for Cu 2p photoelectron regions and curve fitting for the pre-treated AA 2024-T3 alloy following coating for 300 s in a dilute SurTec 650 bath at 40 °C

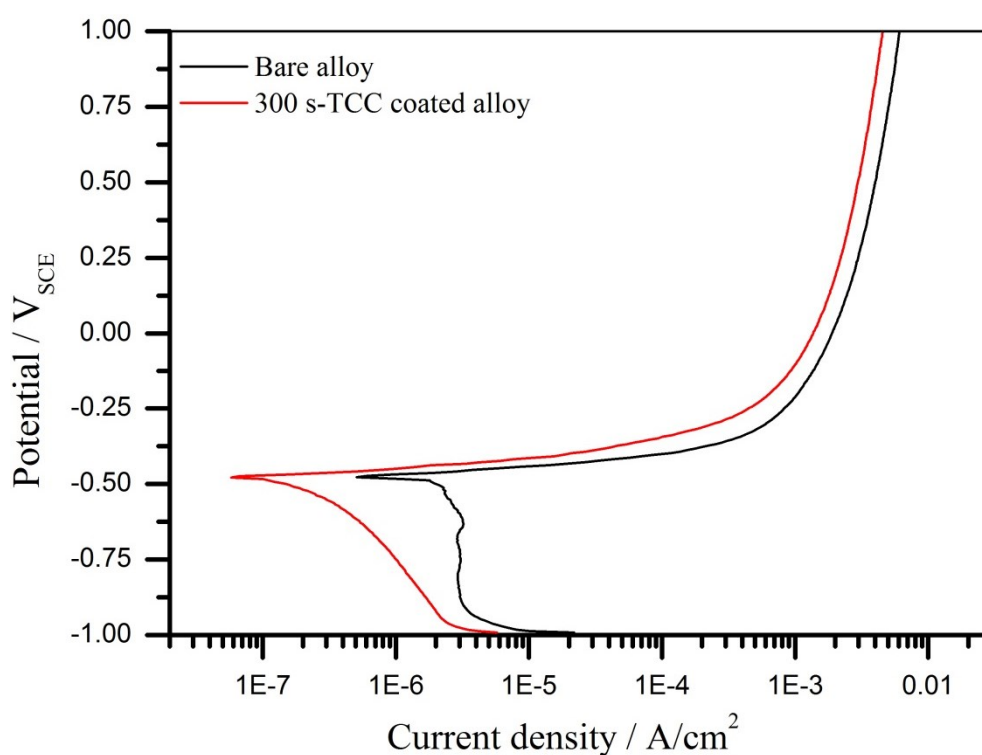


Figure 5. 20 The potentiodynamic polarization curves of the bare AA2024-T351 alloy after alkaline etching and nitric acid desmutting and the coated alloys after immersion in the trivalent chromium bath for 300 s with the standard post-treatment. The open-circuit potentials prior to the polarization scan are ~ -0.5 and -0.6 V vs SCE respectively and both of the corrosion potentials were measured at ~ -0.5 V_{SCE}.

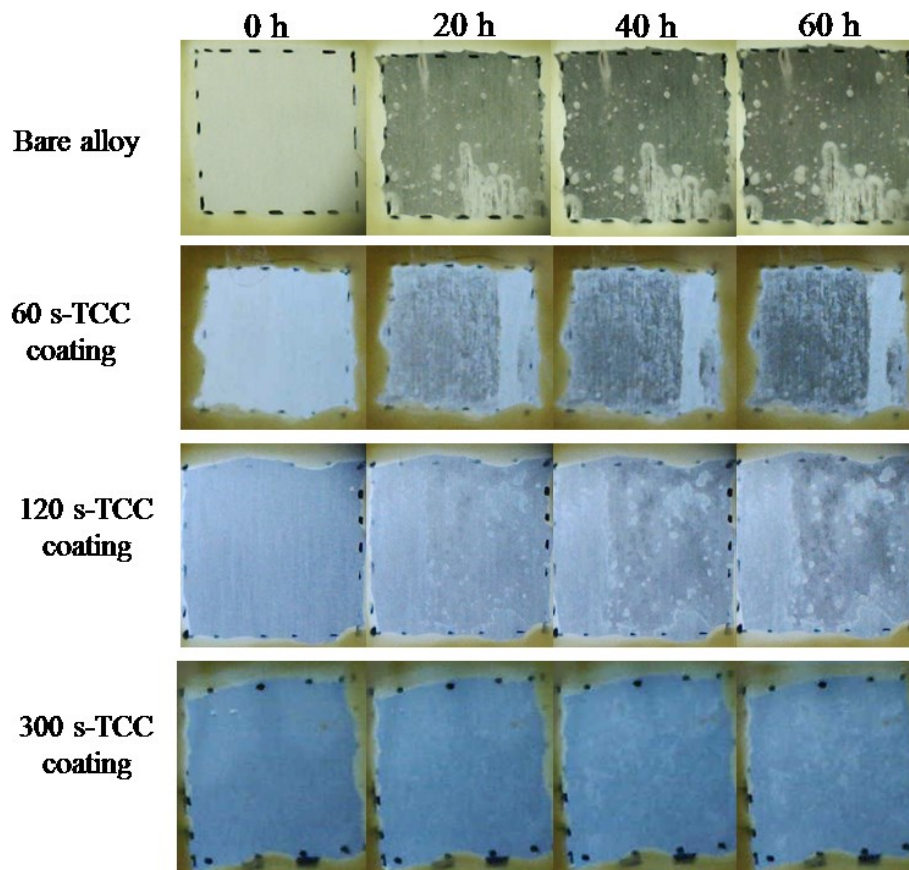


Figure 5. 21 The real-time images with corrosion evolutions up to 60 h for the bare alloy reference and the TCC coating formed for 60, 120 and 300 s in the 3.5 wt.% NaCl electrolyte.

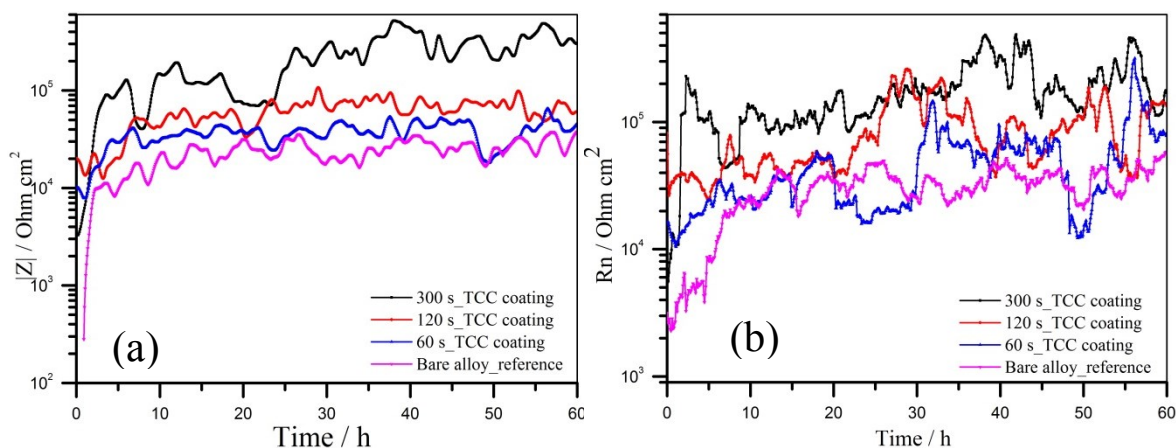


Figure 5. 22 The time evolution of the impedance modulus (left) and noise resistance (right) at 0.005 Hz by the electrochemical noise analysis for the bare alloy reference and TCC coating formed for 60, 120 and 300 s in the 3.5 wt.% NaCl electrolyte.

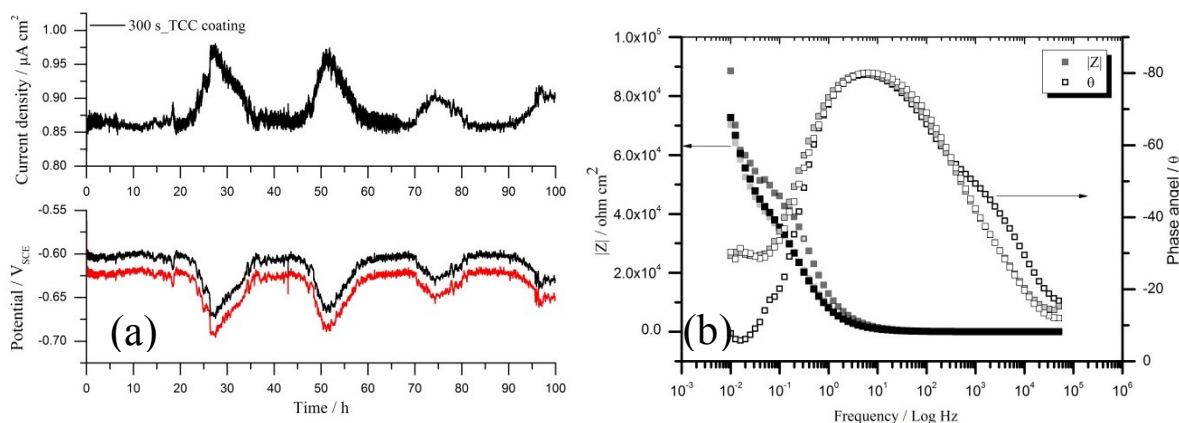


Figure 5. 23 The time evolution of current density and potential at 0.005 Hz (left) by the electrochemical noise analysis in the 3.5 wt.% NaCl electrolyte and the electrochemical impedance spectroscopy analysis (right) for the TCC coating formed for 300 s in the 0.05 M NaCl solution.

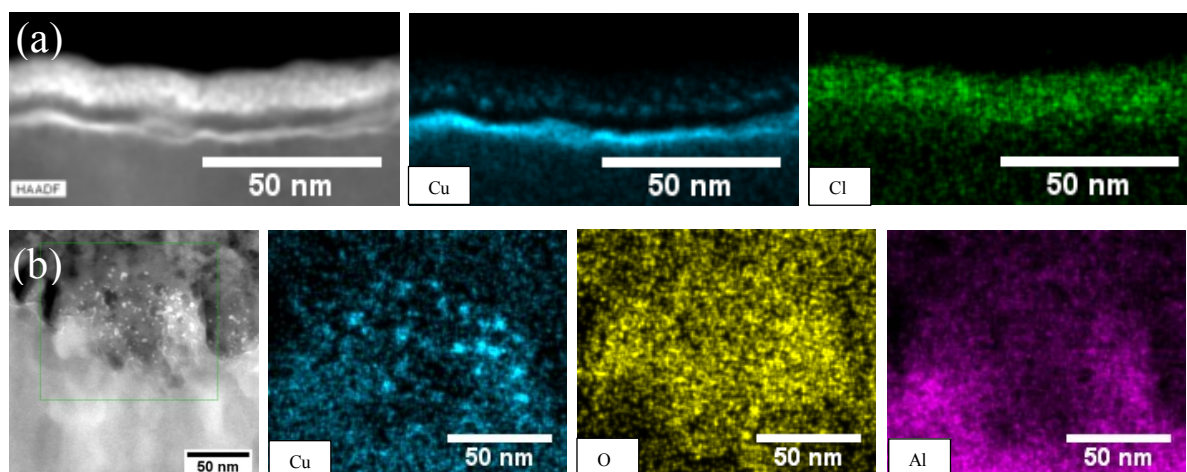


Figure 5. 24 The high-resolution transmission electron micrographs and EDX maps of TCC coating formed for 60 after the long-term ENA test for 138 h in the 3.5 wt.% NaCl electrolyte for two positions (a) and (b).

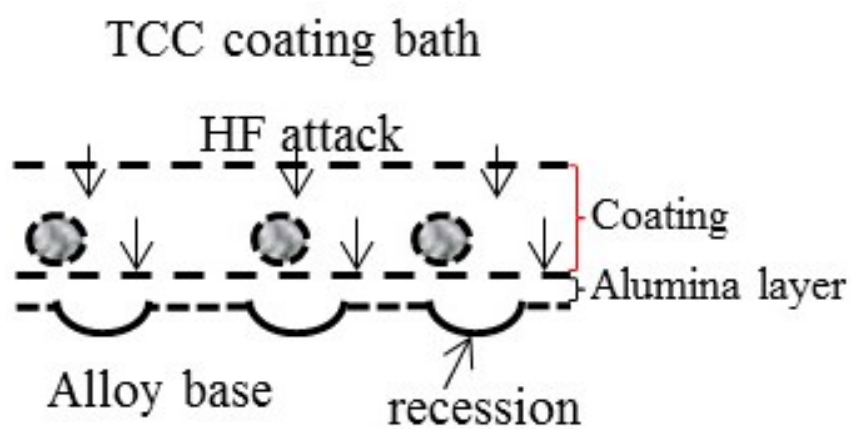


Figure 5. 25 The schematic diagram displaying the trivalent chromium conversion coating formation process with copper evolution into the coating on the pre-treated alloys, where the free copper islands incorporation into the TCC coating by proceeding HF attack, leading to substrate recession features.

Chapter 6 INFLUENCE OF SURFACE PRE-TREATMENTS

The main parts of this chapter include an introduction, results and discussion, and the summary. For the result part, it consists of the influence of the surface pre-treatments on (i) the surface morphology and composition, (ii) the coating formation and composition, (iii) the coating growth kinetics, (iv) electrochemical properties and (v) pre-treatments on as-received alloys, where the effect of concentrated nitric acids on the surface morphology and corrosion protection of mechanically polished and etched alloys was investigated. Accordingly, the discussion part includes the effect of surface pre-treatments on (i) coating morphologies and composition, (ii) the coating formation and growth kinetics, (iii) the electrochemical characterization and (iv) the mechanism of improvement of the TCC coating process.

The pre-treatment of alloys consists of (i) the mechanical polishing, (ii) the alkaline etching and nitric acid desmutting, and (iii) the alkaline etching and D30 desmutting. The experimental procedure of the chemical treatment after mechanically polishing is shown in Table 6.1, where the required temperature of each pre-treatment was maintained in a water-heat bath. All treatments were followed by deionized water rinsing and cool-air stream drying.

6.1. Introduction

AA2024-T3 alloy contains a very complex microstructure, including multiphase second-phase particles (CuMgAl_2 (S), $\text{Al}_2\text{Cu}(\theta)$ and Al-Cu-Fe-Mn-Si (α)), periphery phases around these composite particles and clustering.[5, 6] These heterogeneous copper-containing intermetallics on the alloy surface lead to a high susceptibility to pitting corrosion [10]. Furthermore, the presence and coverage of the second phase particles influence the formation of the conversion coating, e.g. thickness variance and crack defects around particles.[107, 108, 199, 225] In addition, the copper incorporation into the film was revealed at the enrichment of ~ 40 at.%Cu, either as oxidized species [209] or as nano-size metal particles [35]. George et al also proposed one potential relation between the copper incorporation into Zr-based conversion coating and the impedance of mass transport, such as aluminium cations, to slow down coating growth [210]. In this case, we also reported the locally enhanced

copper oxidation by the fluorine attack and dissolved oxygen to give rise to the interfacial defect of substrate recession to reduce the coating integrity.

Thereby, the improvement of copper coverage and amount on the alloy surface prior to the chemical conversion treatment is important to the corrosion protection.[208, 226] In terms of surface pre-treatments, the concentrated nitric acid (70 vol.%) was used to effectively clean surface oxides of as-received AA2024 alloys to provide a homogenous sol-gel coating [226]; however, this treatment on the sputtering-deposited Al-Cu alloy produced copper enrichment on the alloy surface, similar to those achieved during alkaline etching. It is attributed to the enhanced aluminium corrosion and the relatively slow rate of copper dissolution [227]. This is in an excellent agreement with the report of the effect of the HNO_3 , H_2SO_4 and H_3PO_4 alone on the AA2024 alloy by Hughes et al. [22] with the presence of particles that contain a similar composition to the alkaline-etched surface. Further, the mineral acid mixture with the HNO_3 -HF and the HNO_3 -HF- $\text{Na}_2\text{S}_2\text{O}_8$ provided an optimal surface treatment of the AA2024-T3 alloy in the absence of particles and copper-rich smuts.

In this present study, a commercial D30 solution and the nitric acid (50 vol.%) were used to deoxidize the alkaline-etched alloy surfaces of the AA2024-T351 alloys. This D30 solution contains a mixture of sulphuric acid, nitric acid and ferric sulphate (MacDermid Corp. UK) and its cleaning effectiveness of surface particles was investigated as follows. The surface morphologies and composition of the bare alloy and successive TCC coatings were investigated by scanning and transmission electron microscopies, and energy dispersive X-ray spectroscopy (SEM/EDX). In addition, cyclic voltammetry in a deaerated borate buffer solution of pH at 8.4 was used to assess the copper coverage on the AA2024-T3. The linear correlation between current densities and total charges of the $\text{Cu}(0)/\text{Cu}(\text{I})$ oxidation peak indicates that this peak height (current density) can represent the copper coverage alloy [34, 36].

The surface chemistry was investigated by the X-ray photoelectron spectroscopy to further understand the influence of the pre-treated surface on the coating composition. The potentiodynamic polarization, electrochemical impedance spectroscopy and electrochemical noise analyses were used to examine the corrosion protection by the TCC coatings.

6.2 Results

6.2.1 Surface morphology and composition

The scanning electron micrographs of Figures 6.1 (a, b, c, d) show the morphology changes as a result of the pre-treatments. The as-received alloy revealed the pluck lines and scratches along the rolling direction because of the thermomechanical processing (Fig. 6.1(a)). A relatively clean surface with the less protrusion of second-phase particles was investigated on the alloy after the D30 pre-treatment compared with those generated by mechanical polishing and HNO₃ treatments as shown in Fig. 6.1 (b, c, d). Accordingly, the area fractions of the remnant particles on the surface of the alloys after the mechanical polishing, HNO₃ and D30 pre-treatments were manually measured to be ~5.2%, 4.8% and 2.9% respectively. Further, the surface roughness of such specimens of surface area of ~0.15 mm² was assessed by the interferometry contour plots on the base of the optical in Figure 6.2, where the colour variance corresponded to the difference of vertical height. All data were analysed by the Vision64 Software (Version 5.41, Bruker, UK) and the measured roughness indexes of the as-received, polished, HNO₃- and D30-treated alloys were ~2.12, 1.09, 1.49 and 1.06 respectively, where a smaller roughness index indicated a more uniform surface. Furthermore, the root mean squares (RMS) were measured to be ~0.95±0.07, 0.15±0.01, 0.42±0.01, and 0.28±0.02 respectively. Both of them revealed that the D30 treatment provided a smoother and cleaner surface with a smaller roughness compared to the situation of the nitric acid treatment. In addition, the maximum valley depth (R_v) of the surface treated by the nitric acid appeared to be the largest number of ~20 µm among these specimens, indicating the enhanced corrosion on the substrate.

The scanning electron micrographs of the second phase particles and matrix of the alloys after the HNO₃ and D30 treatments are shown in Figure 6.3 and 6.4. The protruded particles with partial dissolution cavities on HNO₃-treated alloy in Figs. 6.3 were evidently observed in the form of the clustered θ (named 'I') and S (named 'II') phase particle, and α (named 'III') phase particles. The dimension of such remnant particles was measured to be up to ~20 µm diameter. By contrast, the microstructures of the alloy surface by the D30 treatment in Figs. 6.4 contained copper-rich sponges (a), cavities left by the removal of second-phase particles (b) and the remnant particles of several micron diameter (c and d). The honeycomb

microstructure of copper-rich sponges (a) was due to the preferential dissolution of aluminium and magnesium on such particles [60]. Accordingly, the SEM/EDX analyses provided a half-quantitative composition examination of particles and the matrix by pre-treatments. For the HNO₃-treated alloy in Table 6.2, concentrated copper levels of ~50, 40 and 20.8 wt.% were detected on the θ phase, S phase and α phase particles in Fig. 6.3 respectively. By contrast, the D30-treated alloy displayed a significant decrease of copper in these particles as shown in Table 6.3. The ~5.8 and 10.4 wt.%Cu components were investigated on the S- and α - phase particles in Fig. 6.4(c and d) respectively, while the isolated copper sponges in Fig. 6.4(a) contained ~90 wt.%Cu in components. These copper sponges of the elongated shape likely correlate with the clustered θ phase particles [4] and the stagnant D30 solution is hard to completely uproot them from the substrate. In terms of the alloy matrix, a small variance of copper content between the HNO₃ and D30 pre-treatment of ~4.6 and 4.9 wt.% respectively was exhibited.

Figure 6.5 shows the cyclic voltammetry during the immersion in a deaerated borate buffer solution of pH at 8.4 of the AA2024-T351 alloys after the mechanical polishing to ~1 μm , alkaline etching and nitric acid demutting, and alkaline etching and D30 deoxidation. In terms of the Cu(0)/Cu(I) oxidation peak at -0.14 V_{SCE}, the current density of the alloys after D30 treatment displayed the maximum value of $\sim 2.1 \times 10^{-6} \text{ A/cm}^2$, while the minimum value of $\sim 2.6 \times 10^{-7} \text{ A/cm}^2$ was observed in the alloy after HNO₃ treatment. This peak area revealed a linear function of the peak height at the slope of 1/10. Thus, the peak areas of Cu(0)/Cu(I) oxidation are $\sim 2.1 \times 10^{-7}$ and $\sim 2.6 \times 10^{-8} \text{ C/cm}^2$ for the alloys after D30 and nitric acid treatments respectively. Accordingly, the copper amount by CV (atomic/cm²) was calculated in the formula of the peak area/F $\times$ N_A, where F and N_A represent the Faraday constant ($9.6485 \times 10^4 \text{ C mol}^{-1}$) and Avogadro constant ($6.022 \times 10^{23} \text{ mol}^{-1}$) respectively. Thus, the surficial copper amounts by the cyclic voltammetry were assessed at 1.6×10^{11} and $1.3 \times 10^{12} \text{ atomic/cm}^2$ for the HNO₃- and D30-treated alloys. In comparison with the Cu(0)/Cu(I) peak area of $\sim 1.61 \times 10^{-6} \text{ C/cm}^2$ on the pure copper, the copper coverage fractions were ~0.02 and ~0.13 respectively.

The presence of the Cu(0)/Cu(I) oxidation peak was suggested to relate to the electroactive copper enriched on the pre-treated surface [37]. The effective deoxidation of the D30 solution by the presence of oxidant Fe(III) ions may produce the thinner oxide on the surface

compared to the single nitric acid desmutting [23], and hence, the more concentration of the electroactive copper on the D30-treated alloy detected by the cyclic voltammetry was reasonable. In addition, a relatively fast removal of the dark etching products was observed in a short period of ~5 seconds when the alloys were immersed in the nitric acid bath. By contrast, this removal in the D30 solution started after a longer period of ~60 seconds. The lower removal rate of the etched oxides by the D30 solution compared to the single nitric acid was probably attributed to the acidity strength of the individual desmutter.

Rutherford backscattering spectroscopy was also used to quantify the surficial amount of copper on the pre-treated AA2024-T351 alloys. The fitted thickness of the individual oxide films on the surfaces was ~4 and 2 nm on the HNO₃- and D30-treated alloys. Further, the amounts of copper in the oxide films were measured at $\sim 7.3 \times 10^{15}$ and 4.8×10^{15} atomic/cm² respectively. In comparison with the early assessed amounts, the cyclic voltammetry revealed a monolayer of the surficial copper, which may play the electroactive role in the reaction with the electrolyte [37]. In sum, the D30 treatment can effectively thin the surface oxide film and the electroactive copper may promote the interfacial reaction kinetics with the electrolyte.

6.2.2 Coating formation and composition

The open-circuit potential evolution of the D30-desmuted alloy during the immersion in the SurTec 650 bath at 40 °C is shown in Figure 6.6. The time-dependent OCP plot displayed an initial quick fall and a subsequent rise to a relatively stable potential around -0.93 V_{SCE}. The minimum -1.07 V_{SCE} OCP was detected around 22 s immersion time, which revealed a shorter period compared to the situation of HNO₃-treated alloys at ~50 seconds. The 70 mV positive shift was measured after the minimum potential.

The scanning electron micrographs of the TCC coatings formed for 300 s on the D30-treated alloy are shown in Fig. 6.7 (a and b). The crack defects were detected around the copper-rich island (Fig. 6.5 (a)), which are initiated by stress in the coating related to drying of the coating. The higher-resolution micrograph on the matrix appeared the fine morphology with some nano-size nodules (Fig. 6.5 (b)). The SEM/EDX analyses for the coatings formed for 300 s on the matrix between HNO₃ and D30 treatments are shown in Figure 6.8. Little

component variance was detected in both coatings. This equivalent composition of both coatings indicates the similarity in their coating thicknesses and compositions in depth.

Table 6.4 shows the quantitative concentrations of the elemental components in the coatings formed for 60, 120 and 300 seconds on the D30-treated alloys by means of RBS analyses. In comparison with the previous analyses of coatings formed on the nitric acid-treated alloys, the concentration ratio of chromium relative to that of zirconium was higher at $\sim 0.76 \pm 0.02$, which were ~ 1.6 times the situation of the coating on the HNO_3 -treated alloy. This increased content of chromium indicated the improvement of the coating composition. The fluorine and sulphur further displayed a significant enrichment, for example, ~ 91.2 and 68.7×10^{15} atomic/cm² fluorine component were investigated in the coatings formed on the D30-treated and HNO_3 -treated alloys respectively. In addition, the copper concentration on the substrate was assessed to be ~ 3.8 , 7.0 and 4.0×10^{15} atomic/cm² in the case of 60, 120 and 300 s, and these were similar to the situation of the bare alloys after D30 treatment. The variance of copper assessments was probably attributed to the surface roughness after the coating treatment. Notably, the concentrations of aluminium (3.0 at.%) and copper (0.3 at.%) in the coatings formed for 300 s on the D30 treated alloys showed a significant decrease compared to the ~ 9.5 and 0.9 at.% contents in the total composition of the coatings formed for 300 seconds on the HNO_3 treated alloys.

The quantitative analyses of the TCC coatings formed for 60, 120 and 300 seconds on the D30-treated alloy were also examined by X-ray photoelectron spectroscopy and the surface elemental concentrations (at.%) are shown in Table 6.5. The carbonaceous contaminations were expected to be present over layer to influence the calculation of the elemental concentration and this Table also includes its correction by Seah's method [193]. Zirconium, chromium, oxygen, aluminium, sulphur, fluorine and copper comprise the TCC coatings, where the primary metal-bearing components are zirconium and chromium with a combined content of more than 29 at.% in all coatings. Aluminium and copper concentrations are relatively constant at ~ 2 at.% and 0.5 at.% respectively. Figures 6.9 (a and b) show the high-resolution XPS spectra and the fittings of (a) the Cr 2p and (b) the Zr 3d photoelectron regions in the coatings formed for 300 seconds. Five peaks were used to fit the Cr 2p_{3/2} photoelectron region, revealing the presence of $\text{Cr}(\text{OH})_3$ (577.3 eV), $\text{Cr}_2(\text{SO}_4)_3$ (578.5 eV), CrO_3 (579.6 eV), CrF_3 (580.1 eV) with one additional Cr 2p_{3/2} peak (581.6 eV). For the Zr

3d photoelectron regions, it showed the fluorinated characteristic with the presence of ZrF_4 (185.2 eV), ZrO_2F_5 (183.5 eV), ZrOF_6 (184.3 eV) and ZrO_2 (182.5 eV). Further, ~93.6% zirconium compounds were detected in the form of zirconium-containing fluorides. Table 6.6 reveals the increasing content of chromium in the form of sulphate, fluoride and hexavalent chromium oxide with the respective maximum concentrations of ~6.0, 2.0 and 1.2 at.% in the coatings formed for 300 seconds. Conversely, chromium hydroxide showed a time-dependent decrease from 4.3 at.% to 3.6 at. %. Additionally, the additional chromium species at 581.6 eV was fitted with an undetectable concentration.

6.2.3 Coating growth kinetics

The cross-sectional TEM micrographs for the TCC coatings on the D30-treated alloy matrix after 5, 15, 300 and 600 seconds of immersion in the dilute SurTec 650 at 40 °C are presented in Figs. 6.10 (a-d). These TCC coatings displayed uniform thicknesses with immersion time. The coating initiation was visibly observed after treatment time of (a) 5 and (b) 15 seconds with coating thicknesses of ~8 and 20 nm respectively. The two-layer coating structure was evident in all coatings in Fig. 6.10(c). This coating consisted of the outer main layer (named 'I' region) and the inner layer (named 'II' region). A dark band beneath the coating was associated with copper enrichment by this pre-treatment. Notably, the interfacial delamination and cracks through the coating were also observed in the coating after conversion treatment for 600 seconds. It possibly indicated the poor adhesiveness of the coatings with the prolonged treatment, although the mechanical damage during the sample preparation may also give rise to these defects.

Figure 6.11 shows the variances of the TCC thickness on the alloy matrix with immersion time. The coating growth kinetics displays an initial linear growth and a subsequent logarithmic kinetics after conversion treatment for 15 seconds. The initial growth rate is ~1.3 nm/s, and the growth rate after 120 seconds of treatment is roughly ~0.04 nm/s to a 50 nm thickness for the coating after conversion treatment for 600 s. In comparison to the situation of the coatings formed on HNO_3 -treated alloys in the previous chapter, the significant increase of the initial growth rate on the D30-treated alloy correlated with the thinner oxides and the more electroactive copper on the surface as evidenced by the cyclic voltammetry.

Furthermore, the logarithmic kinetics after conversion treatment for 15 s was distinct and may relate to the more intact coating structure.

6.2.4 Electrochemical properties

The electrochemical behaviour of the TCC coatings in 0.05 M NaCl solution was measured after a prior stabilization of the open-circuit potentials (OCPs) for 30 min. The OCPs of the bare and TCC coated alloy under HNO₃ were -0.56 and -0.61 V_{SCE} respectively, while the situation of D30 treatment displayed at -0.52 and -0.65 V_{SCE}. The cathodic polarization in Figure 6.12 reveals that the TCC coating formed for 300 s on D30-treated alloys primarily inhibited the cathodic reactions. For example at -0.75 V, the current densities on the bare and coated alloy were $\sim 1 \times 10^{-6}$ and 1×10^{-7} A/cm² respectively. Moreover, the corrosion current densities of the bare and coated alloys were measured to be $\sim 3.0 \times 10^{-7}$ and 2.9×10^{-8} A/cm² respectively. In comparison with the polarization behaviour of TCC coatings on HNO₃-treated alloy of the corrosion current density of $\sim 1.7 \times 10^{-7}$ A/cm², the coatings on the D30-treated alloy provided a better barrier against corrosion as evidenced by $\sim \times 10$ decreases in the corrosion current density.

In terms of the electrochemical impedance measurement, an equivalent circuit (EC) model in the form of $R_e(Q_{coat}(R_{po}(Q_{dl}R_p)))$ is shown and illustrated in Figure 6.13 [228], where the two time constant phase elements (CPEs) of the Q_{coat} and Q_{dl} were used to replace the ideal capacitances. The Zview software was used to fit these data and results are shown in Table 6.7, where the fitting chi-squared error was all around $\sim \times 10^{-3}$ order. The electrolyte resistance, R_e , depended on the electrolyte nature (0.05M NaCl) between the reference electrode and surface morphologies. The HNO₃-treated bare alloy displayed the lowest R_e value ($73 \Omega \text{ cm}^2$) due to the presence of the protruded particles. In contrast, the alloys after the later treatment revealed a stable R_e value around $160 \Omega \text{ cm}^2$. Concerning R_{po} , the resistance of the porous channels or defects in the coating, the coating on D30-treated alloy showed a significant improvement with $\times 100$ increases (around $10^4 \Omega \text{ cm}^2$) compared to that after HNO₃ treatment ($\sim 10^2 \Omega \text{ cm}^2$). It indicates the reduced coating defects and improved coating homogeneity along the substrate resulting from the D30 pre-treatment. The charge-transfer resistance, R_p , is associated with the electrochemical property at the coating/substrate interface. The coatings generated after HNO₃ and D30 pre-treatments showed resistances of

$\sim 7 \times 10^4$ and $\sim 2 \times 10^5 \Omega \text{ cm}^2$ respectively that were $\sim \times 35$ and $\sim \times 20$ increases compared to their respective bare alloys. Notably, the D30-treated bare alloy displays a five-fold increase of the charge transfer resistance, R_p , ($\sim 10^4 \Omega \text{ cm}^2$) compared with $\sim 2.6 \text{ k}\Omega \text{ cm}^2$ for the bare alloy under nitric acid treatment. This more corrosion protection of the bare alloy by the modified desmutting pre-treatment is in good agreement with the report by Guo et al [148].

Impedance modulus- and phase angle-frequency plots for the TCC coatings formed for 300 s and the bare alloys under HNO_3 and D30 treatments during immersion in 0.05 M NaCl solution are shown in Figures 6.14(a and b). For the bare alloy, one constant phase element (CPE) was observed around $\sim 10^1$ Hz. In contrast, two CPEs existed at $\sim 10^0$ and 10^2 Hz for the low and high frequency peaks respectively. The impedance function of the CPE was $Z = (j\omega)^{-n} Q^{-1}$, where the larger n value represented the greater homogeneity of the TCC coating.[165] Concerning Q_{coat} , the constant phase element used in the coating region, the n_{co} values in the coating formed on the HNO_3 -and D30-treated alloy were 0.83 and 0.8 respectively, revealing the more intact coating on the latter alloys. Further, the effective capacitance of this CPE as a response of its distribution of reactivity is defined as $C_{\text{eff}} = Q^{1/n} R^{(1-n)/n}$, where the R symbol represents the ohmic resistance of the electrolyte and the smaller value of the effective capacitance means the better resistance against corrosion[202, 228]. These capacitances $C_{\text{eff-co}}$ for the TCC coatings formed on HNO_3 - and D30-treated alloys were estimated to be ~ 3.04 and $2.35 \mu\text{F}/\text{cm}^2$ respectively, revealing the better corrosion resistance of TCC coating on the latter alloy. At the coating/substrate interface, the coating homogeneity parameter, n , displayed close to the perfect capacitance ($n=1$), revealing the good homogeneity across the surface.

The electrochemical noise analysis (ENA) tests were also used to investigate the long-term performance of TCC coated alloys after the D30 pre-treatment in 3.5 wt.% NaCl solution at the ambient temperature. Figures 6.15 (a and b) show the time evolution of noise resistance of the bare D30-treated alloy and the alloys after TCC coating treatments for 300 and 600 seconds with a standard post-treatment. Calculation by the fast Fourier transforms (FFTs) of potential and current was employed under at 0.01 and 0.005 Hz low frequency. Compared to the time evolution plot under 0.005 Hz, the FFTs at the upper limit of 0.01 Hz removes the evidence of pitting corrosion to provide a time evolution of the general corrosion in this long-term immersion in the Harrison's solution. Furthermore, the real-time macrographs of

specimens during the immersion in NaCl solution showed the corrosion evolution as displayed in Figure 6.16, where selected periods of 0, 20, 40 and 60 h were outlined.

For the noise resistance after FFTs treatment at 0.01 Hz (Fig. 6.15 (a)), the bare alloy after D30 treatment revealed a low resistance and the corrosion products on the surface led to the increased noise resistance from $\sim 3 \times 10^3$ to $4 \times 10^4 \Omega \text{ cm}^2$ after immersion of 40 hours. The real-life macrograph of this bare alloy showed a general corrosion after immersion of 1 hour and generally propagated over the surface. For example in Fig. 6.16, the general corrosion between the periods of 40 and 60 hours showed no significant change, consistent with the relatively constant noise resistances at these periods. By contrast, an efficient resistance against a general corrosion in the TCC coatings formed for 300 and 600 seconds displayed a long-term constant around $1 \times 10^5 \Omega \text{ cm}^2$, which is consistent with the absence of visible corrosion feature on the whole surface. Notably, there exhibited random bubbles on the surface, especially for the case of 600 seconds, correlating with the presence of the localized corrosion such as pits.

In this case, Figure 6.15 (b) shows the noise resistance under FFTs of 0.005 Hz and provides the evidence of pitting corrosion on the specimens. On the bare alloy, the time evolution of noise resistance displayed a similar trend with that under FFTs of 0.01 Hz, indicating its poor resistance after the D30 pre-treatment. Notably, this noise resistance somewhat exhibited a progressive fluctuation in a short period of immersion to relate the pitting propagation in the alloy depth. For example, the resistance of the bare alloy after immersion of 5 hours met a sharp fall-down to $\sim 2 \times 10^3 \Omega \text{ cm}^2$, attributed to the in-depth pitting occurrence. In terms of the TCC coatings, the prolonged treatment for 600 seconds in the trivalent chromium bath likely produced more defects on the surface to yield a relatively unstable resistance response than the situation of 300 seconds. For example, the noise resistance of TCC coating formed for 600 seconds displayed a significant drop from the constant level of $\sim 1 \times 10^5$ to $\sim 4 \times 10^4 \Omega \text{ cm}^2$ after immersion for 70 h in Figure 6.15 (b), indicating the pitting corrosion. By contrast, the TCC coatings formed for 300 seconds revealed a more efficient resistance against the general and localized corrosion during long-term immersion in the NaCl solution. This is also in good agreement with the real-life macrographs where the coating formed for 600 s was covered with more bubbles than the situation of the coating formed for 300 s. This bubble feature may relate to the pits of the TCC coatings beneath the bubbles.

Scanning electron micrographs and EDX point analyses of the corroded TCC coatings formed for 300 and 600 seconds after the long-term immersion in 3.5 wt.% NaCl solution for 240 hours are shown in Figures 6.17 (a-f) and Figures 6.18 (a and b) respectively. Both specimens displayed the evidence of the localized corrosion with some isolated voids, where the circle valleys in Fig. 6.17 (b) probably corresponded to the bubble on the surface macrograph. The SEM/EDX analyses revealed the inhomogeneous distribution of the zirconium component in the matrix as evidenced in Figure 6.18 (a). The zirconium in the No. 3 point revealed a complete removal, while the point of No.2 on the matrix contained an efficient count of zirconium. By contrast, the TCC coatings formed for 600 seconds displayed a relatively low resistance over a long-term immersion in the chloride solution. Support of this fact is that the concentration of zirconium on all selected points in Fig. 6.18 (b) was nearly zero and sodium chloride enriched on the surface with the crystal grid feature outlined by yellow arrows in Figure 6.17 (d). This indicates that TCC coatings formed for 600 seconds probably detached from the alloy surface after a long-term immersion in NaCl solution.

6.2.5 Pre-treatments on as-received alloys

The efficiency of desmutting by the nitric acid on removing copper and second-phase particles is fully examined in this part. Scanning electron microscopy and SEM/EDX analyses combine the electrochemical test of polarization behaviour and EIS to examine the influence of the concentration of the nitric acid on surface morphology, composition and corrosion protection of TCC coatings on the pre-treated alloys.

One series of specimens after acetone degreasing and deionized water rinsing were then mechanically polishing to 4000 grit finish, and then directly deoxidized by the nitric acid solution of concentrations of 50 v/v% and 70 v/v% for 300 seconds to examine the efficiency of nitric acid on removing second-phase particles. In addition, the other series of polished alloys were alkaline etched and then desmuted in such nitric acids. The chemical composition and treatment procedure are shown in Table 6.8. After such pre-treatments, the alloys were immersed in the 20 vol% SurTec 650 solution (pH=3.9, 40 °C) for 300 seconds, soaked in deionized water (40 °C) for 120 s, rinsed by deionized water and dried by a stream of cool air prior to the analytics examination.

Scanning electron micrographs of the specimens I, II, III and IV before and after TCC coatings treatment of 300 seconds and the interferometry of such bare alloys are shown in Figures 6.19 (a-d). In terms of the top-view microstructure, both direct deoxidization with the nitric acid of 50 and 70 vol.% concentrations cannot remove the second-phase particles in comparison to the alloy after the mechanical polishing treatment in Fig. 6.1(b). In terms of the surface roughness, their root mean squares (R_{RMS}) were measured to be $\sim 0.19 \pm 0.04$ and 0.16 ± 0.02 μm respectively. Concerning the desmutting efficiency on the etched products on alloys III and IV, the protruded second-phase particles of dimensions of several micrometres revealed the similar micrographs to the situation of alloys after alkaline etching and 50 vol.% nitric acid desmutting in Figs. 6.3(a and b). The profilometry contour plots (Figs. 6.19 (a-b)) revealed a relative smoother surface on specimens III and IV as evidenced by their root mean squares of $\sim 0.36 \pm 0.01$ and 0.35 ± 0.01 μm respectively, in comparison to the larger value of the root mean squares at ~ 0.42 μm on the alloy after 50 vol.% HNO_3 treatment in Figs. 6.3.

Figures 6.20 (a and b) show the scanning electron micrographs of the TCC coating on such pre-treated alloys. The significant presence of mud cracks around the second-phase particles was observed on the specimens I and II after the direct deoxidization by nitric acid. By contrast, the TCC coating displayed the absence of the cracks, even around the protruded particles, on the specimens III and IV after the mixture treatment of alkaline etching and 70 vol.% HNO_3 desmutting. In addition, the SEM/EDX analyses of the TCC coatings formed for 300 seconds on the matrix of all specimens in Figure 6.21 revealed a similar concentration of zirconium and chromium, indicating similar thicknesses of the TCC coatings.

The corrosion protection by TCC coatings on such pre-treated specimens includes the electrochemical impedance spectra and polarization scan, where the stabilization of the open-circuit potentials prior to each examination was used for at least one hour. The OCPs of specimens I to IV were ~ -0.5 , -0.55 , -0.50 , -0.51 mV respectively. Figure 6.22 shows the polarization curves of the TCC coatings on the specimens I to IV in 0.05 M sodium chloride solution. The corrosion potential of TCC coated specimens from I to IV was measured to be ~ -0.45 , -0.51 , -0.45 and -0.45 V, where its negative shift of ~ 50 mV indicates the barrier coating on the surface. The corrosion current densities were measured to be $\sim 4.5 \times 10^{-7}$, 1×10^{-6} , 2.4×10^{-7} and 3.7×10^{-7} A/cm^2 , where the coatings on specimen II revealed the poorest corrosion protection. In terms of the anodic polarization behaviour, the anodic barrier of the

coatings formed on the alloy II was the least effective in all cases of TCC coatings. For example, at +0.25 V, this current density was around 10^{-2} A/cm², as high as ~10 factors of the other cases ($\sim 10^{-3}$ A/cm²). Thus, the specimens II after pre-treatments of the 70 vol.% HNO₃ deoxidation displayed the poorest corrosion protection. Further, the corrosion potential and current density of the TCC coating formed for 300 s on alkaline-etched and 50 vol.% HNO₃-desmuted alloys were ~ -0.50 V and 1.4×10^{-7} A/cm² respectively (section 5.2.8, Chapter 5). Thus, the corrosion protection by TCC coatings on the alloys after these modified pretreatments did not show a significant enhancement, probably attributed to the presence of the second phase particles to influence the coating inhomogeneity on the whole surface. In terms of the electrochemical impedance examination as shown in Figures 6.22, the equivalent circuit model in Fig. 6.13 was used to calculate the EIS data and the fitting results are shown in Table 6.9, where the chi-squared error was as less as 0.02. The major parameter representing the corrosion protection is the charge-transfer resistance, R_p , which were measured as $\sim 3.5 \times$, $2.2 \times$, $6.8 \times$ and 6.0×10^4 Ω cm² in the TCC coated specimens I to IV respectively. In comparison to the EIS data in Table 6.7, the TCC coatings on these modified specimens from I to IV cannot provide one comparable corrosion protection to the case under the alkaline etching and D30 deoxidization.

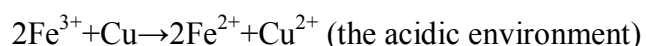
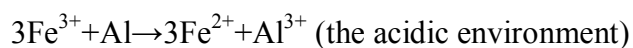
6.3 Discussion

6.3.1 Coating morphologies and compositions

The inhomogeneity of conversion coating on the aluminium alloy has been reported to directly result from the presence of protruded second-phase particles [226]. Thus, the reduction of the area fraction of these particles represents the pre-treatment effectiveness. Compared to 5.2 area% of the total surface on the mechanically polished alloy in the form of particles, D30 treatment displays the best removal effectiveness of particles with an ~ 1.2 area% particles, while $\sim 4.8\%$ particles were detected on the HNO₃-treated alloy. Moreover, the dimensions of the remnant particles on the D30-desmuted surface were also considerably reduced to around one micron dimension. In addition, the decreased copper content was investigated on the remnant S and α phase particles on the D30-treated surface by SEM/EDX analyses. Notably, the effective desmutters of the D30 solution may produce the thinner oxides on the surface to lead to the higher peak height of Cu(0)/Cu(I) oxidation by the cyclic

voltammetry, which correlates with the presence of the electroactive coppers on the surface. The presence of more electroactive copper correlates with the enhanced initiation kinetics.

In terms of the cleaning mechanism of the deoxidation solution, the 50 vol.% nitric acid alone is revealed to be effective in removing the etching products, but it cannot clean the surface particles, possibly attributed to the formation of surface phase to inhibit the oxidation of particles [22]. By contrast, the D30 deoxidation bath is an aqueous mixture of nitric and sulphuric acid and ferric sulphates, and it has revealed to be effective to clean the second-phase particles. Further, the presence of Fe(III) sulphate in this bath probably plays an oxidant role in promoting the dissolution of copper and aluminium as follows.



Thus, the cleaning of second-phase particles can proceed at a higher etched rate of alloying component in the Fe(III)-bearing D30 desmutter. This is in an excellent agreement with the report by Hughes et al [22, 23].

Furthermore, RBS examinations reveal the increased concentrations of the combined zirconium and chromium in the coatings formed on the D30-treated alloys. These concentrations on D30- and HNO₃-treated substrates were detected as ~17.1 at.% and ~13.1 at.% respectively. However, the concentration of aluminium (3.0 at.%) and copper (0.3 at.%) display a significant decrease on the D30-treated alloys compared to ~9.5 at.%Al and 0.9 at.%Cu in the coatings formed on HNO₃-treated alloys. Concerning the chemical states of the chromium, XPS analyses revealed that the hexavalent chromium oxides, and sulphate and fluoride of chromium (Cr (III)) showed much concentrated compared to the coatings on nitric acid treated alloys. Notably, zirconium components display the fluorinated characteristic, with ~94.6% of zirconium being in the form of fluorides and oxyfluorides. By contrast, only 3% ZrF₄ exhibited in the Zr 3d photoelectron region in the coating formed for 300 seconds on the HNO₃-treated alloys. This enrichment of the fluorinated compounds of zirconium and chromium in the coatings on the D30-treated alloy may effectively limit the single fluorine

that has been revealed to be more aggressive than the chloride ions to corrode the aluminium[81].

6.3.2 Coating formation and growth kinetics

The OCP evolution of the D30-treated alloy during immersion in the SurTec 650 bath displayed a similar trend to the situation of the HNO₃-treated alloy, and thus this coating formation starts after the efficient dissolution of air-formed oxide to form appreciable electron tunnelling. Subsequently, the cathodic reactions of oxygen reduction and/or hydrogen evolution result in the interfacial pH increase and then to initiate coating deposition. For the initial OCP, the shorter period to the minimum level on the D30-treated alloys is consistent with the early hypothesis that a thinner oxide was generated on the surface compared to the situation of nitric acid treatment. Moreover, the developed coating on the surface leads to the surface passivity, accordingly, the OCPs generally increased to a relatively stable potential around -0.83 V_{SCE} with an ~ 87 mV positive shifts relative to the minimum OCPs. By contrast, such a positive shift on HNO₃-treated alloy (~150 mV) approximately two times the situation on D30-treated alloy, possibly attributed to the presence of the protruded particles on the former surface. The cathodic reactions around these particles were regarded to be more aggressive in comparison to those on the matrix [150, 159].

Concerning the coating growth kinetics, a significant increase on the D30-treated alloys is displayed at the early stage of coating growth. The initial growth rate of ~1.3 nm/s kinetics up to 15 s (~20 nm) is a ~×5 increased order in comparison to that under HNO₃ treatment (~0.23 nm/s). For the D30-treated alloys, the more electroactive coppers by the higher Cu(0)/Cu(I) oxidation peak of the CVs promote the cathodic reactions kinetics on the matrix to induce the fast coating precipitation. After this coating initiation, the logarithmic kinetics were observed and probably correlate with the inhibition of the reactant diffusion through the coating channels or pores. This is in good agreement with the logarithmic equation of the oxide density with respect to the number of oxide pores, where the pores in the oxide film can be mutually blocked by the compressive strain of the neighbouring pores [207, 229]. Due to the presence of the protruded particles left by the pre-treatment, the inhomogeneous coatings formed on the particles and matrix display increased stress and it cannot be fully relieved

during the coating formation to produce the mud cracks around particles. These cracks accelerate the local mass transport and locally enhance the linear kinetics of coating growth. In this case, the large population of the protruded particles on the mechanically polished and HNO₃-treated alloy is probably responsible for the absence of the logarithmic kinetics after coating initiation.[207] This is also consistent with our previous report of the TCC coating growth on superpure aluminium, where the occurrence of cracks on the coatings correlates with the linear growth kinetics after treatment for 300 seconds [224].

6.3.3 Electrochemical characterization

The polarization curves reveal that the TCC coatings on the pre-treated alloy primarily display the cathodic barrier behaviour to reduce the oxygen availability near the substrate by the coating blocking. This cathodic inhibition of TCC coatings is in good agreement with the report by Guo et al [148]. By contrast, the cathodic current density and the corrosion current densities of the TCC coating formed for 300 s on the D30-treated alloys shows a ten-fold decrease than those of the coating on HNO₃-treated alloy. This reveals that the former coatings display a better barrier inhibition.

In terms of the corrosion resistance by EIS examinations, it also discloses the best corrosion protection by the TCC coatings formed on the alloy after D30 pre-treatment. This coating reveals the largest charge-transfer resistance $R_p \sim 2 \times 10^5 \Omega \text{ cm}^2$, and the low effective capacitance $C_{eff} = 2.04 \mu\text{F}/\text{cm}^2$, comparable with the corrosion resistance of CCC.[64, 155] Moreover, the resistance of coating pores or defects R_{po} ($\sim 10^4 \Omega \text{ cm}^2$) revealed a $\times 100$ increase than that on HNO₃-treated alloy, in a good agreement with the bigger homogeneity coefficient n_{co} (0.96). Li et al [165] reported the best corrosion protection of TCC coatings formed for 600 seconds on the AA2024-T3 alloy, including the charge transfer resistances R_p , resistance of coating pores or defects R_{po} and effective capacitance of the coating C_{co} as $\sim 3.3 \times 10^5 \Omega \text{ cm}^2$, $525 \Omega \text{ cm}^2$ and $2.49 \mu\text{F}/\text{cm}^2$ respectively. By contrast, our coatings formed for 300 seconds on the D30 treated alloy provide the equivalent and even better corrosion protection as evidenced by a ten-fold increase of coating resistance and the smaller effective capacitance of this coating ($\sim 2.04 \mu\text{F}/\text{cm}^2$).

6.3.4 Mechanism of the improvement of TCC coating process

The D30 pre-treatment effectively removes the copper-rich particles to reduce the surface inhomogeneity to form the relatively uniform TCC coating, where fluorine enrichment by the attraction of the cathodic copper-rich particles was restricted. Zirconium hydroxide in the coatings provides the exchange ligands between the hydroxide ion with the fluorine anion[230]. Thus, the fluorine ions combine the zirconium hydroxides to yield a more stable form of oxyfluoride [231], limiting the single fluorine anions [54, 81]. Furthermore, the presence of zirconium oxyfluoride component has been revealed to promote the reactivity with organic primer by facilitating Zr-hydroxylation via H-F extraction in the aqueous environment [231, 232]. This may correlate with the increased bonding of TCC coating with a top paint primer. Accordingly, a significant improvement of corrosion protection was realized by the TCC coatings on the D30-treated alloy, although the equivalent thicknesses were observed in these coatings on the alloys under both pre-treatments.

Notably, ~1.2 at.% Cr(VI) oxides in the coatings formed for 300 seconds on the D30-treated alloy also reveal a significantly increase compared to that coatings of ~0.15 at.% Cr(VI) for the nitric acid pre-treatment. This eco-friendly concern relates to the Cr(III)/Cr(VI) transformation in the oxygenated environment, either in the coating formation process or in the air ageing. The presence of the hexavalent chromium species also enhances the corrosion protection afforded to the AA2024-T351 alloys.[64]

6.4. Summary

1. Surface pre-treatment by the D30 deoxidation can effectively remove the protruded particles generated by the alkaline etching and provide a cleaned surface beneath a thinner oxide film. This cleaned surface promotes the formation of the more uniform coatings.
2. An $\sim \times 5$ increased initiation rate on the D30 treated substrate is related to the thinner oxides on the matrix. The subsequent logarithmic kinetics correlates with the inhibition of mass transport through the mutual blocking pores in the intact coating.

3. The TCC coatings on the D30-treated alloy consist of the concentrated fluorinated compounds of zirconium and chromium, with the decreased contents of copper and aluminium by XPS analyses, revealing a more stable composition.
4. A significant improvement of corrosion protection was revealed on the D30-treated alloy after conversion treatment of 300 seconds in the SurTec 650 solution followed by water immersion for 120 seconds and air ageing for 24 h.
5. The concentrated nitric acid plays a limited role in removing the surface particles on the polished alloys and the protruded particles on the etched alloys. This leads to the poor corrosion protection by the successive TCC coatings.

Figure Captions 6.1-6.23

Figure 6.1 Scanning electron micrographs of the AA2024-T351 alloy. (a) As-received alloy with the pluck lines along the rolling directions, (b) mechanically polished alloy to 4000 grit finish with grinding scratches and second-phase particles, (c) alkaline etched-HNO₃ deoxidized surface with protruded particles up to 20 microns dimensions and (d) alkaline etched-D30 deoxidized surface that is relatively clean with the reduced protrusion of particles.

Figure 6.2 Interferometry contour plots of AA2024-T351 alloy specimens. (a) As-received alloy, (b) mechanically polished alloy to 4000 grid finish, (c) alkaline etched-HNO₃ deoxidized surface and (d) alkaline etched-D30 deoxidized surface. The primary roughness parameters of the root mean square and the maximum valley depth were shown in (e) and (f) respectively.

Figure 6.3 Scanning electron micrographs of the AA2024-T351 alloys after the HNO₃ treatment. A cluster of θ phase (a, labelled 'I') and S phase (a, labelled 'II'); α phase (b, labelled 'III') particles.

Figure 6.4 Scanning electron micrographs of the surface of AA2024-T351 alloys after the D30 treatment. (a) The Cu-rich sponges (labelled 'I') with a honeycomb structure, (b) the cavity by the removal of the second-phase particle (labelled 'II'), (c) S phase particle present on the grain boundary (labelled 'III') and (d) α phase particle (labelled 'IV').

Figure 6.5 The cyclic voltammetry of AA2024-T351 alloys after the mechanical polishing to 1 μ m finish, alkaline etching and nitric acid desmutting, and alkaline etching and D30 deoxidation in the deaerated borate buffer solution.

Figure 6.6 The open circuit potential plot with dependence on the immersion time in the SurTec 650 bath at 40°C for the D30-treated alloy.

Figure 6.7 Scanning electron micrographs of the TCC coatings formed for 300 s. (a) Plan-view morphology with cracks as outlined by arrows and (b) the fine coating on the matrix with nano-size nodules.

Figure 6.8 The comparative EDX point analyses for 300 s TCC coating on the matrix by two pre-treatments, and the average amount of three points was used. No much variance of coating composition was detected.

Figure 6.9 The high resolution XPS spectra for (a) the Cr 2p_{3/2} and (b) and the Zr 3d photoelectron regions and curve fitting in the coating formed for 300 seconds on D30-treated alloy.

Figure 6.10 Transmission electron micrographs of the ultramicrotomed sections of the TCC coating attached to the alloy substrate after different formation times. (a) 5 s, (b) 15 s, (c) 300 s and (d) 600 s in the dilute SurTec 650 at 40 °C. The two-layer coating structure consists of the outer main layer (labelled 'I') and the inner layer (labelled 'II').

Figure 6.11 Thickness plot of the TCC coatings with immersion determined by TEM measurements

Figure 6.12 The potentiodynamic scans in 0.05 M NaCl solution for the alloy treated by HNO₃ and D30 deoxidization, consisting of the bare alloys and the TCC coatings formed for 300 s.

Figure 6.13. The equivalent circuit model $R_e(Q_{coat}(R_{po}(Q_{dl}R_p)))$ applied to the TCC coating system. R_e , R_{po} and R_p represent the electrolyte resistance, the resistance of coating defects and charge-transfer resistance respectively; the constant phase elements (Q_{co} and Q_{dl}) represent the region in the coating and coating/substrate interface respectively.

Figure 6.14 (a) Impedance modulus-frequency plot and (b) phase angle-frequency plot for the bare alloys and the TCC coatings formed for 300 s on the alloys after either HNO₃ or D30 treatment. The 0.05 M NaCl solution was used. The TCC coating on the D30-treated alloy reveals the best corrosion resistance.

Figure 6.15 Time evolution of noise resistance by the electrochemical noise analysis for the bare alloy reference and the TCC coatings formed for 300 and 600 s in the 3.5 wt.% NaCl electrolyte, where the calculation of fast Fourier transforms (FFTs) of potential and current were employed under the low frequencies of (a) 0.01 and (b) 0.005 Hz.

Figure 6.16 The real-life macrographs with corrosion evolutions up to 60 h for the bare alloy reference and TCC coating formed for 300 and 600 s in the 3.5 wt.% NaCl electrolyte.

Figure 6.17 Scanning electron micrographs of corrosion in the TCC coatings formed for (a-c) 300 and (d-f) 600 seconds with a standard post-treatment after long-term immersion in 3.5 wt.% NaCl solution for 240 hours.

Figure 6.18 The SEM/EDX spectra of selected points in the corroded TCC coatings formed for 300 and 600 seconds after long-term immersion in 3.5 wt.% NaCl solution for 240 hours.

Figure 6.19 Scanning electron micrographs (left) and optical profilometry contour plots (right) of the bare specimens. (a) Specimen I, (b) specimen II, (c) specimen III and (d) specimen IV. The analyses area of the interferometry contour plots was $\sim 0.15 \text{ mm}^2$.

Figure 6.20 Scanning electron micrographs of the TCC coatings formed for 300 seconds on the alloys after pre-treatments. (a) Specimen I, (b) specimen II, (c) specimen III and (d) specimen IV. The analysis area of the interferometry contour plots was $\sim 0.15 \text{ mm}^2$.

Figure 6.21 SEM/EDX spectra of TCC coatings formed on the matrix of all specimens, where the normalized counts with respect to the count of aluminium were used.

Figure 6.22 The potentiodynamic scans of the TCC coatings in 0.05 M NaCl solution on the treated alloys. (a) Specimen I, (b) specimen II, (c) specimen III and (d) specimen IV.

Figure 6.23 The impedance- and angle-frequency plots of TCC coatings on the specimens I to IV.

Table 6.1 The chemical treatment for AA2024-T3 specimens after the mechanical polishing

Sample code	Etching	Desmutting
HNO ₃ treatment	1 min-5 wt.% NaOH-60 °C	30 s-50 v/v% HNO ₃ -25 °C
D30 treatment	30 s-10 wt.% NaOH-60 °C	90 s-15 v/v% D30-30 °C

Table 6.2 The average composition (weight %) of particles and the matrix on the alloy after HNO₃ treatment by SEM-EDX point analyses

	Al	Cu	Mg	Fe	Mn	Si	O
θ-phase (1)	45.05	53.14	0.84	-	-	-	0.97
S-phase (2)	41.84	42.38	14.24	-	-	-	1.53
α-phase (3)	54.03	20.81	-	15.43	7.30	1.39	1.03
matrix	93.57	4.61	1.21	-	-	-	0.62

Table 6.3 The average composition (weight %) of particles and matrix on the alloy after D30 treatment by SEM-EDX point analyses

	Al	Cu	Mg	Fe	Mn	Si	O
Cu sponges (1)	3.60	95.40	-	-	-	-	1
S phase (3)	91.56	5.83	1.91	-	-	-	0.71
α phase(4)	70.22	10.41	-	9.08	5.73	3.34	1.23
matrix	92.50	4.92	1.92	-	-	-	0.65

Table 6.4 RBS analyses ($\times 10^{15}$ atomic/cm²) of TCC coatings formed for different times on D30-treated alloys.

	Zr	Cr	Hf	S	F	Al	Cu	O _{RBS}	Cr/Zr
60 s	17.0	12.9	0.2	3.2	42.8	16.2	1.6	72.7	0.76
120 s	21.6	16.5	0.2	4.1	92.3	20.6	2.1	92.3	0.76
300 s	29.9	22.8	0.3	5.7	91.2	28.5	2.9	125.8	0.76

Table 6.5 The surface elemental concentration (atomic%) of TCC coatings formed on D30-treated alloys after immersion in the SurTec 650 solution at 40 °C for 60, 120 and 300 seconds: (a) before and (b) after the carbonaceous over layer correction.

Samples	Zr		Cr		O		Al		S		F		Cu		C
	a	b	a	b	a	b	a	b	a	b	a	b	a	b	a
60 s	9.6	19.6	4.5	10.1	36.0	56.1	1.7	2.4	0.7	1.2	5.7	10.1	0.1	0.5	37.9
120 s	9.5	18.9	5.1	11.1	36.3	55.6	1.4	2.0	0.7	1.1	6.2	10.8	0.1	0.5	36.2
300 s	7.9	16.5	5.6	12.8	35.0	56.0	1.6	2.3	1.3	2.0	5.2	9.5	0.2	0.9	37.2

Table 6.6 The concentration (atomic%) of each chromium component in the Cr 2p_{3/2} photoelectron region of the D30-treated alloys after immersion in the SurTec 650 solution at 40 °C for 60, 120 and 300 seconds.

	Cr(OH) ₃	Cr ₂ (SO ₄) ₃	Cr(VI) Oxide	CrF ₃	Cr5
60 s	4.0	4.4	0.8	0.9	0
120 s	3.7	5.0	0.9	1.4	0.1
300 s	3.7	5.8	1.1	2.1	0.2

Table 6.7 Parameters of TCC coatings/alloy systems obtained from fittings of EIS data with equivalent circuits, such as R(QR) model for the bare alloy and R(Q(R(QR))) model for the coated alloy. (a) and (b) represent alloys after nitric acid and D30 treatments respectively.

Experiments	Re Ωcm ²	Rpo Ωcm ²	Rp kΩ cm ²	Q co (×10 ⁻⁶ s ⁿ /(Ω cm ²))	nco	Ceff-co μF/cm ²	Qdl (×10 ⁻⁶ s ⁿ /(Ω cm ²))	ndl
Bare alloy_(a)	73	-	2.6	-	-	-	100	0.88
300 s-TCC_(a)	153	79	69.2	14.1	0.80	3.04	2.06	0.99
Bare alloy_(b)	159	-	10.6	-	-	-	17.1.	0.86
300 s-TCC_(b)	170	8230	205.2	8.9	0.83	2.35	2.8	0.96

Table 6.8 The chemical treatment for AA2024-T351 specimens after mechanical polishing

Sample code	Etching	Desmutting
I-50 % HNO ₃ treatment	-	5 min-50 v/v% HNO ₃ -25 °C
II-70 % HNO ₃ treatment	-	5 min-70 v/v% HNO ₃ -25 °C
III-NaOH+70 % HNO ₃	30 s-10wt.% NaOH-60 °C	5 min-70 v/v% HNO ₃ -25 °C
IV-NaOH+70 % HNO ₃	30 s-10wt.% NaOH-60 °C	90 s-70 v/v% HNO ₃ -25 °C

Table 6.9 Parameters of TCC coatings/alloy systems obtained from the best fittings of the experimental EIS data with the equivalent circuit of $R(Q(R(QR)))$ for the coated alloy.

Experiments	Re Ωcm^2	Rpo Ωcm^2	Rp k Ω cm^2	Q co $\times 10^{-5} \text{ s}^n / (\Omega$ $\text{cm}^2)$	nco	Ceff-co $\mu\text{F}/\text{cm}^2$	Qdl $\times 10^{-5} \text{ s}^n / (\Omega$ $\text{cm}^2)$	ndl
50 % HNO ₃ treatment	112	199	34.9	44.8	0.47	0.35	7.78	1
70 % HNO ₃ treatment	18	41	22.2	39.6	0.46	0.03	42.9	0.91
NaOH+70 % HNO ₃	103	183	68.0	6.8	0.65	0.24	17.4	0.90
NaOH+70 % HNO ₃	116	138	59.8	29.6	0.66	2.4	20.2	0.97

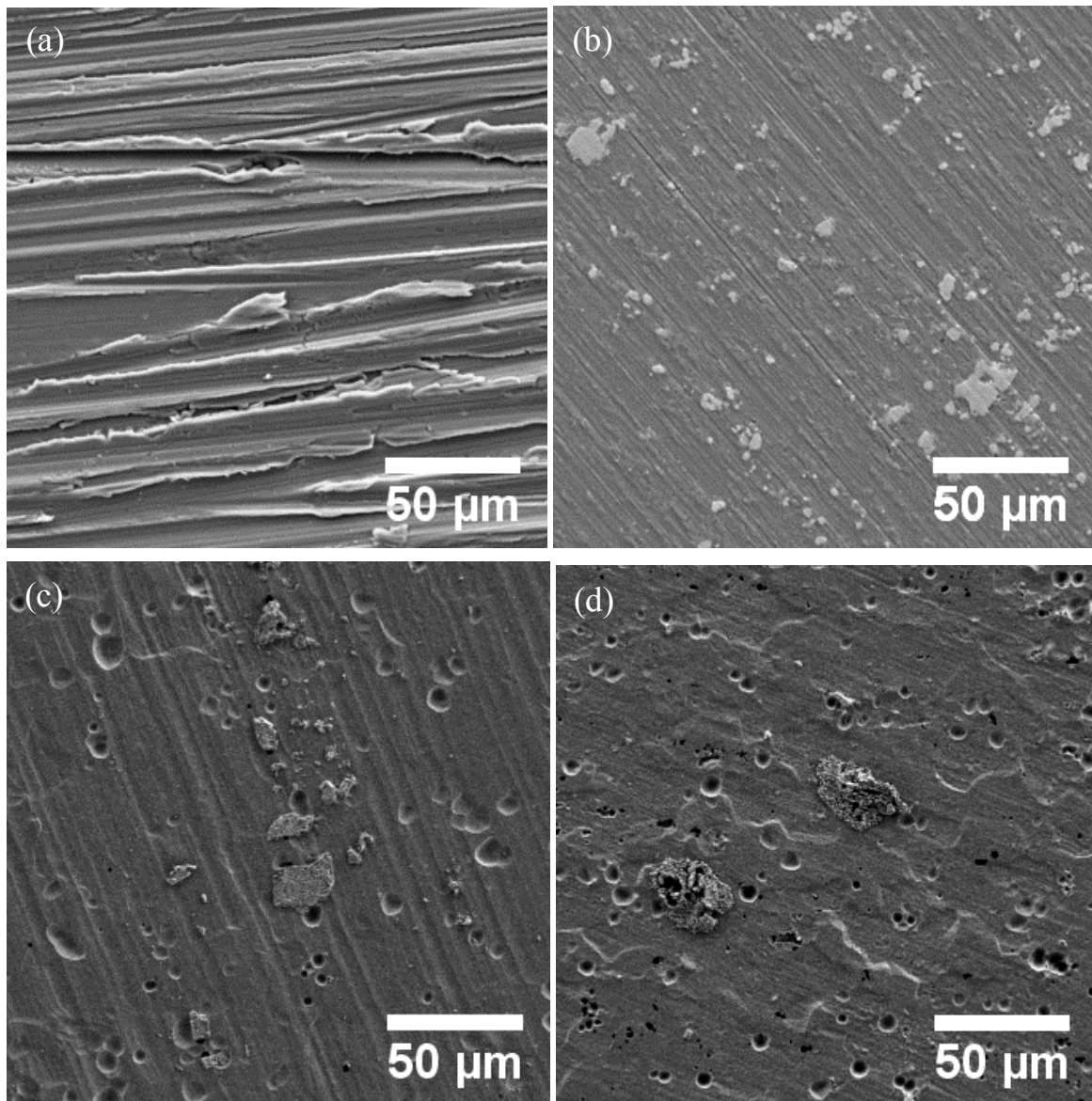


Figure 6. 1 Scanning electron micrographs of the AA2024-T351 alloy. (a) As-received alloy with the pluck lines along the rolling directions, (b) mechanically polished alloy to 4000 grit finish with grinding scratches and second-phase particles, (c) alkaline etched-HNO₃ deoxidized surface with protruded particles up to 20 microns dimensions and (d) alkaline etched-D30 deoxidized surface that is relatively clean with the reduced protrusion of particles.

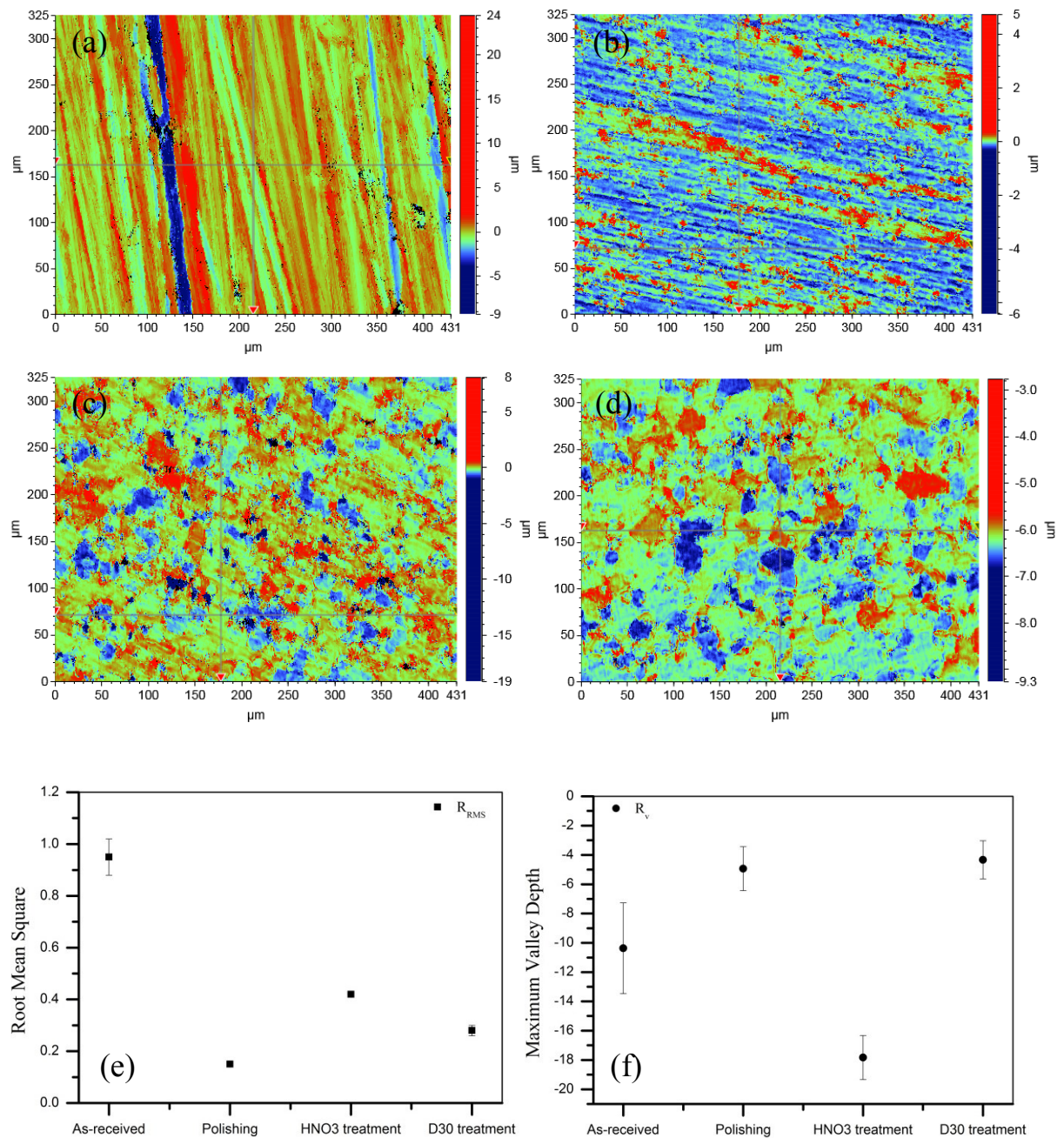


Figure 6. 2 Interferometry contour plots of AA2024-T351 alloy specimens. (a) As-received alloy, (b) mechanically polished alloy to 4000 grid finish, (c) alkaline etched-HNO₃ deoxidized surface and (d) alkaline etched-D30 deoxidized surface. The primary roughness parameters of the root mean square and the maximum valley depth were shown in (e) and (f) respectively.

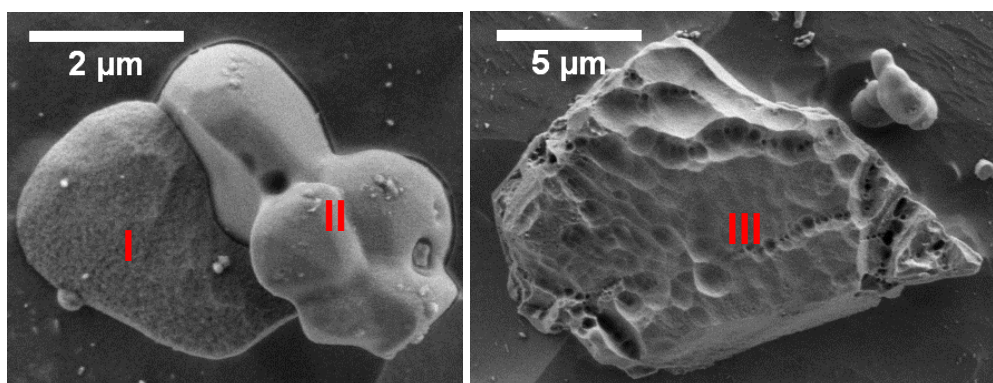


Figure 6. 3 Scanning electron micrographs of the AA2024-T351 alloys after the HNO_3 treatment. A cluster of θ phase (a, labelled 'I') and S phase (a, labelled 'II'); α phase (b, labelled 'III') particles.

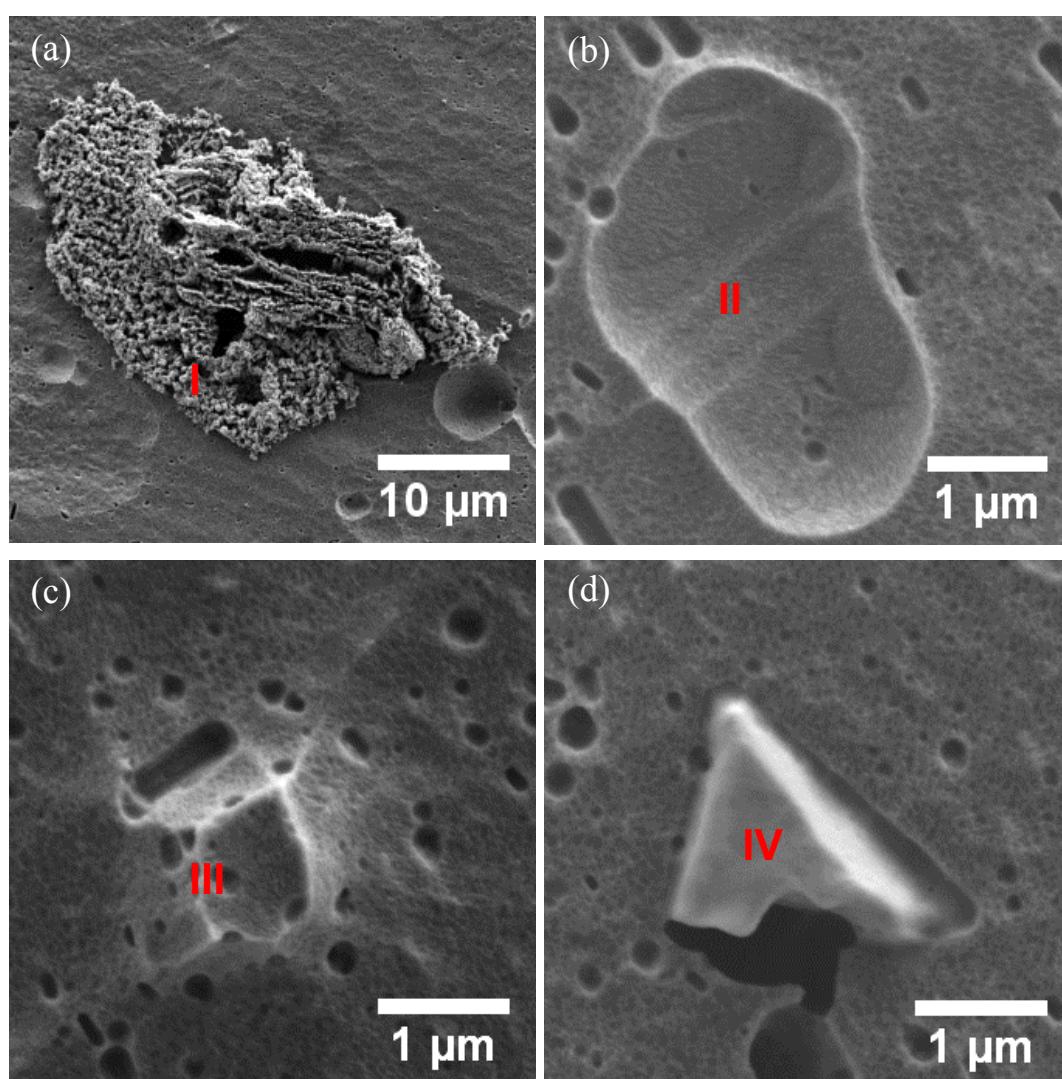


Figure 6. 4 Scanning electron micrographs of the surface of AA2024-T351 alloys after the D30 treatment. (a) The Cu-rich sponges (labelled 'I') with a honeycomb structure, (b) the cavity by the removal of the second-phase particle (labelled 'II'), (c) S phase particle present on the grain boundary (labelled 'III') and (d) α phase particle (labelled 'IV').

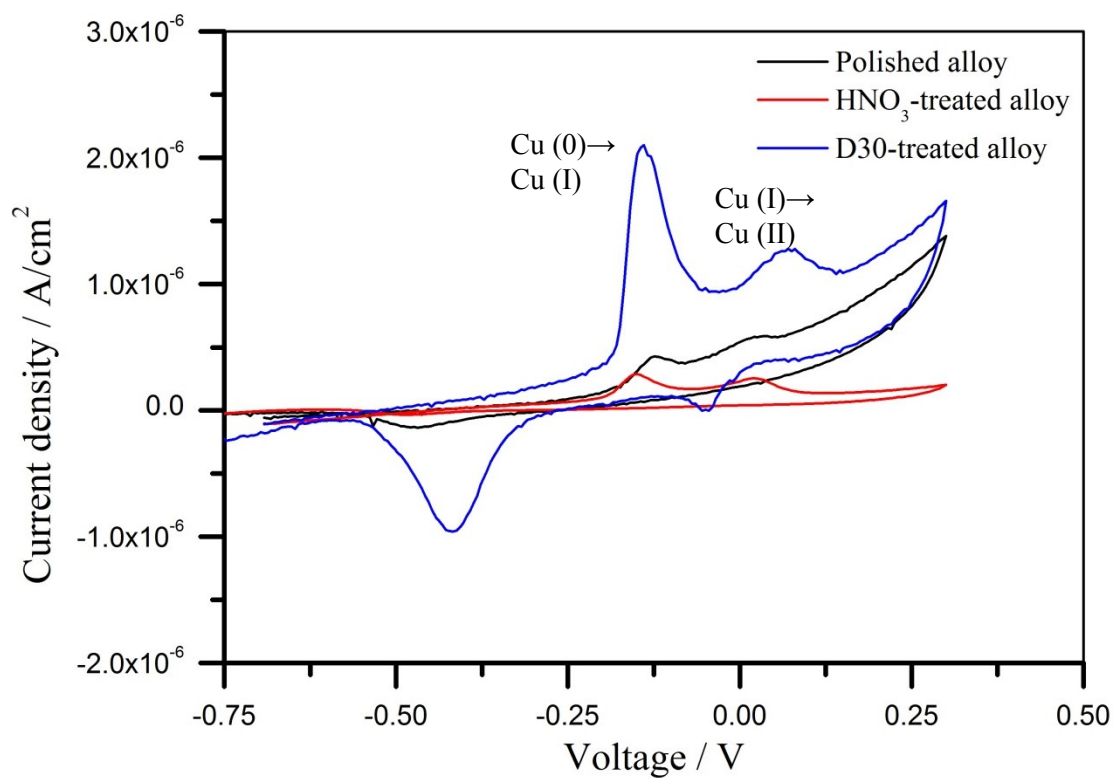


Figure 6. 5 The cyclic voltammetry of AA2024-T351 alloys after the mechanical polishing to $1 \mu\text{m}$ finish, alkaline etching and nitric acid desmutting, and alkaline etching and D30 deoxidation in the deaerated borate buffer solution.

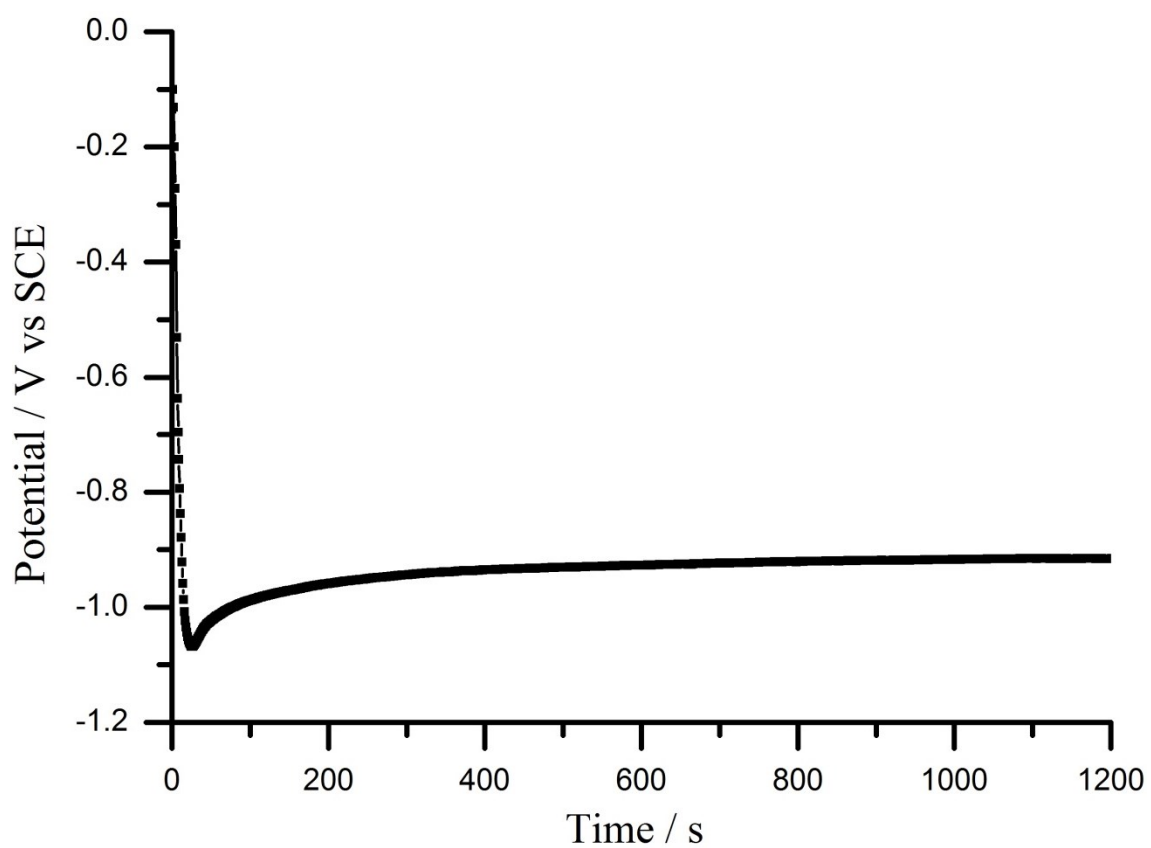


Figure 6. 6 The open circuit potential plot with dependence on the immersion time in the SurTec 650 bath at 40 °C for the D30-treated alloy.

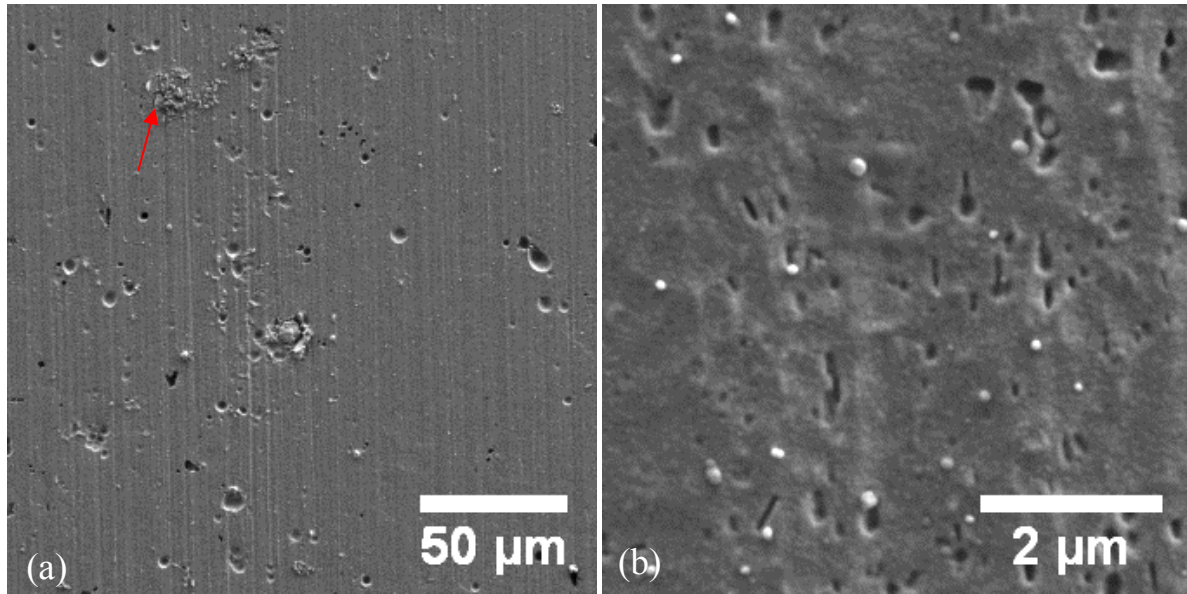


Figure 6. 7 Scanning electron micrographs of the TCC coatings formed for 300 s. (a) Plan-view morphology with cracks as outlined by arrows and (b) the fine coating on the matrix with nano-size nodules.

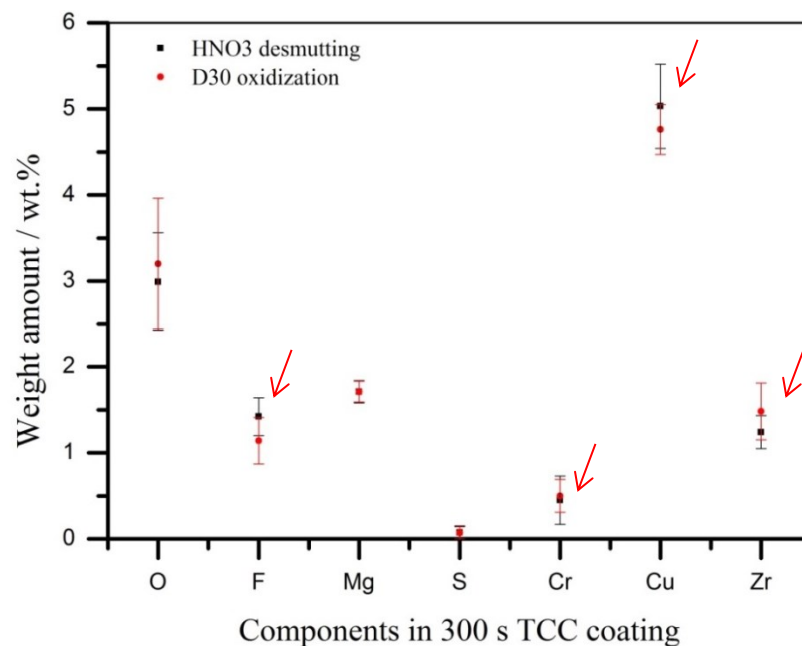


Figure 6. 8 The comparative EDX point analyses for 300 s TCC coating on the matrix by two pre-treatments, and the average amount of three points was used. No much variance of coating composition was detected.

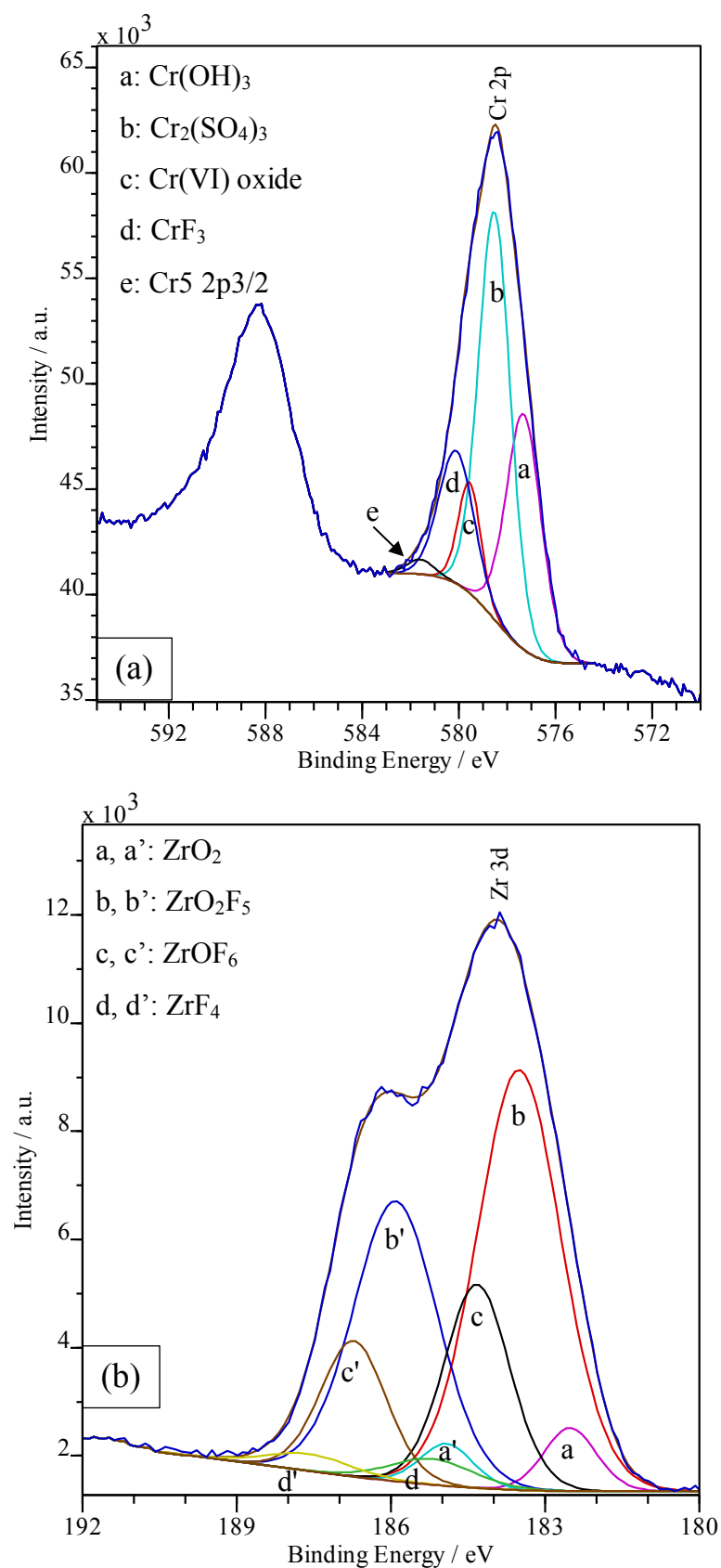


Figure 6. 9 The high resolution XPS spectra for (a) the Cr 2p_{3/2} and (b) and the Zr 3d photoelectron regions and curve fitting in the coating formed for 300 seconds on D30-treated alloy.

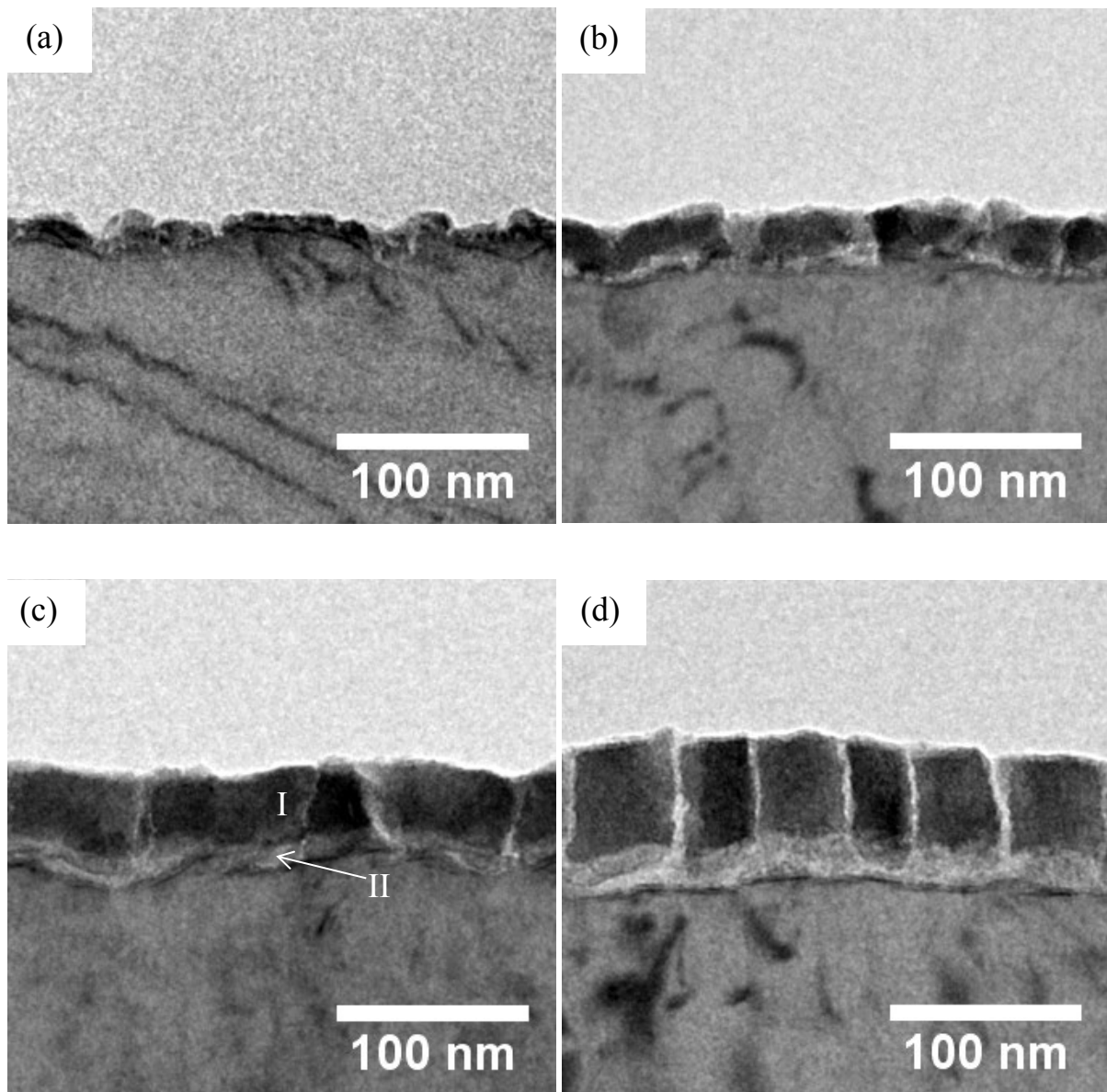


Figure 6. 10 Transmission electron micrographs of the ultramicrotomed sections of the TCC coating attached to the alloy substrate after different formation times. (a) 5 s, (b) 15 s, (c) 300 s and (d) 600 s in the dilute SurTec 650 at 40 °C. The two-layer coating structure consists of the outer main layer (labelled 'I') and the inner layer (labelled 'II').

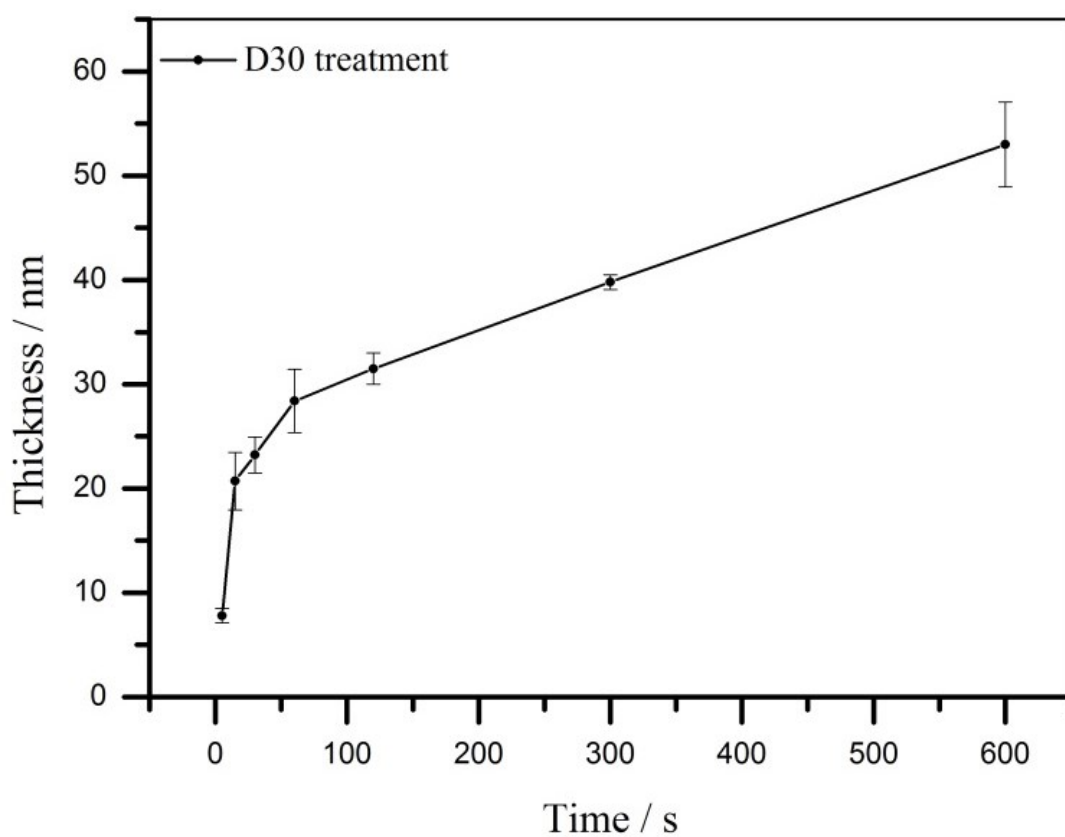


Figure 6. 11 Thickness plot of the TCC coatings with immersion determined by TEM measurements

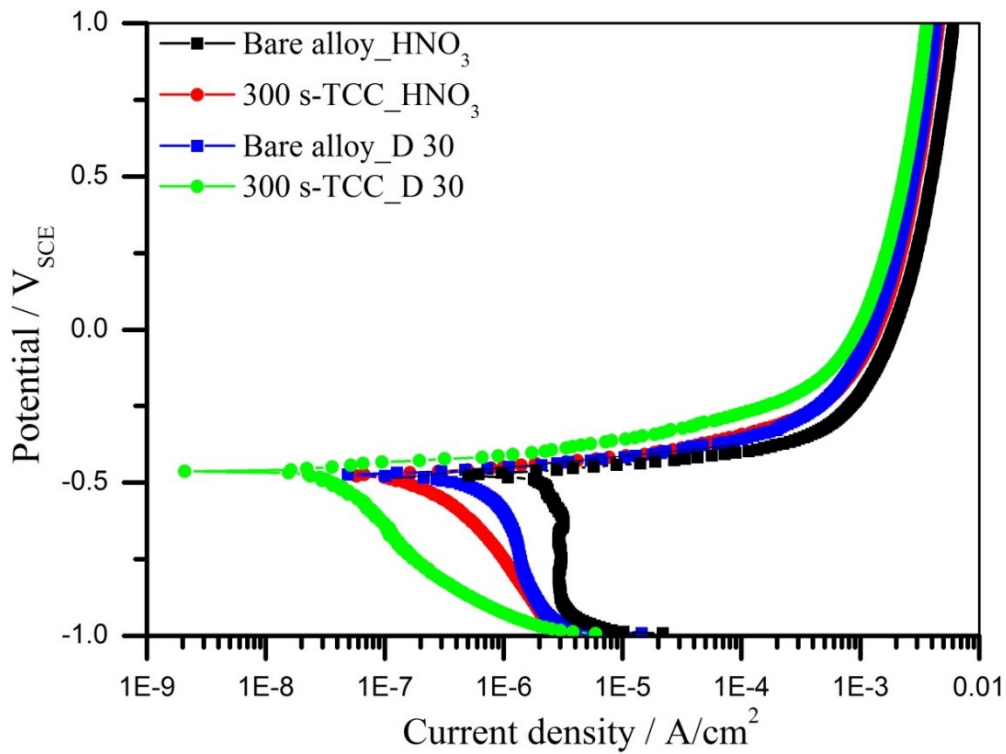


Figure 6. 12 The potentiodynamic scans in 0.05 M NaCl solution for the alloy treated by HNO₃ and D30 deoxidization, consisting of the bare alloys and the TCC coatings formed for 300 s. The TCC coating on D30-treated alloy displays the best cathodic barrier with the corrosion current density and potential values of $\sim 2.9 \times 10^{-8}$ A/cm² and -600 mV respectively.

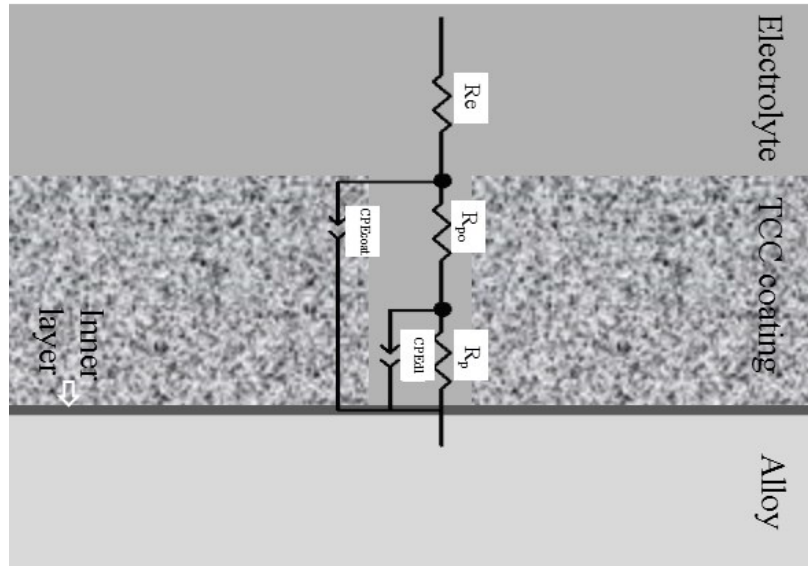


Figure 6. 13 The equivalent circuit model $R_e(Q_{coat}(R_{po}(Q_{dl}R_p)))$ applied to the TCC coating system. R_e , R_{po} and R_p represent the electrolyte resistance, the resistance of coating defects and charge-transfer resistance respectively; the constant phase elements (Q_{co} and Q_{dl}) represent the region in the coating and coating/substrate interface respectively.

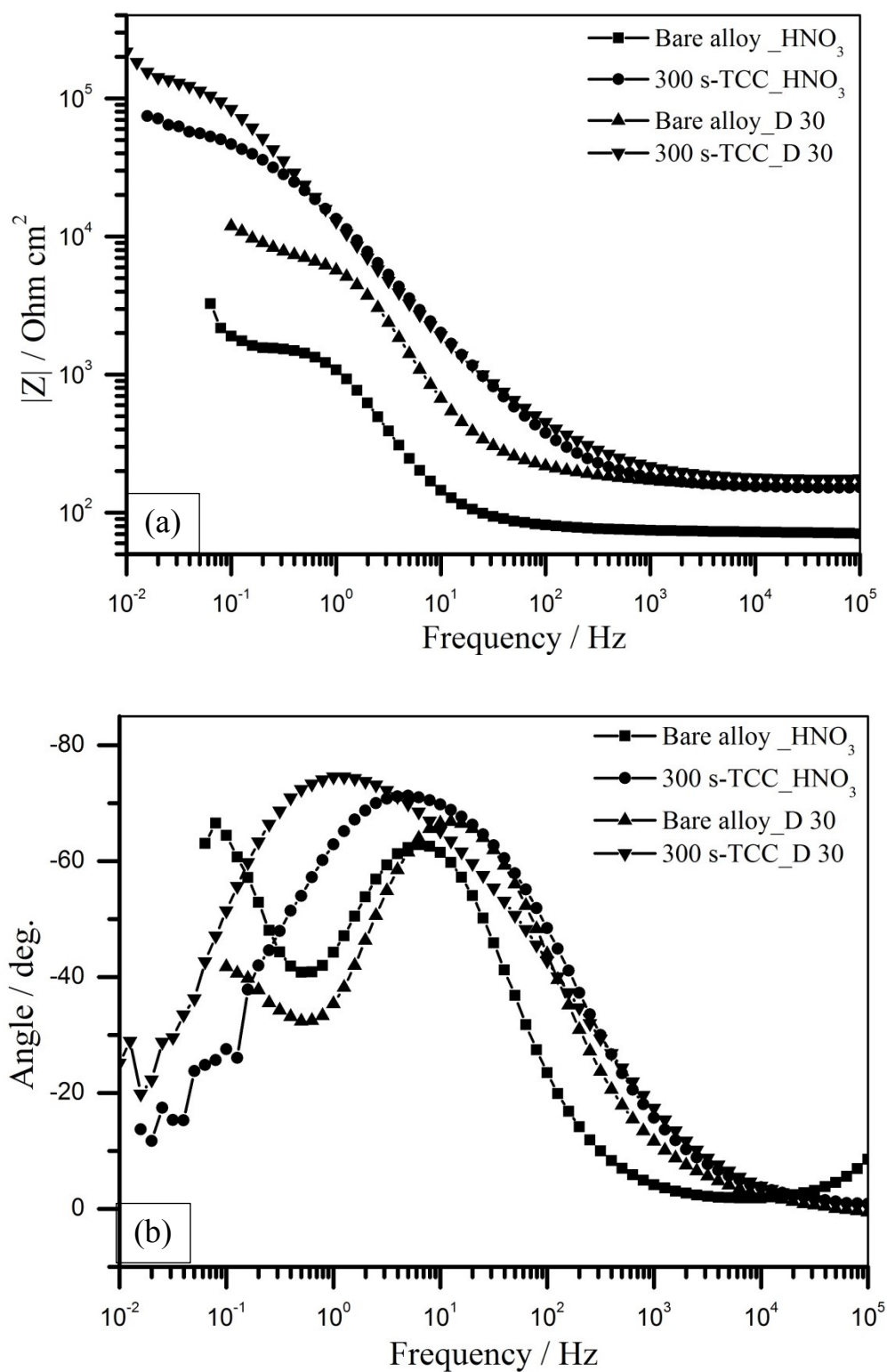


Figure 6. 14 (a) Impedance modulus-frequency plot and (b) phase angle-frequency plot for the bare alloys and the TCC coatings formed for 300 s on the alloys after either HNO₃ or D30 treatment. The 0.05 M NaCl solution was used. The TCC coating on the D30-treated alloy reveals the best corrosion resistance.

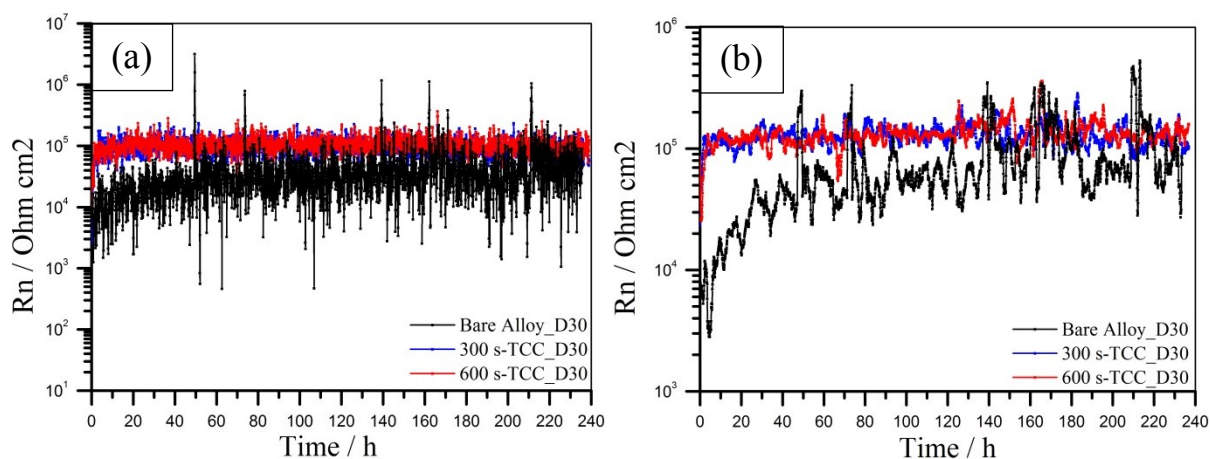


Figure 6. 15 Time evolution of noise resistance by the electrochemical noise analysis for the bare alloy reference and the TCC coatings formed for 300 and 600 s in the 3.5 wt.% NaCl electrolyte, where the calculation of fast Fourier transforms (FFTs) of potential and current were employed under the low frequencies of (a) 0.01 and (b) 0.005 Hz.

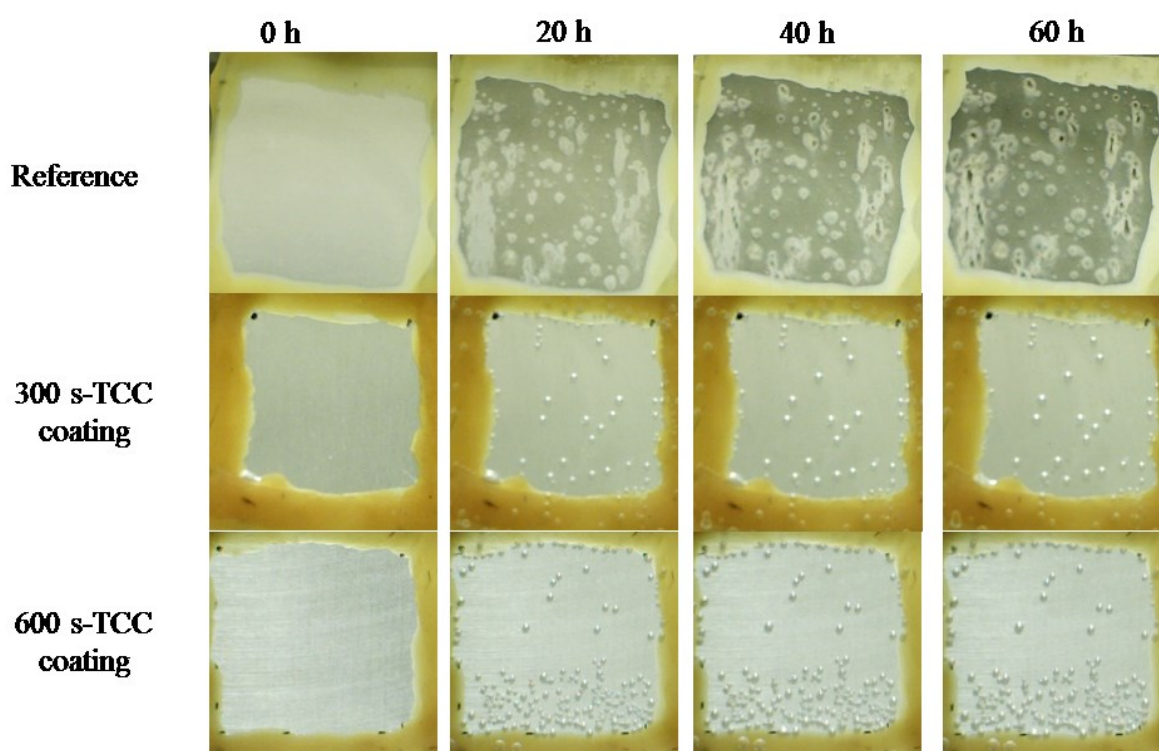


Figure 6. 16 The real-life macrographs with corrosion evolutions up to 60 h for the bare alloy reference and TCC coating formed for 300 and 600 s in the 3.5 wt.% NaCl electrolyte.

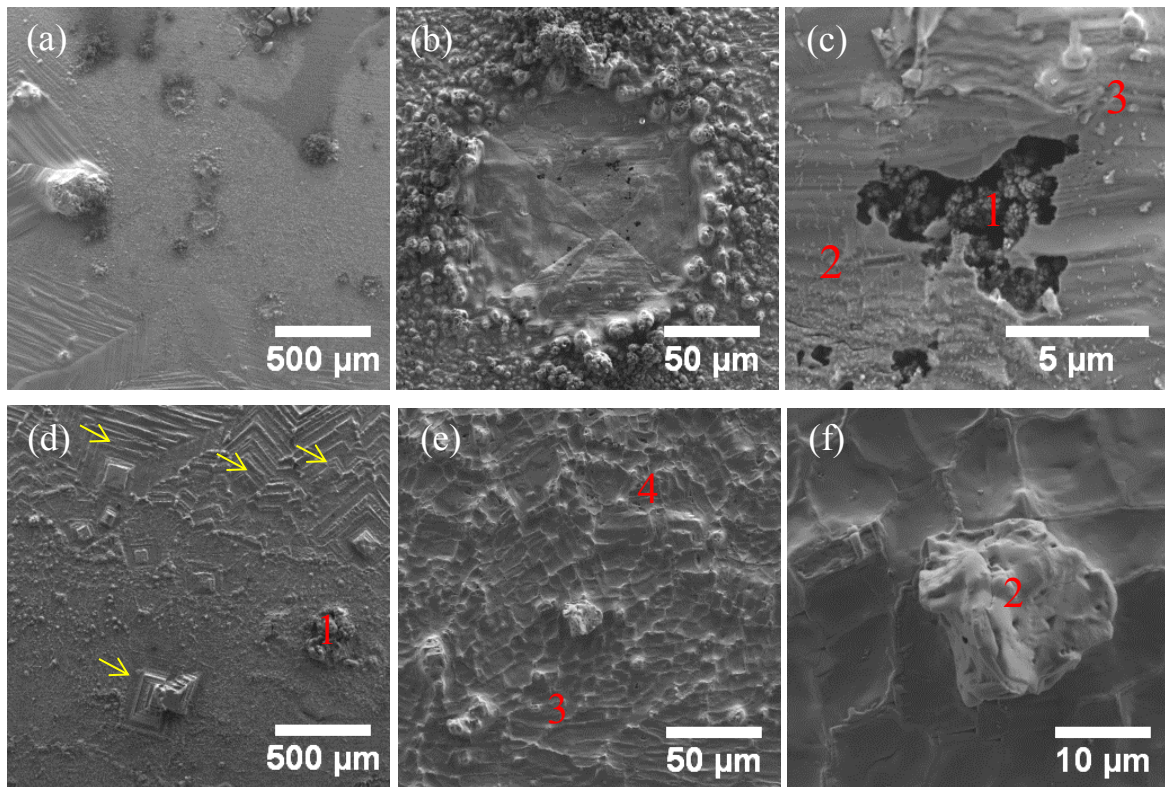


Figure 6. 17 Scanning electron micrographs of corrosion in the TCC coatings formed for (a-c) 300 and (d-f) 600 seconds with a standard post-treatment after long-term immersion in 3.5 wt.% NaCl solution for 240 hours.

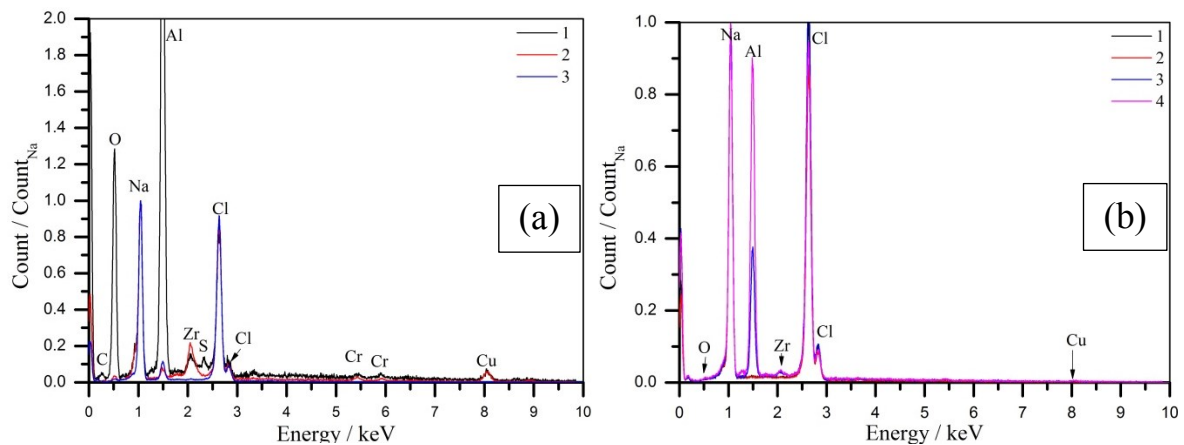


Figure 6. 18 The SEM/EDX spectra of selected points in the corroded TCC coatings formed for 300 and 600 seconds after long-term immersion in 3.5 wt.% NaCl solution for 240 hours.

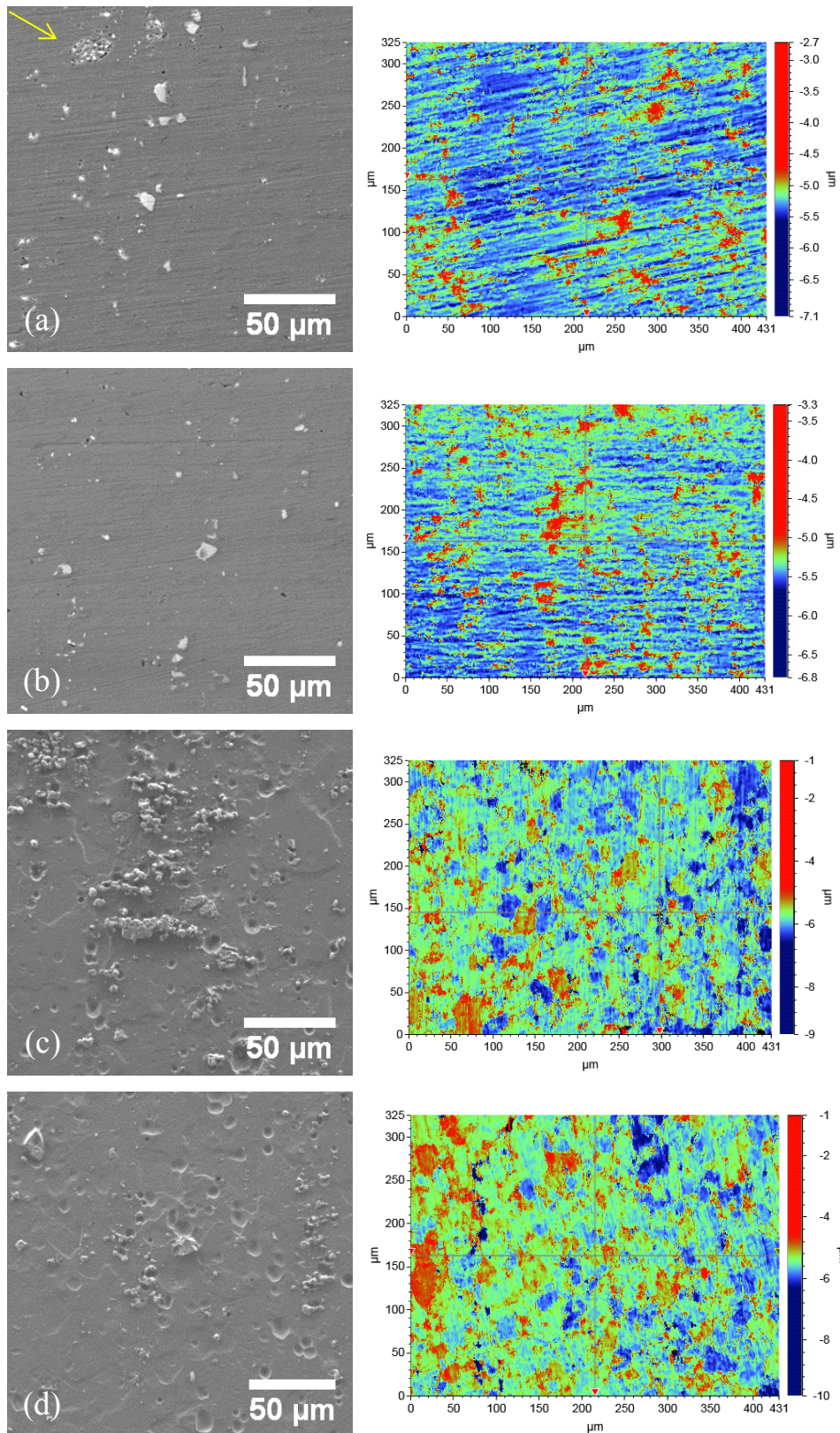


Figure 6. 19 Scanning electron micrographs (left) and optical profilometry contour plots (right) of the bare specimens. (a) Specimen I, (b) specimen II, (c) specimen III and (d) specimen IV. The analyses area of the interferometry contour plots was $\sim 0.15 \text{ mm}^2$.

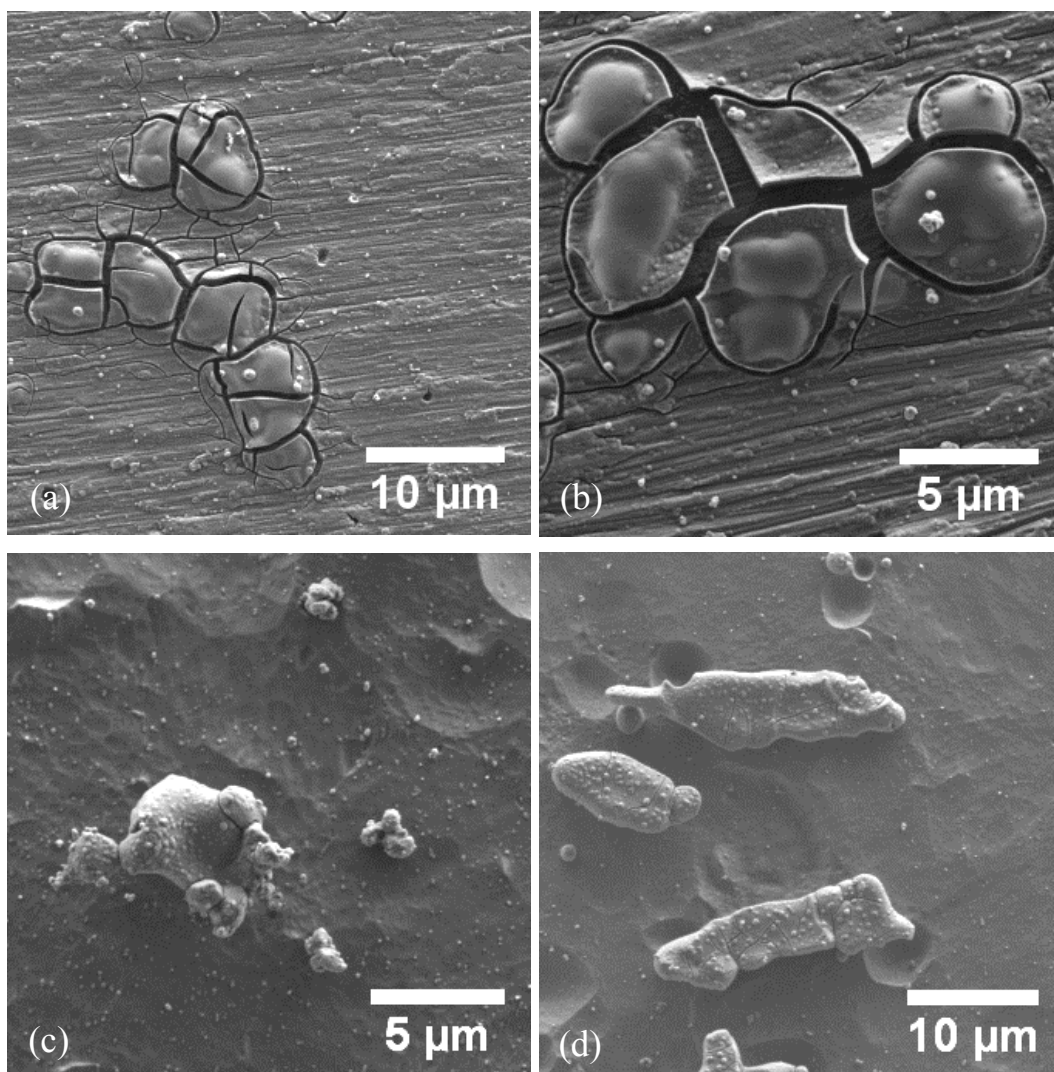


Figure 6. 20 Scanning electron micrographs of the TCC coatings formed for 300 seconds on the alloys after pre-treatments. (a) Specimen I, (b) specimen II, (c) specimen III and (d) specimen IV. The analysis area of the interferometry contour plots was $\sim 0.15 \text{ mm}^2$.

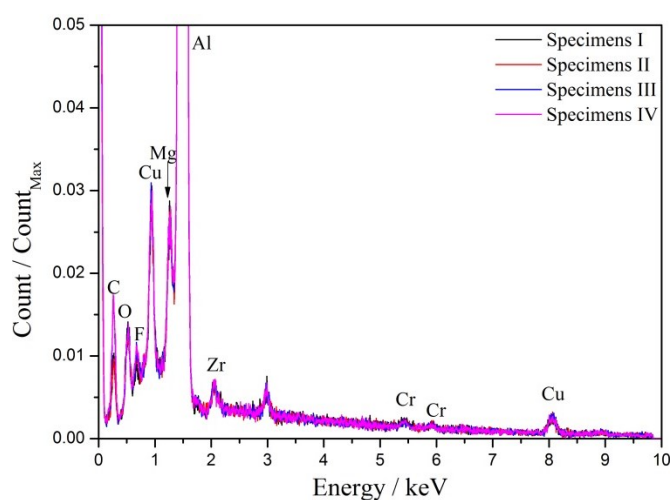


Figure 6. 21 SEM/EDX spectra of TCC coatings formed on the matrix of all specimens, where the normalized counts with respect to the count of aluminium were used.

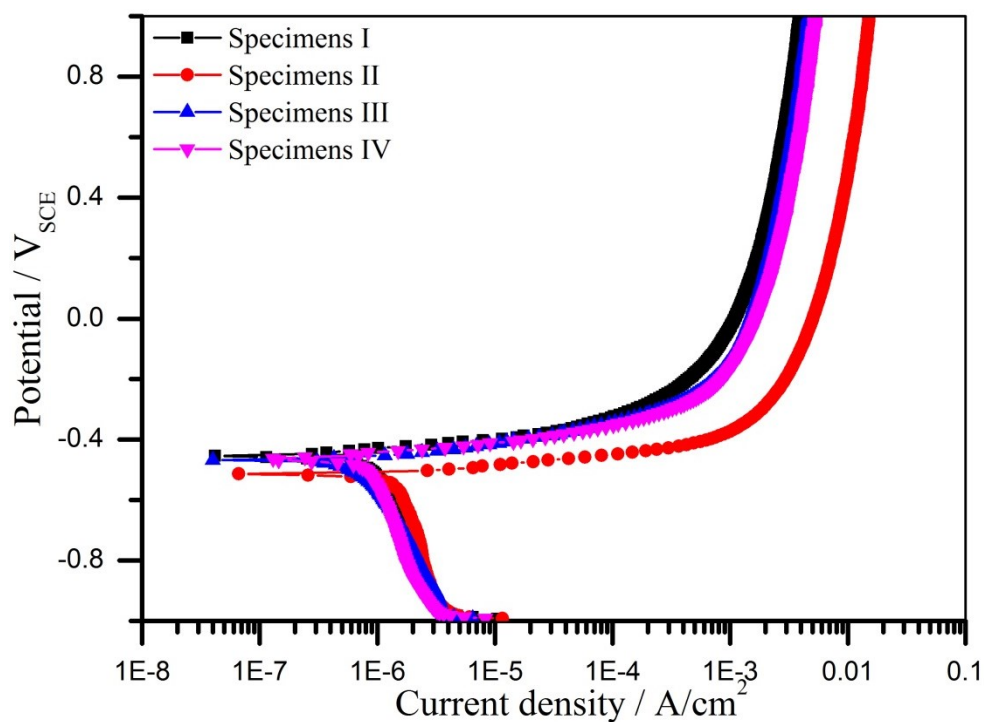


Figure 6. 22 The potentiodynamic scans of the TCC coatings in 0.05 M NaCl solution on the treated alloys. (a) Specimen I, (b) specimen II, (c) specimen III and (d) specimen IV.

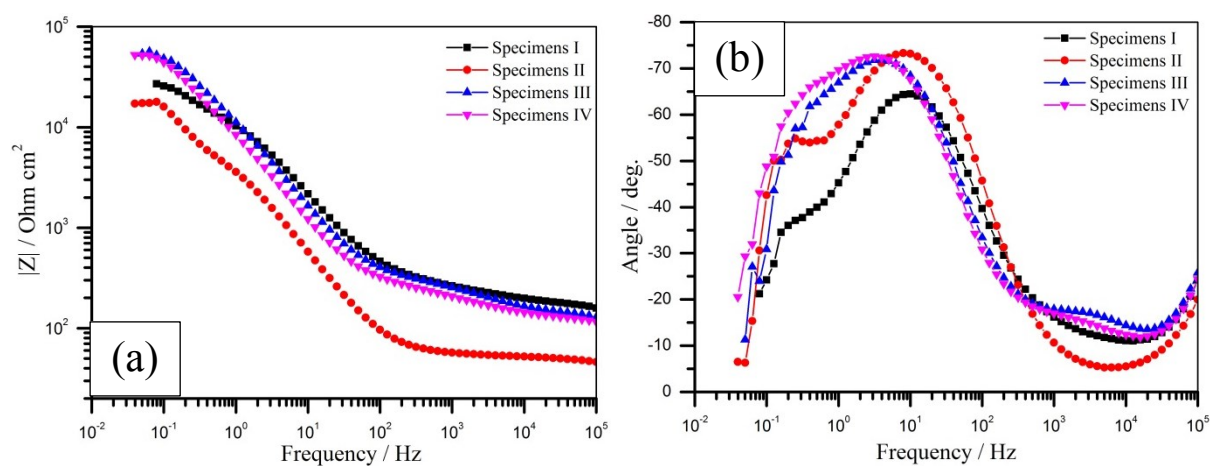


Figure 6. 23 The impedance- and angle-frequency plots of TCC coatings on the specimens I to IV.

Chapter 7 INFLUENCE OF COATING POST-TREATMENTS

This chapter comprises four main parts, including an introduction, results and discussion and the summary. The results consist of (i) the water temperature influence on surface morphology, (ii) the water temperature influence on coating composition, (iii) the water pH influence, (iv) electrochemical properties and (v) the influence of sodium sulphite addition in the water bath. Therefore, the subsequent discussion part contains (i) the influence of water temperature, (ii) the influence of the pH value of the water bath and (iii) the influence of sodium sulphite.

In this chapter, the alloys were pre-treated by alkaline etching and nitric acid desmutting; the influence of sodium sulphite was examined on the alloys after pre-treatment by alkaline etching and D30 desmutting. The underlying experimental condition of such pre-treatment was presented in Chapter 6. The post-treatment of the coated alloys consists of the immediate immersion in deionized water for 120 s, a deionized water rinse and drying in a cool air stream. Prior to examination, the specimens were stored in the laboratory environment for 24 hours. In order to reduce the transient Cr(VI) species in the TCC coatings, the sodium sulphite solution was used soon after the conversion coating treatment to provide an eco-friendly coating. These solutions, of 10, 50 and 100 g/l Na₂SO₃ are ~0.08, 0.40 and 0.80 M respectively are used to investigate their efficiency of the removal of Cr(VI) species. Further, the pH value of the 100 g/l Na₂SO₃ solution was also examined for the influence on the corrosion protection, where 5 wt.% sulphuric acid was used to adjust the solution pH to ~8.5 and 7.5. The specimens were dried in a cool-air stream and were then investigated by Raman spectroscopy and X-ray photoelectron spectroscopy.

7.1. Introduction

TCC coatings generally consist of one outer main layer of hydrated zirconium-and chromium-rich oxides over a fluoroaluminate inner layer. [143, 148, 150] The concentrated presence of fluorine along the substrate in Chapter 5 was revealed to enhance the local oxidation to generate substrate recessions. Moreover, this supply of the fluorine ions from the bulk bath towards the substrate was suggested to proceed without the blocking effect of the thickening coating [210]. These fluorine ions were revealed to be more aggressive than

chloride to corrode the aluminium substrate [76]. Furthermore, the presence of the fluorine ions and the dissolved oxygen promotes the copper dissolution rate with the first-order kinetics of each concentration of the fluorine and oxygen [54, 55]. The primary form of the fluoride component was revealed as fluoride and oxyfluoride of zirconium and aluminium, and chromium (III) fluoride by means of XPS analyses, which is consistent with the hard-soft acid-base (HSAB) theory [59]. Considering the presence of the free fluorine ions in the bath and the continuous supply into the substrate, there probably exhibits a balance between the formation of these fluorides and oxyfluorides and the free fluorine ions. In terms of the transport influence factor, the $t^{1/2}$ temperature-dependent kinetics were revealed as an inter-diffusion process of the single fluorine ions during dissolution of fluorozirconate glasses [233]. In this case, the water immersion with the increased temperature soon after conversion coating treatment may promote the egress of the fluorine enrichment beneath the coating outwards to the bulk water.

Concerning the effect of the post-treatments, the air aging treatment was revealed to improve the corrosion performance as evidence by a $4\times$ increased charge-transfer resistance after 7-day air aging when the coating was immersed in a 0.5 M Na_2SO_4 solution [153]. However, this prolonged air aging leads to coating dehydration with water loss and results in mud-crack defects, and the coatings become more hydrophobic as evidenced by an increased water contact angle up to 100° [234]. In this case, the overnight air aging was used in this study. This effect was expected to be similar to that of chromate conversion coating for an ageing period of 24 hours in the air [80, 90]. In addition, the immediate water rinse for 120 seconds after the coating treatment was suggested to stabilize the near-surface coating prior to this air aging, especially using the tap water of pH 6.8. That tap water is relatively more basic than the deionized water (pH=5.8) [150, 153, 228].

Thus, our standard post-treatment process consists of the deionized water immersion for 120 s soon after coating treatment, deionized water rinsing, a cool-air stream drying and the air ageing for 24 hours in the laboratory air. In order to comparatively study the effect of water immersion post-treatment, the coatings without the water immersion were used as a control (named I). Further, the factors of water immersion post-treatments include the temperatures of 20, 40 and 60 $^\circ\text{C}$, the pH values of 5, 7 and 9, and the addition of sodium sulphite into the water at a concentration of 50 and 100 g/l. The specimen codes of the water temperatures at

20 and 40 °C were named as treatments II and III respectively. In this present study, the high-resolution transmission electron microscopy with energy dispersive spectroscopy (TEM/EDX) was used to determine the elemental distributions across coatings. The electrochemical impedance spectroscopy (EIS) was employed to investigate the corrosion protection by the TCC coatings.

7.2 Results

7.2.1 Water temperature influence on morphologies

The cross-sectional transmission electron micrographs of the TCC coatings formed for 120 s with and without water immersion treatment are shown in Figure 7.1. The effect of water treatment appeared in the inner layer, where a minimum presence of defects was observed in the coating after treatment III (Fig. 7.1(b)). Further, the average coating thickness from six measurements in Figure 7.2 revealed that the coating appeared more homogeneous after treatment III. Support of this fact is the coating thicknesses of 37 ± 1.67 , 40 ± 0.62 , 39 ± 0.76 nm for the cases of I, II and III treatments respectively, although the mechanical defects can be produced by the ultramicrotomy. For the TCC coating formed for 300 s, the cross-sectional morphologies after the water immersion post-treatment are shown in Figure 7.3. The TCC coating formed for 300 s with treatment III (Fig. 7.3 (b)) displayed the most uniform inner layer over the macroscopic alloy surface. In contrast, the evident delamination of the coating of treatment I (Fig. 7.3 (a)) and the defects of the substrate recession for the coating of treatment II (Fig. 7.3(c)) were also investigated. The coating of treatment III revealed the maximum coating thicknesses of 47 ± 1.44 nm in Figure 7.4.

7.2.2 Water temperature influence on compositions

The half-quantitative TEM/EDX analyses of the elemental components in TCC coatings formed for 300 s followed by the water immersion are shown in Figure 7.5, where the average measurement of three different areas was used. For the inner layer of the TCC coating (Fig. 7.5 (a) and the corresponding area in Fig. 7.5(c)), the amount of oxygen as the component of oxide and hydroxide appeared to be similar for all coatings. The concentration of aluminium as a component of the alumina film showed the maximum value for the coating

after treatment III. By contrast, the minimum aluminium content was observed in the coating after treatment I. In addition, zirconium and chromium were most concentrated in the inner layer of the coating after treatment I that also contained the minimum amount of carbon. The presence of carbon is possibly attributed to the contribution from organic contamination of the deionized water [195]. Notably, the concentration of fluorine in the case of treatments II and III displayed a decrease compared to the situation of treatment I and the atomic ratios of fluorine relative to the metals of Al, Zr and Cr in the coatings after treatment of III and II were ~ 0.13 , 0.13 and 0.19 . This indicated the promoted diffusion of fluorine away from the coating/substrate interface.

In terms of the outer layer of Fig. 7.5 (b) and the analysis area outlined in Fig. 7.5 (d), the water treatment was revealed to reduce the concentration of fluorine compared to the coating of treatment I with the maximum fluoride of ~ 5 wt.%. Further, the fluorine contents (at.%) with respect to the combined metals of Al, Zr and Cr are ~ 0.04 , 0.05 and 0.15 for the specimens after treatment III, II and I respectively. This revealed that the water treatment can reduce the free fluorine ions in the outer coating layer to stabilize the coating. For oxygen concentration, ~ 40 and 30 wt. % contents were observed in the coatings after treatments III and I respectively. Moreover, the ratios of oxygen relative to the combined contents of zirconium, chromium and aluminium (at.%) after treatments of III, II and I are ~ 3.4 , 4.3 , and 2.4 respectively. This indicated the more hydrated nature of the outer coating layer after the water treatment. In addition, the copper and sulphur concentrations showed a little variation in the outer and inner layers for all the treatment conditions. Further, aluminium was revealed to concentrate in the inner layer as evidenced by the level of $\sim 20+$ wt. % compared with <10 wt. %Al in the outer layer, which is consistent with the alumina inner layer in the TCC coatings [224].

7.2.3 Water pH influence

Figures 7.6(a, b, c and d) and Figures 7.7 (a, b, c and d) show the transmission electron micrographs of the TCC coatings formed for 120 and 300 s of treatment III respectively, with dependence on the pH values. For the coating microstructure, no significant change was revealed with the pH variance. In terms of the coating thickness, the coating formed for 120 s of treatment III (pH=7) appeared to significantly shrink by a factor of $\sim 25\%$ compared to the

situation of the pH values at 5 and 9 (Fig. 7.6 (d)). By contrast, the minimum thickness (~ 34 nm) for the TCC coatings formed for 300 seconds occurred at the situation of the pH value at 9 (Fig. 7.7 (d)), and the coatings after III water treatment (pH=5 and 7) displayed a relatively stable coating of ~ 44 nm thick in Figure 7.7 (a and b).

7.2.4 Electrochemical behaviours

The influence of the water parameters on the corrosion performance of the TCC coated substrates was examined by the electrochemical impedance spectroscopy (EIS) in the 3.5 wt.% NaCl solutions. The equivalent circuit model of Figure 7.8 was used to interpret the impedance responses; the fitted results are shown in Tables 7.1, 7.2 and 7.3 where the chi-squared error was all less than 0.01. The impedance modulus- and phase angle-frequency evolution in Figures 7.9, 7.10 and 7.11 revealed the electrochemical behaviours of the coatings with dependence on water temperatures and water pH respectively. The open-circuit potentials after the prior stabilization period of 30 min were all around ~ -0.60 mV_{SCE}.

The charge-transfer resistance, R_p , for the TCC coatings after treatment II (Table 7.1), revealed a $\sim \times 10$ -20 increase with the prolonged treatment in comparison to the resistance value of the bare alloy ($\sim 1.8 \times 10^3 \Omega \text{ cm}^2$). The relative lower coating resistances, R_{po} , of tens of $\Omega \text{ cm}^2$ suggested a porous microstructure of the coating, which is consistent with the interfacial defects in the SEM observations. In Figure 7.9 (b), one time constant was observed around $\sim 10^1$ Hz on the bare alloys, while two visible time constants existed at $\sim 10^1$ and 10^4 Hz for the low and high frequency peaks, revealing the coating capacitance property. The constant phase elements (CPEs) were used to represent the non-ideal capacitance (Q) because their phase angles were less than 90° . The effective capacitance function of these CPEs was defined as $C_{eff} = (j\omega)^{-n} Q^{-1}$, where the smaller effective capacitance means the better corrosion protection and the larger value of n represents the greater homogeneity of the coatings. For the double-layer capacitance Q_{dl} , TCC coating formed for 600 seconds revealed a significantly lower value of $\sim 3.92 \mu\text{F}/\text{cm}^2$ C_{eff-dl} compared to that in the bare alloy ($\sim 79.2 \mu\text{F}/\text{cm}^2$). Furthermore, a relatively higher ratio n_{dl} at ~ 0.92 is in good agreement with such improved homogeneity after 600 seconds of treatment. By contrast, the effective capacitances for the coatings region ($C_{eff-coat}$) revealed an increased trend with the prolonged treatment, relating to the presence of mud cracks with drying of the coating in the air to deteriorate the

coating homogeneity. For example, the $C_{\text{eff-coat}}$ value of the coating formed for 600 s was $\sim 2.13 \mu\text{F}/\text{cm}^2$ while that in the coating formed for 120 s was the lowest at $\sim 0.49 \mu\text{F}/\text{cm}^2$.

Table 7.2 shows the electrochemical behaviour of the TCC coatings after the treatment III, where the alloys after conversion treatment for 600 seconds displayed the best corrosion protection with a $\sim \times 50$ increase of the charge-transfer resistance R_p . In comparison to those after treatment II (Table 7.1), the resistances of the coating pores or defects, R_{po} , and the charge-transfer resistances showed significant improvement after treatment III. For example, an $\sim \times 8$ increase was observed in the coating formed for 300 s ($\sim 290 \Omega \text{ cm}^2$) compared to the case of II treatment ($\sim 39 \Omega \text{ cm}^2$). This indicated that the treatment III reduced the coating defects to enhance the corrosion protection of the coated alloy. In addition, the charge-transfer resistance of the coating formed for 600 s ($\sim 10^5 \Omega \text{ cm}^2$) revealed an $\sim \times 3$ increase compared to the coating after treatment II ($\sim 4 \times 10^4 \Omega \text{ cm}^2$). Concerning the effective capacitance, C_{eff} , the treatment III also revealed a great role in stabilizing the inner coating layer as evidenced by the lower $C_{\text{eff-dl}}$ values. For example, the coatings formed for 300 seconds with treatments III and II revealed the effective capacitance values at $\sim 1.49 \mu\text{F}/\text{cm}^2$ and $\sim 6.21 \mu\text{F}/\text{cm}^2$ respectively. In terms of the effective capacitance in the coating region $C_{\text{eff-coat}}$, the coatings formed for 600 seconds after treatments III and II did not display a significant change after treatment III and II as evidenced by the values of 2.45 and $2.13 \mu\text{F}/\text{cm}^2$ respectively. Notably, the larger value of the $C_{\text{eff-coat}}$ in the coating formed for 120 s after treatment III was revealed in comparison to the case after treatment II. These discrepancies of the treatment III effect on the effective capacitances of the coating region are possibly related to how homogeneous the coating formed on the surface [165]. The TCC coating formed for the short immersion period revealed the preferential coating formation on the second phase particles to result in the surface inhomogeneity. During the prolonged treatment, the developed coating on the second phase particles inhibited the substrate oxidation to slow down the coating thickening, and thus the lateral coating growth on the matrix improved the thickness variance with that on the particles. In this case, the coating formed for 120 s significantly swells in the treatment III to become more inhomogeneous and to deteriorate the capacitance property.

The influence of the pH value of the treatment III on the corrosion protection of TCC coatings formed for 600 s was also investigated, as shown in Figure 7.11 with the fitted

results listed in Table 7.3. With increasing pH value from 5, 7 to 9, the resistances of the pores in the coating R_{po} and the charge-transfer resistance R_p revealed the evident decreases, possibly relating to the shrinking coatings in the alkaline solution. The effective capacitances, C_{eff-dl} , were reduced from ~ 3.86 to $\sim 2.16 \mu F/cm^2$, which means that the inner layer became more intact and stable to maintain the larger capacitance property. By contrast, the outer layer revealed a visible deterioration as evidenced by the increased value $C_{eff-coat}$ from 2.45 to $\sim 5.25 \mu F/cm^2$. Thus, the best coating process on the alloy after the pre-treatment of alkaline etching and nitric acid desmutting is the conversion treatment for 600 seconds, followed by the post-treatment of immersion the deionized water for 120 seconds. The water solution is at 40 °C and pH 5.

7.2.5 Influence of sodium sulphite in the water bath

The addition of sodium sulphite into the water bath that was used soon after the coating treatment has revealed the effectiveness in reducing the near-surface chromium (VI) in the TCC coatings formed on pure Al (Chapter 4). In this case, the reaction mechanism of sulphite and Cr (VI) species was expected to occur on the coated alloy and this additive may influence the corrosion protection of TCC coatings. Thus, the comparative study of corrosion protection of TCC coatings with and without the presence of sodium sulphite in the water bath was employed on the alloys after D30 treatment, where the conversion treatment was for 300 and 600 seconds. In order to distinguish the variance of treatment of TCC coatings, Table 7.4 shows the sample codes with respect to the examined specimens, where the standard post-treatment used in present study included the warm water immersion for 120 s, water rinsing and drying in a cool-air stream.

Figures 7.12 (a and b) show the impedance modulus- and phase angle-frequency evolution of all specimens I to V in the 0.05 M NaCl solution respectively, where both of the prior OCP stabilization runs for 30 min and revealed potentials of $\sim -0.51 V_{SCE}$. In comparison to the low-frequency resistance of specimen I control in Fig. 7.12 (a), the application of sodium sulphite into the water bath decreased the corrosion protection, especially in the case of specimens V with the lowest impedance modulus at 10^{-2} Hz ($\sim 8 \times 10^4 \Omega cm^2$). Moreover, the time constants (Fig. 7.12(b)) existed at $\sim 10^1$ Hz for the low frequency peaks exhibited a similar phase angle around -75° , indicating the comparable capacitance property between

these specimens. The equivalent circuit model in Fig. 7.8 of $R(Q(R(QR)))$ formula was employed to fit all data with chi-squared error as less than 0.03 as shown in Table 7.5.

Specimen I was used as a control in the absence of the sodium sulphite in the water bath. By contrast, the resistance of the pores in TCC coatings, R_{po} , displayed a significant decrease, especially on the specimen IV (100 g/ L sodium sulphite of pH $\approx$ 7.5) of a reduced factor of $\sim \times 80$. Furthermore, the charge-transfer resistance, R_p , of the specimens IV was decreased by $\sim \times 2$, indicating the possible damage by this chemical on the inner layer of TCC coating. In terms of the coating capacitance property $C_{eff-coat}$, specimens II and III showed an increased value up to $\sim 4.3 \mu F/cm^2$ compared to the specimen I ($\sim 2.35 \mu F/cm^2$). Notably, the reduced pH environment of sodium sulphite solution in specimen IV revealed no significance of the capacitance ($\sim 2.56 \mu F/cm^2$). The larger effective capacitance corresponds to the poorer capacitance and to the lesser extent of corrosion protection; thus, the specimens II and III revealed the relatively poorer corrosion protection by these coating regions. In addition, the similar capacitance (Q_{dl}) of the coating/substrate interface on the specimens I to IV revealed that the sulphite penetration either cannot penetrate into the coating bottom or it cannot damage the capacitance of the coating/substrate interface if this chemical may diffuse inwards to the substrate. Furthermore, the EIS examination of the influence of sodium sulphite of pH=7.5 was employed on the TCC coating formed for 600 seconds. The resistance of coating region and the charge-transfer resistance were evidently lower than specimen I, indicating the deterioration of the sulphite ions on the corrosion protection. However, the effective capacitance of coating/substrate interface exhibited the lowest value at $\sim 0.46 \mu F/cm^2$, indicating the most homogeneous microstructure and the intact interfacial bonding.

7.3 Discussion

7.3.1 Influence of the water temperature

The cross-sectional morphologies of the TCC coatings formed for 120 and 300 s reveal that the water treatment III (40 °C) provides the best improvement compared to the specimen I without the water treatment and that after the water treatment II (20 °C). This improvement

mechanism by rising water temperature possibly relates to the temperature-dependent diffusion of the coating components [235] as follows.

For the outer coating layer, the higher ratios of oxygen relative to the combined metal components revealed that the coating became more hydrated. The decayed fluorine concentration by weight and the reduced atomic ratios of fluorine relative to the combined concentration of metals after treatment III and II identified that the water treatment promoted the diffusion kinetics of the free fluorine ions to stabilize the outer coating layer. The coating thickness correlates with the temperature effect on the gel-like coating, which may shrink sufficiently at low temperature and swell at the high temperature [236]. Thus, the water bath III at 40 °C was increased by $\sim \times 8$ factors of the resistance of the porous region compared to that after the treatment II.

For the inner coating layer, the treatments II and III also revealed the promoted outward egress of the free fluorine ions as evidenced by the decreased ratio of fluorine relative the combined metal components. Notably, the ratios of fluorine relative to the combined metal components in the inner layer displayed great significance compared to the outer layer even after the water treatment. This correlates with the presence of oxyfluorides that were relatively stable. In addition, the concentrated aluminium in the specimens after treatment III revealed the presence of more alumina in the inner coating layer, indicating the more stable coating/substrate interface. These improved components are in good agreement with the decrease of the effective capacitance, $C_{\text{eff-dl}}$, that represents the enhanced distribution of reactivity along the substrate [155].

In summary, the post-treatment of immersion in the warm water can produce a more hydrated outer layer and the stronger bonding strength of the inner coating layer with the substrate. Consequently, the corrosion protection of these TCC coatings was improved.

7.3.2 Influence of pH values of the water bath

The pH effect profile on the silicate growth was assigned to the combined rates of condensation, hydration and dissolution process in the aqueous solution [237, 238]. The hydrated TCC coating was regarded as a gel-like film with the nanosized channels to be

influenced by these effects of the pH variance in the solution [153]. Considering the negligible effect of coating dissolution in the deionized water, the competition between the hydration and condensation rates determines the TCC coating thickness variance. The thickness of the coating formed for 120 s displays a ‘V’-shape plot with the dependence on water pH of 5, 7 and 9. The significant condensation may occur in the pH 7 case to significantly reduce the coating thickness, which is consistent with the peak condensation rate and the negligible hydrolysis effect in the silicate growth [237]. In contrast, the ~20 % reduced coating thickness of the coatings formed for 300 s was observed in the case of pH 9, while thicknesses at pH 5 and 7 cases were relatively stable around 44 nm. This indicates that the condensation rate of this coating after immersion in a pH=9 water bath becomes more significant. In this case, the reduced corrosion resistances in the coating formed for 600 s (R_{po} and R_p) were revealed when the pH value of the water bath increased from 5, 7 up to 9, possibly attributed to the decreased thickness by the significant condensation effect. In addition, the effective capacitance for the coating/substrate interfaces (C_{eff-dl}) decreases with increasing water pH value, revealing the improved distribution of reactivity along the substrate. In summary, the pH-dependent influence of the water bath on coating thickness was a complex function of the hydration and condensation rates. The water treatment (pH 5 and 40 °C) provides the best barrier performance as evidenced by the $\sim 10^5 \Omega \text{ cm}^2$ charge-transfer resistance that is increased by ~ 50 factors compared to the bare alloy ($\sim 2 \times 10^3 \Omega \text{ cm}^2$).

7.3.3 Influence of sodium sulphite

The presence of the reductant sodium sulphite in the water bath (40 °C) at concentrations of 50 and 100 g/l was revealed to significantly destroy the microstructure of the TCC coating from the surface to the bottom. In terms of the chemical reaction mechanism, the reduction of the chromium (VI) component was expected to occur as follows.



However, the side effect of this reaction was revealed by the considerable decrease of the resistances of the coating pores, R_{po} , with a reduced factor of ~ 80 , which is consistent with the increase of the effective capacitance of coating regions. In terms of the coating/substrate

interface, the evident reduction of the charge-transfer resistance may result from the deterioration of the outer coating layer after immersion in the sulphite solution. However, the relatively stable capacitances in the TCC coatings formed for 300 and 600 seconds suggested that the sulphite either may not penetrate into the inner coating layer or it cannot influence the interfacial bonding if the chemical diffused inwards to the substrate. The effect of the post-treatment with the presence of sodium sulphite reveals a complex function of the concentration of the additive and solution pH value.

7.4. Summary

1. Rising temperature of the water bath from 20 °C to 40 °C can improve the cross-sectional morphology and the distribution of the coating components. This imparts good consistency to the improvement of the corrosion resistances of the coating.
2. The influence of pH variation of water bath on the coating thickness is a complex function of the rates of hydration and condensation, and the deionized water bath (40 °C, pH=5) can provide the best barrier inhibition of the coated alloy with an appreciable coating thickness.
3. The best TCC coating process on the alloys after alkaline etching and nitric acid desmutting consists of the conversion treatment for 600 seconds and the immediate water treatment (40 °C, pH=5) for 120 seconds and water rinsing and the air aging for 24 h. The charge-transfer resistance of this coating reveals a ~50-fold increase.
4. The sodium sulphite addition in the water bath of 50 and 100 g/l can destroy the coating microstructure to reduce the corrosion protection. The effect of the post-treatment in the sodium sulphite solution is influenced by the factors of solution concentration and pH value.

Figure Captions 7.1-7.12

Figure 7.1 Transmission electron micrographs of ultramicrotomed cross-sections of the TCC coatings formed for 120 s in a dilute SurTec 650 bath at 40 °C. The coatings were post-treated with (a) no water, (b) the warm water ($t=40$ °C) and (c) the cold water immersion ($t=20$ °C).

Figure 7.2 The average thickness of the coating formed for 120 seconds by six measurements. The coatings were after the post-treatments I, III and II. The coating after the treatment III displayed the highest thickness with the least error.

Figure 7.3 Transmission electron micrographs of ultramicrotomed cross-sections of the TCC coatings formed for 300 s in a dilute SurTec 650 bath at 40 °C. The coatings were post-treated with (a) no water, (b) the warm water (40 °C) and (c) the cold water (20 °C) immersion.

Figure 7.4 The average thickness of the coating formed for 300 seconds determined by six measurements. The coatings were post-treated as follows: no water; warm water (40 °C) and cold water (20 °C) immersion. The coating after the warm water immersion displays the highest thickness with the least error.

Figure 7.5 The elemental profiles in weight of the TCC coating formed for 300 s measured by TEM/EDX maps analyses: (a) for the inner coating layer and (b) for the outer coating layer. The following yellow squares in (c) and (d) correspond to the inner and outer coating layer respectively that are the TCC coatings formed for 300 s after treatment III. The post-treatments were outlined with colours of the red, black and green colours for the cases after the treatments I, II and III respectively.

Figure 7.6 (a,b,c) Transmission electron micrographs and (d) the average thickness of the TCC coatings formed for 120 seconds in a dilute SurTec 650 bath at 40 °C. The coatings were post-treated after the treatment III with dependence on the pH at: (a) 5, (b) 7 and (c) 9.

Figure 7.7 (a,b,c) Transmission electron micrographs and (d) the average thickness of the TCC coatings formed for 300 seconds in a dilute SurTec 650 bath at 40 °C. The coatings were after the treatment III (40 °C) with dependence on the pH at (a) 5, (b) 7 and (c) 9.

Figure 7.8 The equivalent circuit model $R(Q(R(QR)))$ was used to represent the coating system on the alloys, where R_e , R_{po} and R_p represent the resistances of the electrolyte among the reference electrode and coating surface, the resistance by coating defects or channels and the charge-transfer resistance respectively. The time constant elements CPEs were represented by the Q symbol.

Figure 7.9 (a) Impedance modulus-frequency plot and (b) phase angle-frequency plot for the bare and coated alloys in 3.5% NaCl solution, where the coatings were formed for 120, 300 and 600 s after the treatment II. The coated alloy after conversion treatment for 600 s revealed the best corrosion resistance.

Figure 7.10 (a) Impedance modulus-frequency plot and (b) phase angle-frequency plot for the coated alloys in 3.5% NaCl solution, where the coatings were formed for 120, 300 and 600 s after the treatment III. The coated alloys after the conversion treatment for 600 s revealed the best corrosion resistance.

Figure 7.11 (a) Impedance modulus-frequency plot and (b) phase angle-frequency plot for the coated alloys in 3.5% NaCl solution, where the TCC coatings were formed for 600 s after the treatment III (40 °C, pH=5, 7 and 9). The coated alloys in the pH=5 condition displayed the best corrosion resistance.

Figure 7.12 (a) Impedance modulus-frequency plot and (b) phase angle-frequency plots for all specimens I to V in the 0.05 M NaCl solution respectively, where both of the prior OCP stabilization for 30 min revealed at $\sim -0.51 V_{SCE}$.

Table 7.1 Fitted results of TCC coatings/alloy systems obtained on the base of equivalent circuits: R(QR) for the bare alloy; R(Q(R(QR))) for the coated alloy, where coatings were after the treatment II (20 °C). Parameters of the $C_{\text{eff-dl}}$ and $C_{\text{eff-coat}}$ represent effective capacitances of coating/substrate interface and coating regions. Bare alloys was used as a control and named as '0 s'.

	R_e $\Omega \text{ cm}^2$	R_{po} $\Omega \text{ cm}^2$	R_p $k\Omega \text{ cm}^2$	Q_{dl} $\times 10^{-5} \text{ s}^n / (\Omega \text{ cm}^2)$	n_{dl}	$C_{\text{eff-dl}}$ $\mu\text{F}/\text{cm}^2$	Q_{coat} $\times 10^{-6} \text{ s}^n / (\Omega \text{ cm}^2)$	n_{coat}	$C_{\text{eff-coat}}$ $\mu\text{F}/\text{cm}^2$
0 s	13	-	1.83	15.1	0.88	79.2	-	-	
120 s	13	15	16.46	1.97	0.88	7.83	3.22	0.82	0.49
300 s	13	39	36.28	1.17	0.92	6.21	3.50	0.89	1.22
600 s	13	70	41.49	0.67	0.92	3.39	8.20	0.85	2.13

Table 7.2 Parameters of TCC coatings/alloy systems obtained from the best fittings of the experimental EIS data according to the equivalent circuit R(Q(R(QR))), where coatings were after the treatment III (40 °C).

	R_e $\Omega \text{ cm}^2$	R_{po} $\Omega \text{ cm}^2$	R_p $\Omega \text{ cm}^2$	Q_{dl} $\times 10^{-6} \text{ s}^n / (\Omega \text{ cm}^2)$	n_{dl}	$C_{\text{eff-dl}}$ $\mu\text{F}/\text{cm}^2$	Q_{coat} $\times 10^{-6} \text{ s}^n / (\Omega \text{ cm}^2)$	n_{coat}	$C_{\text{eff-coat}}$ $\mu\text{F}/\text{cm}^2$
120 s	13	38	25644	6.19	0.94	3.73	12.0	0.87	4.05
300 s	13	290	33387	2.61	0.94	1.49	8.53	0.87	2.74
600 s	14	209	92784	4.62	0.98	3.86	7.43	0.88	2.45

Table 7.3 Parameters of TCC coatings/alloy systems obtained from the best fittings of the EIS data, where coatings were formed for 600 s and soon immersed in the water bath for 120 s (40 °C). The effect of the pH dependence was investigated as follows.

	R_e $\Omega \text{ cm}^2$	R_{po} $\Omega \text{ cm}^2$	R_p $\Omega \text{ cm}^2$	Q_{dl} $\text{s}^n / (\Omega \text{ cm}^2)$	n_{dl}	$C_{\text{eff-dl}}$ $\mu\text{F}/\text{cm}^2$	Q_{coat} $\text{s}^n / (\Omega \text{ cm}^2)$	n_{coat}	$C_{\text{eff-coat}}$ $\mu\text{F}/\text{cm}^2$
pH=5	14	209	92784	4.62E-6	0.98	3.86	7.43E-6	0.88	2.45
pH=7	14	110	46164	6.29E-6	0.91	2.88	7.86E-6	0.88	2.76
pH=9	14	91	25612	2.16E-6	1	2.16	1.63E-5	0.86	5.25

Table 7.4 Sample codes with respect to examined specimens for the influence of sodium sulphite, including the concentration and pH factors, where the standard post-treatment includes deionized water immersion for 120 s, water rinsing and drying in a cool-air stream.

Sample codes	Specimens
Sample I	TCC coating formed for 300 s with a standard post-treatment in absence of Na_2SO_3
Sample II	TCC coating formed for 300 s with a standard post-treatment in presence of 50 g/ L Na_2SO_3
Sample III	TCC coating formed for 300 s with a standard post-treatment in presence of 100 g/ L Na_2SO_3 (pH $\sim$ 8.5)
Sample IV	TCC coating formed for 300 s with a standard post-treatment in presence of 100 g/ L Na_2SO_3 (pH $\sim$ 7.5)
Sample V	TCC coating formed for 600 s with a standard post-treatment in presence of 100 g/ L Na_2SO_3 (pH $\sim$ 7.5)

Table 7.5 Parameters of TCC coatings/alloy systems obtained from the best fittings of the experimental EIS data with dependence on the concentration and pH values of sodium sulphite solution (40 °C).

	Re Ωcm^2	Rpo Ωcm^2	Rp $\text{k}\Omega\text{cm}^2$	Q co $(\times 10^{-6} \text{ s}^n/(\Omega\text{cm}^2))$	nco	Ceff-co $\mu\text{F}/\text{cm}^2$	Qdl $(\times 10^{-6} \text{ s}^n/(\Omega\text{cm}^2))$	ndl
I	170	8230	205.2	8.9	0.83	2.35	2.8	0.96
II	190	530	95.1	13.4	0.84	4.30	1.5	1
III	144	504	110.9	12.8	0.85	4.21	1.5	1
IV	130	111	93.2	12.7	0.80	2.56	1.2	1
V	135	1024	90.9	11.1	0.86	3.85	0.46	1

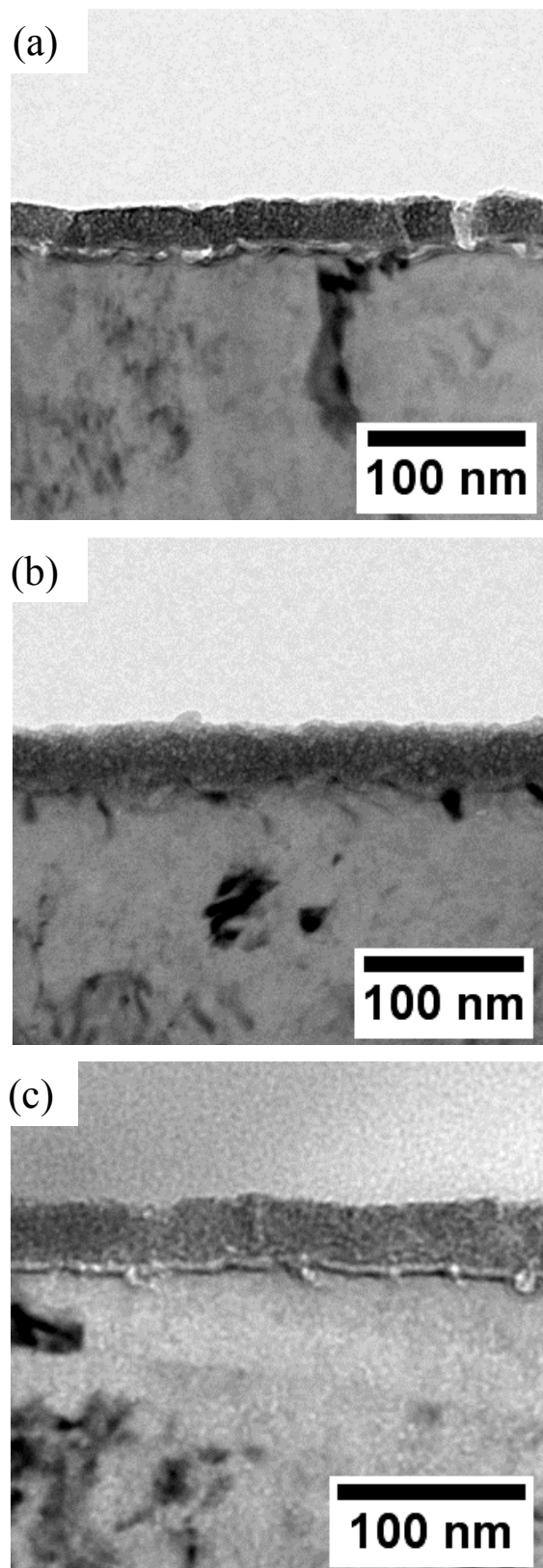


Figure 7. 1 Transmission electron micrographs of ultramicrotomed cross-sections of the TCC coatings formed for 120 s in a dilute SurTec 650 bath at 40 °C. The coatings were post-treated with (a) no water, (b) the warm water ($t=40$ °C) and (c) the cold water immersion ($t=20$ °C).

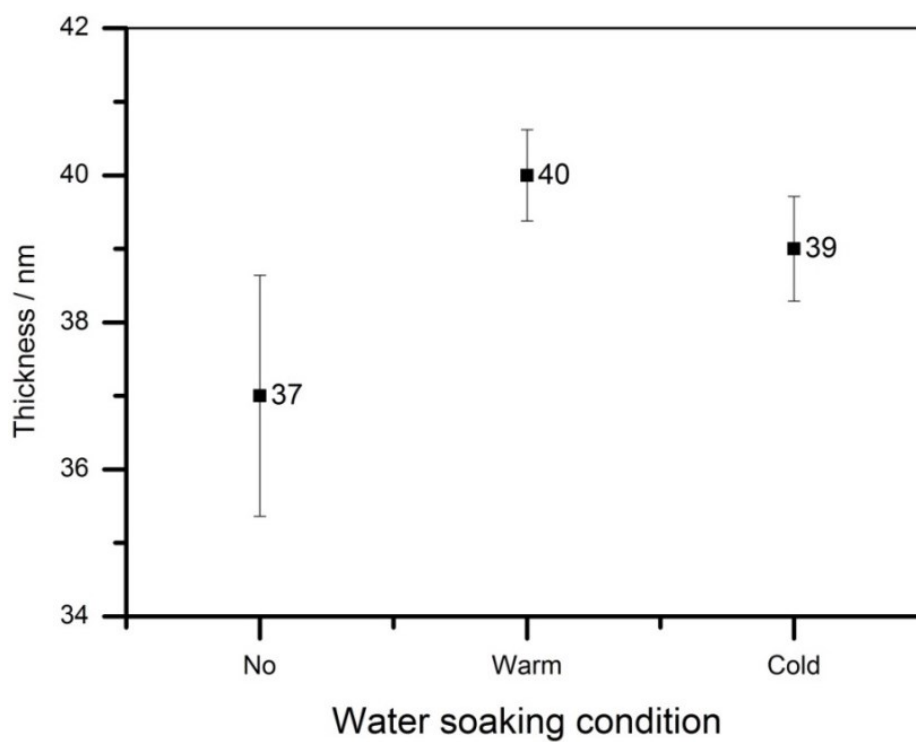


Figure 7. 2 The average thickness of the coating formed for 120 seconds. The coatings were after the post-treatments I, III and II. The coating after the treatment III displayed the highest thickness with the least error.

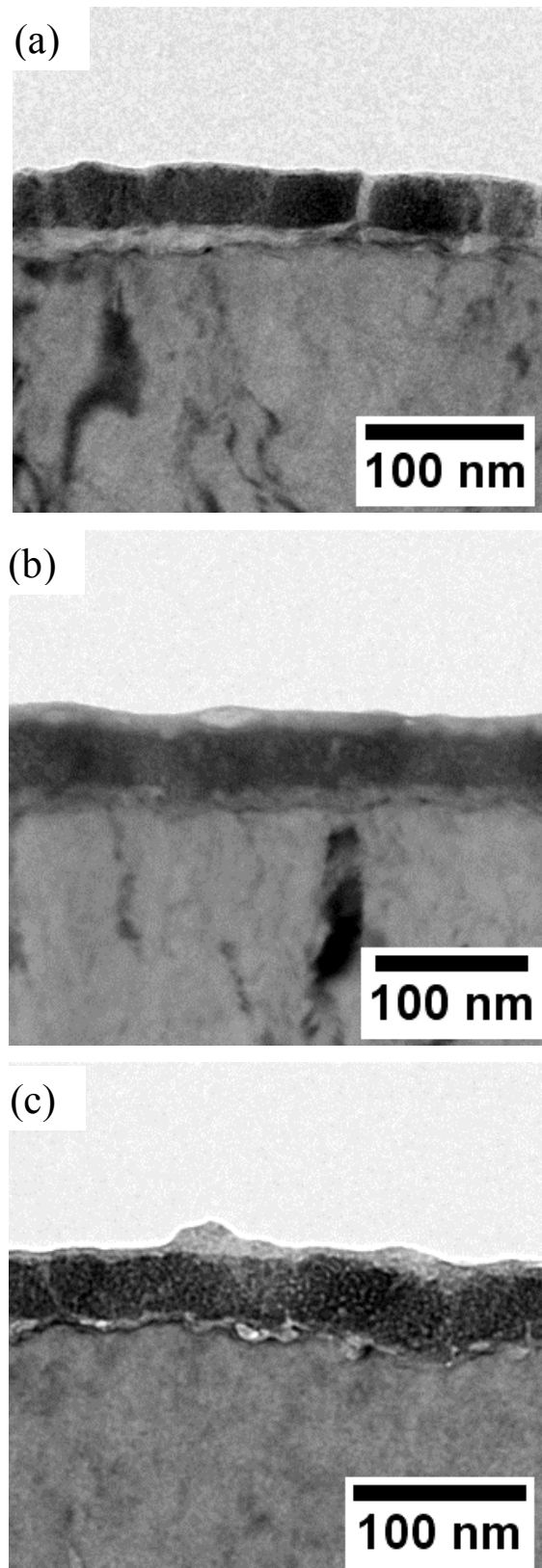


Figure 7. 3 Transmission electron micrographs of ultramicrotomed cross-sections of the TCC coatings formed for 300 s in a dilute SurTec 650 bath at 40 °C. The coatings were post-treated with (a) no water, (b) the warm water (40 °C) and (c) the cold water (20 °C) immersion.

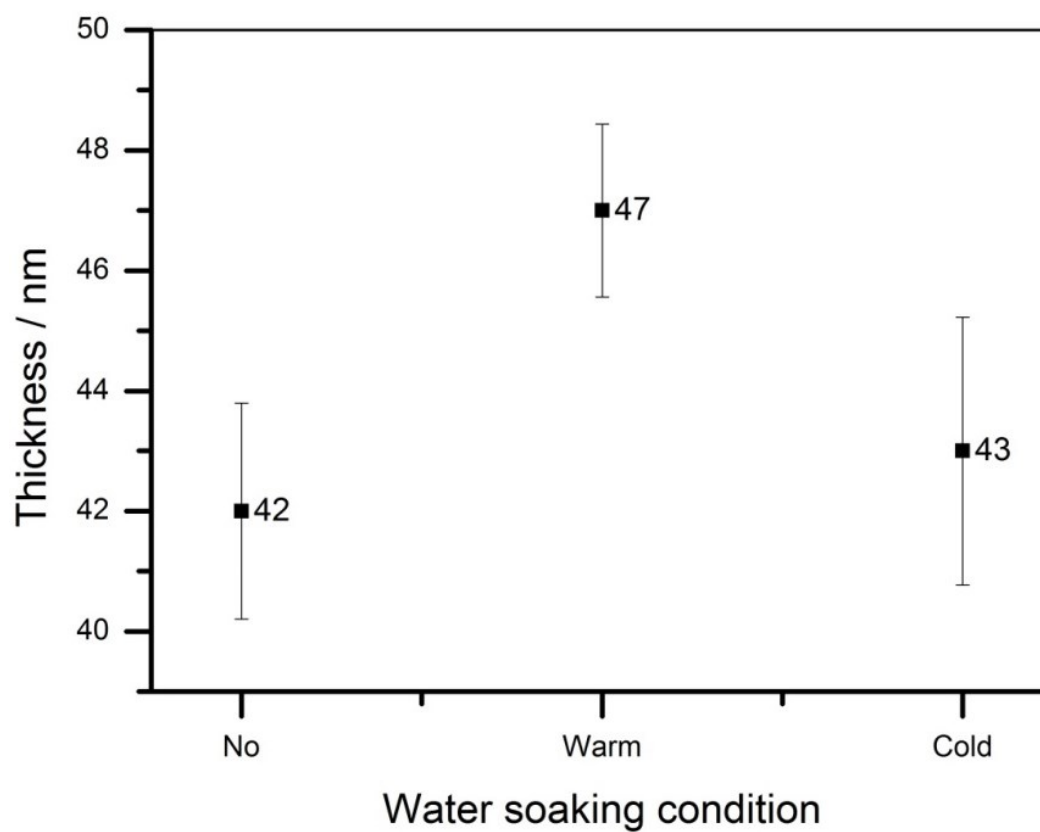


Figure 7. 4 The average thickness of the coating formed for 300 seconds determined by six measurements. The coatings were post-treated as follows: no water; warm water (40 °C) and cold water (20 °C) immersion. The coating after the warm water immersion displays the highest thickness with the least error.

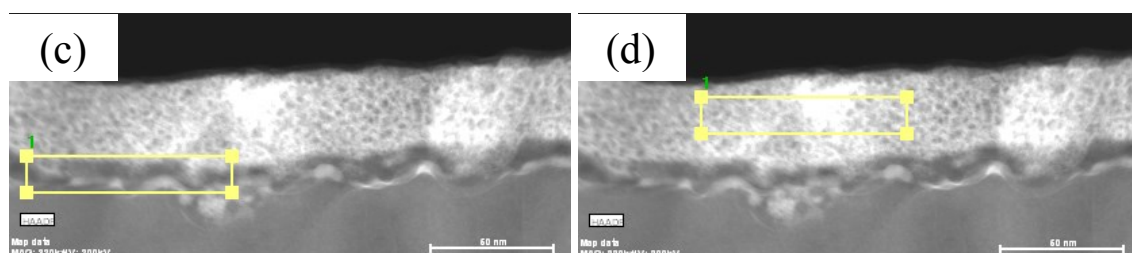
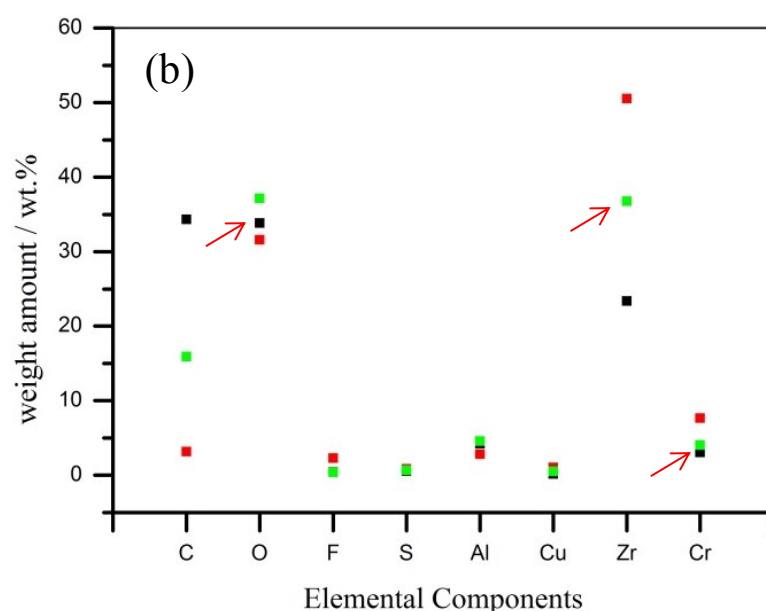
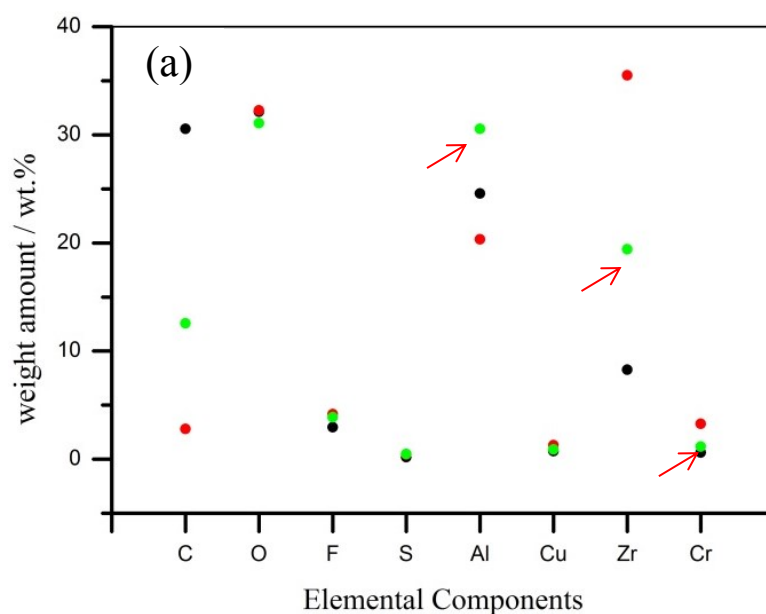


Figure 7. 5 The elemental profiles in weight of the TCC coating formed for 300 s measured by TEM/EDX maps analyses: (a) for the inner coating layer and (b) for the outer coating layer. The following yellow squares in (c) and (d) correspond to the inner and outer coating layer respectively that are the TCC coatings formed for 300 s after treatment III. The post-treatments were outlined with colours of the red, black and green colours for the cases after the treatments I, II and III respectively.

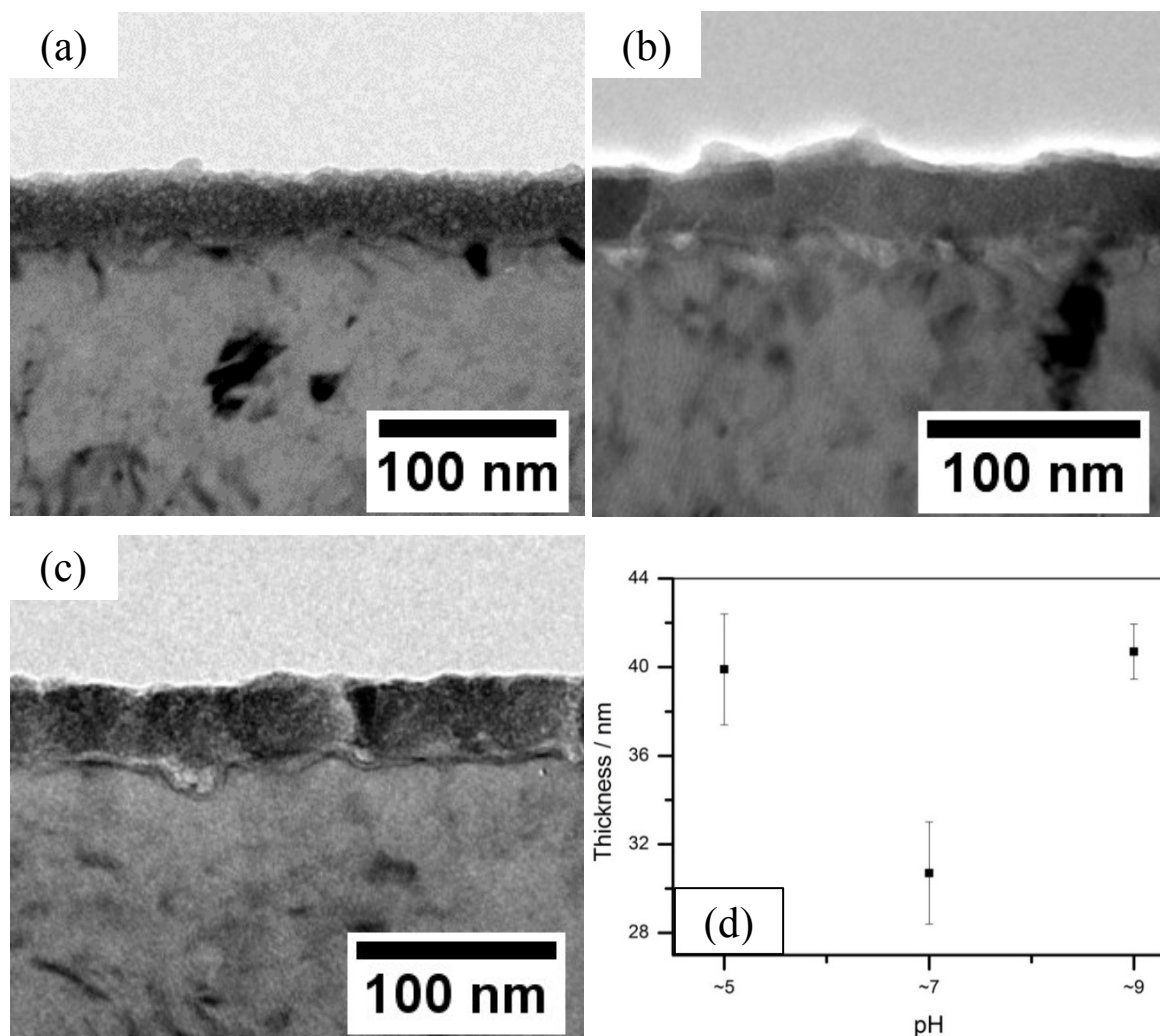


Figure 7. 6 (a,b,c) Transmission electron micrographs and (d) the average thickness of the TCC coatings formed for 120 seconds in a dilute SurTec 650 bath at 40 °C. The coatings were post-treated after the treatment III with dependence on the pH at: (a) 5, (b) 7 and (c) 9.

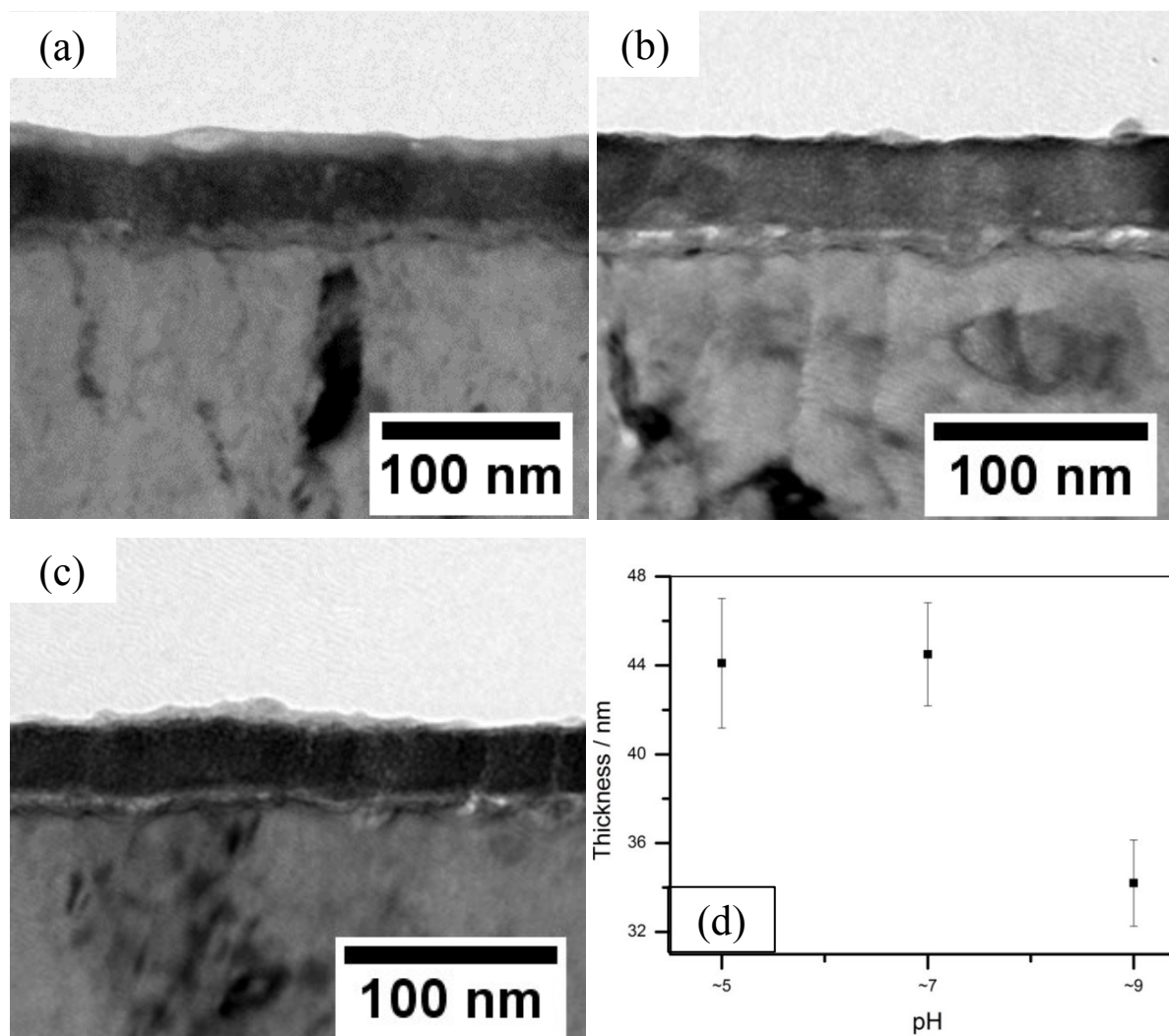


Figure 7. 7 (a,b,c) Transmission electron micrographs and (d) the average thickness of the TCC coatings formed for 300 seconds in a dilute SurTec 650 bath at 40 °C. The coatings were after the treatment III (40 °C) with dependence on the pH at (a) 5, (b) 7 and (c) 9.

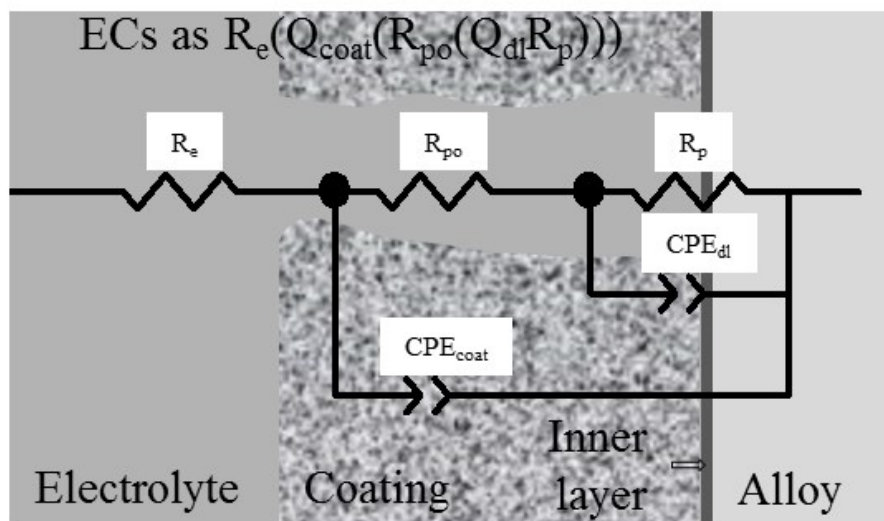


Figure 7. 8 The equivalent circuit model $R(Q(R(QR)))$ was used to represent the coating system on the alloys, where R_e , R_{po} and R_p represent the resistances of the electrolyte among the reference electrode and coating surface, the resistance by coating defects or channels and the charge-transfer resistance respectively. The time constant elements CPEs were represented by the Q symbol.

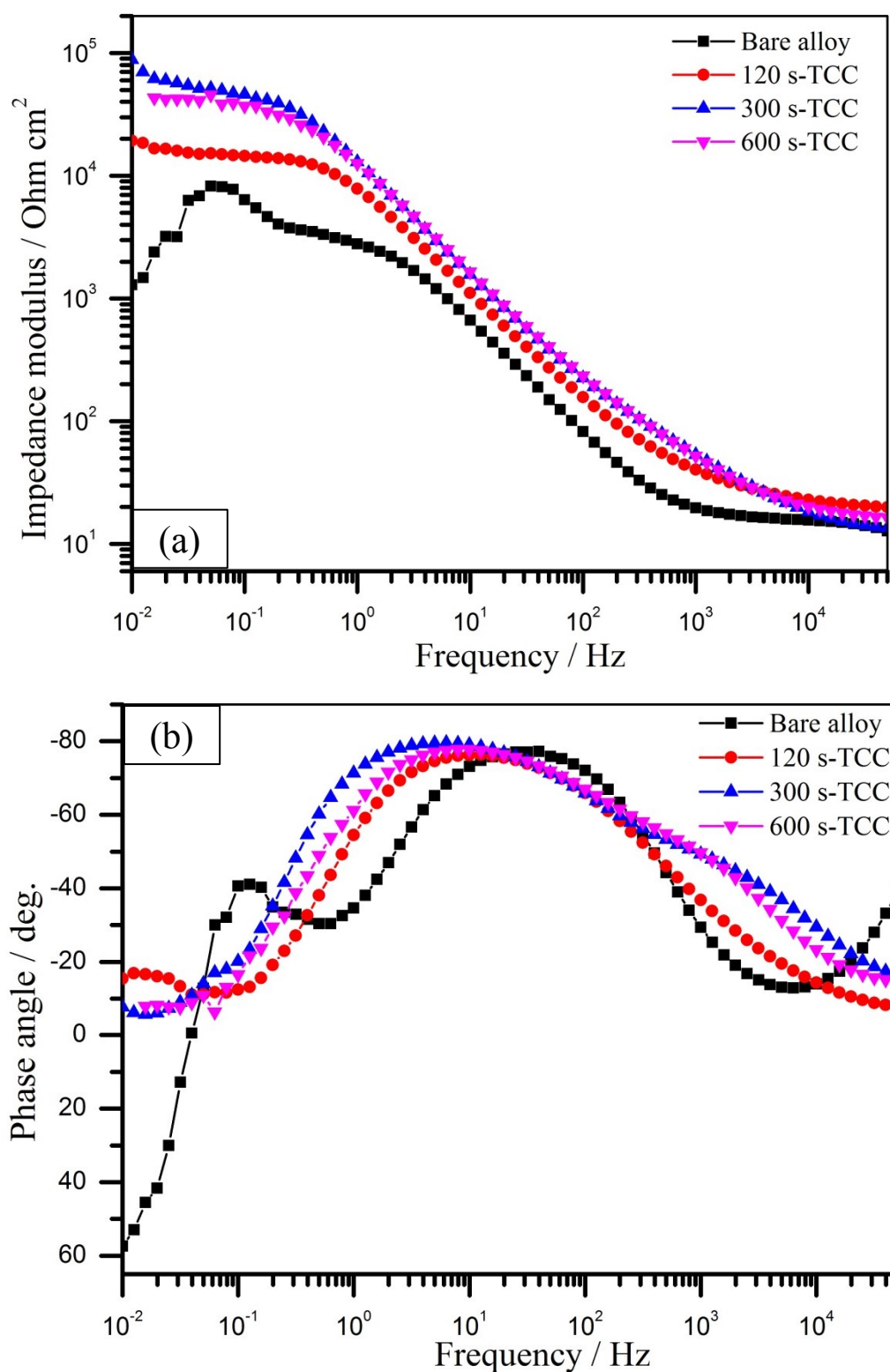


Figure 7. 9 (a) Impedance modulus-frequency plot and (b) phase angle-frequency plot for the bare and coated alloys in 3.5% NaCl solution, where the coatings were formed for 120, 300 and 600 s after the treatment II. The coated alloy after conversion treatment for 600 s revealed the best corrosion resistance.

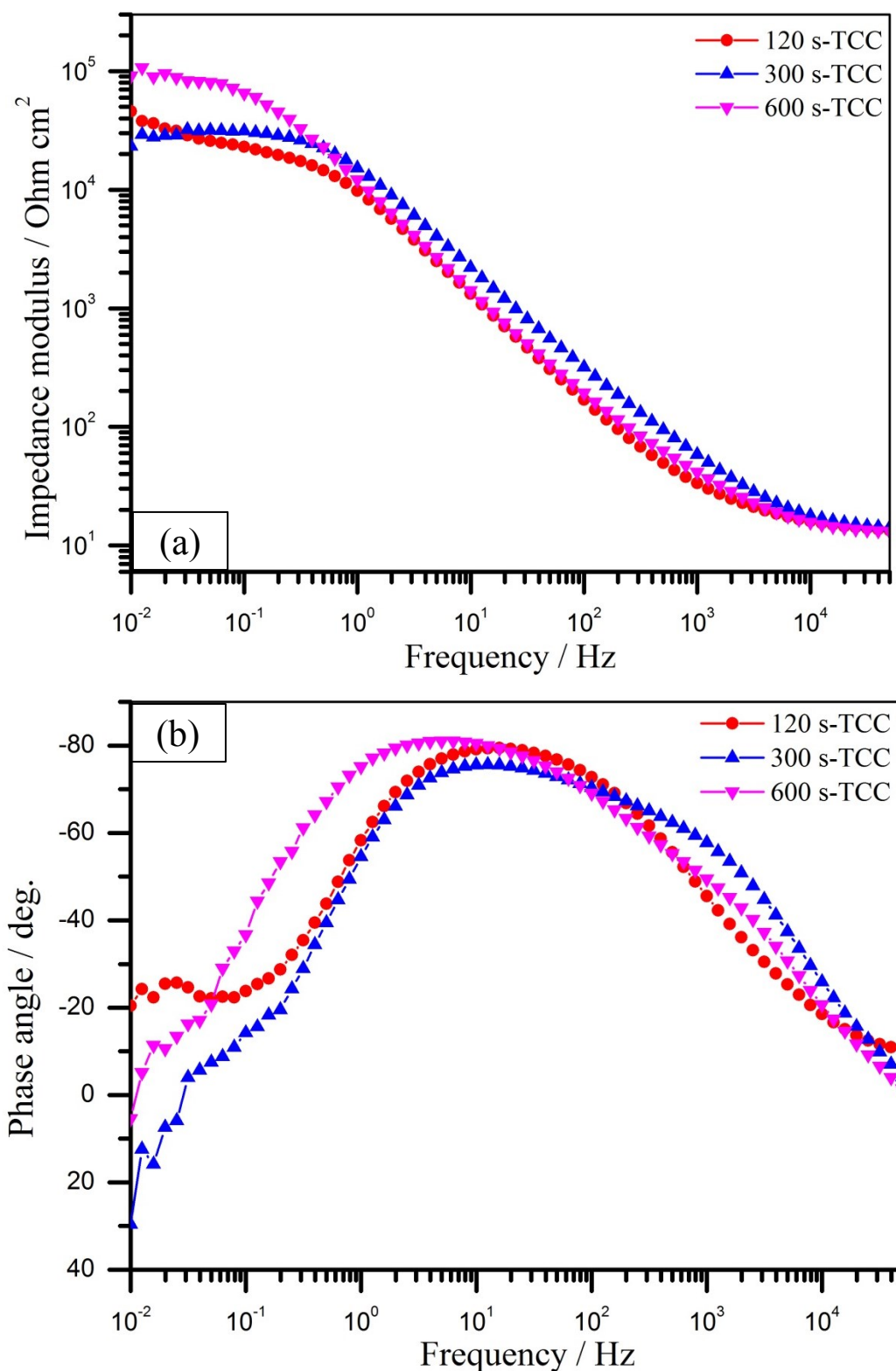


Figure 7. 10 (a) Impedance modulus-frequency plot and (b) phase angle-frequency plot for the coated alloys in 3.5% NaCl solution, where the coatings were formed for 120, 300 and 600 s after the treatment III. The coated alloys after the conversion treatment for 600 s revealed the best corrosion resistance.

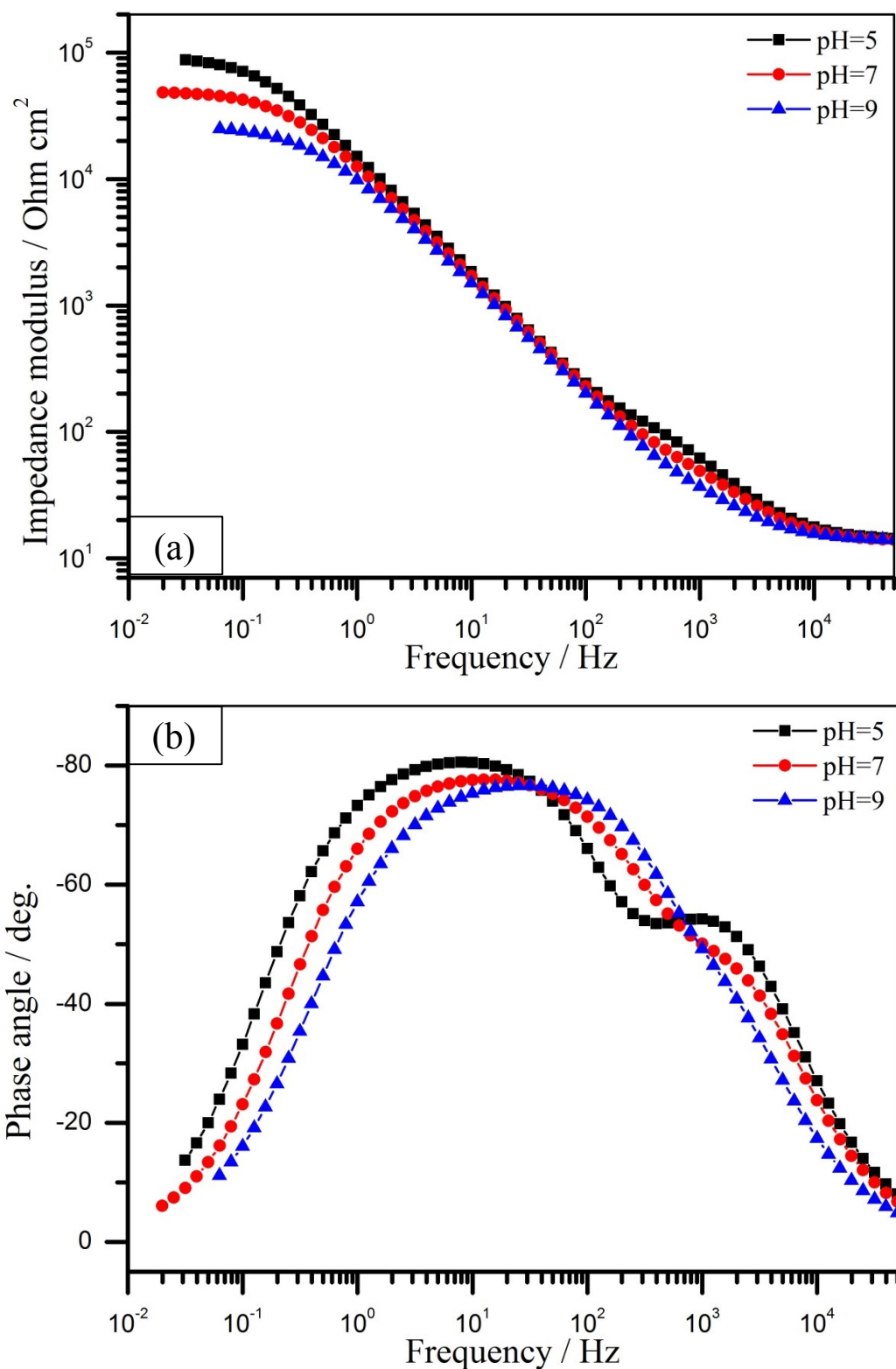


Figure 7. 11 (a) Impedance modulus-frequency plot and (b) phase angle-frequency plot for the coated alloys in 3.5% NaCl solution, where the TCC coatings were formed for 600 s after the treatment III (40 °C, pH=5, 7 and 9). The coated alloys in the pH=5 condition displayed the best corrosion resistance.

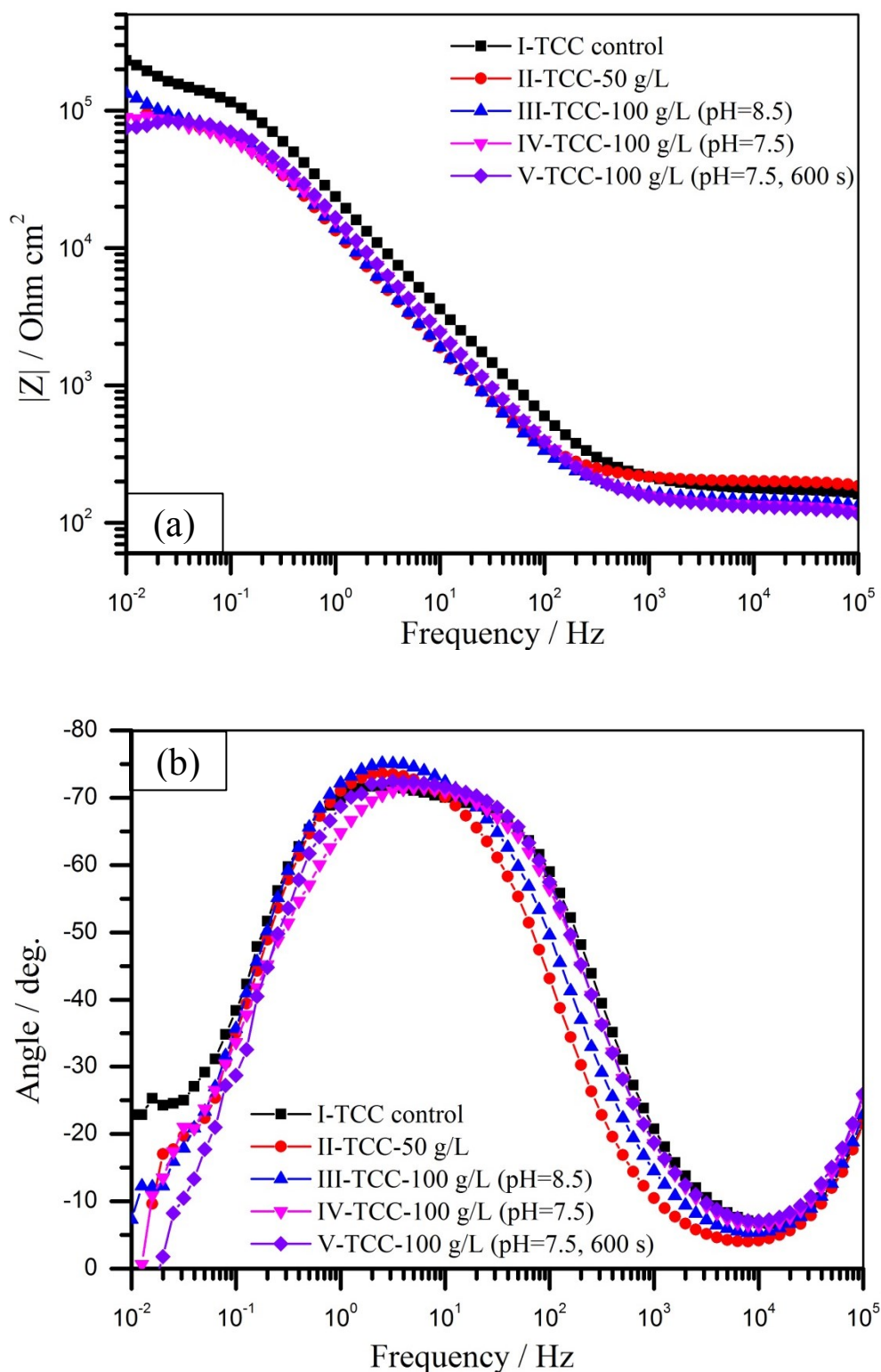


Figure 7. 12 (a) Impedance modulus-frequency plot and (b) phase angle-frequency plots for all specimens I to V in the 0.05 M NaCl solution respectively, where both of the prior OCP stabilization for 30 min revealed at ~ -0.51 V_{SCE}.

Chapter 8 INFLUENCE OF COPPER CONCENTRATION IN Al-Cu ALLOYS

This chapter contains four main parts comprising an introduction, results, discussion and the summary. The results consist of (i) the tomographic characteristic, (ii) OCP behaviour and the cross-sectional characteristic, (iii) the coating composition by Rutherford backscattering spectroscopy/Raman spectra, (iv) the copper concentration effect on coating growth, (v) the effect of copper sulphate addition into the trivalent chromium bath, (vi) the influence of copper in alloys on the transient formation of Cr (VI), and (vii) the influence on electrochemical behaviours. Correspondingly, the discussion includes (i) the influence of the copper in alloys, (ii) the influence of copper sulphate addition into the bath, and (iii) copper and Cr (VI) chemistry.

The superpure aluminium contains ~50 ppm copper in the nominal composition. The pre-treatment of the electropolishing in a perchloric acid-ethanol electrolyte at 20 V for 240 s can lead to the near-surface copper enrichment, which influences the surface chemistry to probably change the pH-sensitive deposition process of TCC coatings. By contrast, the magnetron sputtering-deposited Al, Al-2 at.%Cu, Al-24 at.%Cu, Al-40 at.%Cu and Al-64 at.%Cu alloys on the electropolished aluminium were used to compare the effect of solid-solution copper on the formation and composition of TCC coatings. In addition, the copper sulphate addition into the trivalent chromium bath was also employed in concentrations of 0.5 and 50 mg/l to examine the role of copper deposits on the formation and chemical composition of resultant TCC coatings.

8.1 Introduction

The surface chemistry of aluminium alloys can be controlled by the pre-treatment such as mechanical polishing and chemical treatment. Consequently, the pH-sensitive deposition of TCC coatings correlated to the pre-treated surface as reported in Chapter 6. The presence of copper-rich particles and matrix by pre-treatments greatly influences the homogeneity of TCC coating deposition. The coatings preferentially deposited around the cathodic copper-rich particles. After this coating initiation, the coating formed on the matrix and the growth kinetics revealed a decreased trend with the prolonged treatment. It is attributed to the

possible incorporation of copper particles into the coating to inhibit the mass transport of reactant and products. [148, 150, 210]

Furthermore, the effect of copper deposits from the conversion coating bath on the coating reveals a great dependence on the substrate.[199, 225, 239] Copper deposits on the AA6014 alloy were in the form of isolated islands to form zirconium-based conversion coatings of minimum thickness. By contrast, the situation on the hot dip galvanized steel and cold rolled steel displayed the uniform distribution of copper deposition and the resultant thicker coating [225]. Moreover, intermetallic particles in AA6014 alloys played a preferential nucleation role of these Cu-rich deposits due to the cathodic nature of these intermetallics, and then the limited contact with the Al surface in initial phases led to the copper-deposit saturation. The presence of these cathodic deposits enhanced the oxide precipitation in the vicinity, while the minor coating components were detected on copper deposits [199].

In terms of cathodic copper-rich particles in alloys, the promoted Cr(III)/Cr(VI) transformation was suggested in TCC coatings when either the atmospheric oxygen was sufficient around these particles or the chloride aggressively corroded the matrix [159]. In this case, Raman spectroscopy was used to examine hexavalent chromium species using the fingerprint evidence of the Raman shift between 840 and 904 cm^{-1} [78, 94, 157]. Here, the effect of copper concentration on the Cr(VI) formation was compared in TCC coatings formed on electropolished Al and sputtering-deposited Al and Al-Cu alloys by such a Raman fingerprint.

In this present study, surface characterization techniques include the scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM). Electrochemical properties were monitored by polarization scans and electrochemical impedance spectroscopy (EIS). Concerning the detection of Cr(VI) species, Raman peak of 840-904 cm^{-1} is used as an evidence and the relationship of Cr(VI) transformation with copper deposits is also discussed.

8.2 Results

8.2.1 Topographic characteristic

Atomic force microscopy (AFM) was used to record the surface tomographic characteristics of the sputtering-deposited and electropolished Al prior to the TCC coating treatment as shown in Figures 8.1 (a, b) respectively. The spherical particles of dimension of hundreds of nanometres were visible in Fig. 8.1(a), where the voids of depth up to 30 micrometres are outlined by the red arrows. By contrast in Fig.8.1(b), the highly-ordered furrow was examined, which was in good agreement with the feature of (1 1 0) Al single crystals in the report by Konovalov et al [29]. The preferential adsorption of alcohol molecules on surface ridges was possibly responsible for this pattern formation [240, 241].

8.2.2 OCP behaviour and cross-sectional characteristic

The open-circuit potentials of the sputtering aluminium during the immersion in the SurTec 650 solution at 40°C for 1200 seconds are shown in Figure 8.2 along with the early report of the OCP evolution of electropolished Al. Initially both OCPs fall down and then generally increase to a constant level up to 1200 s. The minimum OCP and final constant level for both substrates were similar, being -1.54 and -1.50 V_{SCE} respectively. Compared to the short period (less than 100 s) of the initial OCP fall on electropolished Al, this stage seems more prolonged on the sputtering Al of ~200 seconds.

Transmission electron micrographs of the bare and TCC coated aluminium after the electropolishing pre-treatment are shown in Figures 8.3 (a and b), where the resin was used to seal the specimens to prepare the transparent thin cross sections and the red arrows highlighted the presence of copper enrichment. Figure 8.3 (a) shows the dark band of several nanometres on the surface of the bare Al, which correlates with the copper enrichment due to the electropolishing [221]. In terms of the TCC coated aluminium in Fig. 8.3 (b), the treatment in the trivalent chromium bath (pH≈3.9) for 60 seconds generated a film of ~18 nm thickness and a two-layer structure. The evident dark band of ~5 nm thickness under the inner TCC layer is a copper-rich layer.

Figures 8.4 (a, b, c and d) display the transmission electron micrographs of the sputtering-deposited aluminium layer of ~399 nm thickness and the TCC coatings formed for 60, 120

and 300 seconds on this substrate with the resultant thicknesses of ~ 7 , 16 and 42 nm respectively. This rate of coating thickening increased in the initial stage and then fast decreased after the prolonged treatment of 300 s. The respective average rates of growth at these two stages were measured to be ~ 0.14 and 0.04 nm s^{-1} . Compared with the coating growth rates of ~ 0.27 and 0.08 nm s^{-1} on electropolished aluminium, the sputtering-deposited aluminium showed the impeded growth kinetics with the decreased kinetics by $\sim \times 2$. It possibly resulted from the reduced cathodic reaction kinetics due to the absence of copper enrichment on the sputtering-deposited Al. In terms of the rate of the aluminium oxidation rate, it also exhibited a significant decrease after the treatment time for 300 seconds and a relative constant rate proceeded up to 1200 seconds. The ratio of coating thickness to the loss of aluminium in the period of 1200 s was roughly ~ 3 .

Considering the thin layer of copper enrichment generated by electropolishing, the diffraction pattern of transmission electron microscopy in a FEI Tecnai F30 instrument was employed to examine the evidence of copper-rich phase at the coating/substrate interface. Figures 8.5 (a and b) show the TEM diffraction patterns of the interfacial areas on the electropolished and sputtering-deposited Al respectively, where both TCC coatings were formed for 60 seconds. Figure 8.5(a) displayed the mixture TEM diffraction patterns of Al and Al_2Cu . The Al matrix was determined in good agreement with the (1 0 0) Al lattice plane spacing. By contrast, the measured distances of the copper-enriched layer corresponded to the d-values for (0 2 0) plane of θ' (Al_2Cu) phase of a tetragonal structure ($a=0.404 \text{ nm}$ and $c=0.58 \text{ nm}$) [223]. In terms of the sputtering-deposited aluminium (Fig. 8.5(b)), it showed the single diffraction pattern in good agreement with (1 1 1) FCC Al and revealed in the absence of copper impurities on the substrate.

8.2.3 Coating composition by RBS and Raman spectroscopy

Rutherford backscattering spectroscopy was used to analyse the compositional variance on the sputtering-deposited Al. Figure 8.6 shows the example of the coating formed for 300 seconds, where oxygen, fluorine, aluminium, chromium, sulphur, zirconium and hafnium elements are detected. The fitted results of the spectra are given in Table 8.1 for specimens treated for times of 60, 120 and 300 seconds. The relatively low concentration of either zirconium or chromium in all coatings is consistent with the thinner cross-sections compared

with the situations on electropolished Al (Chapter 4). The atomic ratio of chromium relative to zirconium of ~ 0.75 is higher than that of ~ 0.47 Cr/Zr ratios on electropolished aluminium, indicating the impeded kinetics of zirconium deposition. Furthermore, the concentrated aluminium components on the sputtering Al were distinct. For example, it was around two times the concentration of aluminium in the TCC coating formed for 300 seconds on the electropolished Al.

In comparison to the situation on electropolished Al, the stifled cathodic reactions probably occur during the coating formation on the sputtering-deposited Al due to the reduced impurities on the surface. Thus, the pH increases at solution/substrate interface consequently slow down with the resulting generation of the thinner TCC coatings of the reduced components. Considering the hexafluorozirconate component in the bath, it primarily plays a role in decreasing the interfacial tension between the bath and air-formed oxide coated substrate. Further, their reactions between this chemical and alumina oxide are probably catalysed by the presence of copper to form the fluoride-complex nodules of Na_3AlF_6 and K_3AlF_6 [82]. Thus, the copper absence on the sputtering-deposited Al consequently reduced this reaction kinetics, and thus slowed the deposition of zirconium component. By contrast, the bath component of the trivalent chromium was in the form of Cr^{3+} ions, which deposition was independent with the substrate and proportionally related to pH sensitivity.

Figure 8.7 shows the Raman spectra of TCC coatings formed for 1200 seconds in the naturally-aerated bath and the bare sputtering-deposited aluminium. Compared to the bare aluminium substrate with the Raman peak at 805 as the evidence of aluminium hydroxides along a shoulder peak at 945 cm^{-1} [198], the Zr-O and Cr(III)-O bands were revealed in this coating as evidenced by peaks at 470 and 536 cm^{-1} respectively [159, 199, 242]. Further, sulphate in the form of zirconium sulphate was detected at 998 cm^{-1} [201]. Concerning the fingerprint evidence of Cr(VI) oxides, an intense and broad peak was observed at 864 cm^{-1} , revealing the formation of Cr(VI) species on the sputtering-deposited aluminium. By contrast, the TCC coating formed for 1200 seconds in the deaerated bath exhibited an evident absence of Cr(VI) species at $840\text{--}904\text{ cm}^{-1}$ [78]. This further revealed the role of dissolved oxygen in the transformation of the trivalent chromium into hexavalent chromium species.

8.2.4 Copper concentration effect on coating growth

The sputtering-deposited Al-2 at.%Cu alloys were cleaned by acetone and deionized water prior to TCC coating treatment in the SurTec 650 solution. This coating was analysed by transmission electron microscopy, using the JOEL 2000 FX II instrument under the accelerating voltage of 120 kV. Figure 8.8 shows the thickness plot of the coating and loss of matrix on these sputtering-deposited Al and Al-2 at.%Cu alloys during immersion in the trivalent chromium bath up to 600 seconds. For both substrates, the rates of the coating growth and loss of matrix in the early period of ~300 seconds are evidently higher than the situations of the treatment between 300 and 600 seconds. Further, the presence of copper in the alloy layer significantly promotes both processes of matrix dissolution and coating deposition. In terms of the substrate of Al-2 at.%Cu alloys, the average rate of coating growth and loss of matrix during the treatment of 600 seconds are roughly ~ 0.11 and 0.12 nm s^{-1} , and this ratio of coating formation relative to aluminium oxidation at ~ 0.9 revealed a significant decrease compared to the case of the sputtering-deposited Al (~ 3).

Figures 8.9 (a-f) show transmission electron micrographs of the TCC coatings on (a, b) Al-24 at.%Cu, (b, c) Al-40 at.%Cu and (e, f) Al-64%Cu alloys, where the treatment times in the SurTec 650 solution at 40°C were for (a, c, e) 300 seconds and (b, d, f) 1200 seconds respectively. A corrosion layer by substrate dissolution was observed beneath the TCC coatings on the Al-24 at.%Cu and Al-40 at.%Cu alloys and outlined by red arrows in Figs. 8.9 (a-d). By contrast, the absence of this corrosion layer occurred on the Al-60 at.%Cu alloys. Further, the more aggressive corrosion was evident on the Al-40 at.%Cu alloys after prolonged treatment for 1200 s (Fig. 8.9 (d)), which corrosion layer was of thickness of $\sim 33 \pm 2.6 \text{ nm}$.

The rates of coating thickening and substrate oxidation are shown in Figures 8.10 (a, b and c), which correspond to the cases of the Al-24 at.%Cu, Al-40 at.%Cu and Al-64 at.%Cu alloys respectively. For the matrix dissolution, the former two alloys displayed the continuous dissolution during the conversion treatment up to 1200 seconds with the final thickness of the matrix dissolution at 73.8 ± 5.7 and $56.0 \pm 4.1 \text{ nm}$ respectively. In contrast, the thickness of the matrix dissolution on the Al-64 at.%Cu alloys displayed a constant value at $\sim 20 \pm 3.1 \text{ nm}$ in the treatment period of between 300 and 1200 seconds, which thickness was a significant

decrease than the situations on the former two alloys. Further, the thickness of the TCC coatings on the Al-64 at.%Cu alloys displayed a distinct increase compared to the thickness of the matrix dissolution. The average rates of the coating growth and matrix dissolution with increasing copper concentration on the Al-24 at.%Cu after the conversion treatment for 600 seconds were ~ 0.075 and 0.092 nm s^{-1} respectively. In comparison, such rates were ~ 0.078 and 0.088 nm s^{-1} on the Al-40 at.%Cu alloys, and ~ 0.087 and 0.035 nm s^{-1} on the Al-64 at.%Cu alloys. Thus, the ratios of the coating formation relative to the aluminium oxidation were ~ 0.9 , 0.9 and 2.5 respectively. Hence, the effect of copper addition into the aluminium substrate highly depended on the concentration of copper and the Al-64 at.%Cu alloys displayed the enhanced coating growth kinetics in compared to the situations on the alloys of less than 40 at.% copper concentration.

8.2.5 Effect of copper sulphate addition into the bath

The OCP evolutions of electropolished aluminium during the immersion in the trivalent chromium bath, containing either 50 mg/l or 0.5 g/l concentration of copper sulphate, are shown in Figure 8.11, where the as-received bath was used as a control. All OCP evolutions displayed the similar trend of the initial fall of the potential and the successive rise to a constant value. The minimum and the final constant OCP values in the as-received bath were $\sim -1.55 V_{\text{SCE}}$ and $-1.50 V_{\text{SCE}}$ respectively. For the 50 mg/l copper-containing bath, the minimum and the final constant OCP values were measured at $\sim -1.10 V_{\text{SCE}}$ and $-0.70 V_{\text{SCE}}$. In the bath containing the 0.5 g/l copper sulphate, the $\sim -1.10 V_{\text{SCE}}$ and $\sim -0.40 V_{\text{SCE}}$ OCP represented the minimum and final constant values. By contrast, the copper sulphate addition into the bath led to the positive shift of the OCP evolution and further the more concentrated copper ions resulted in the more positive OCP values after the prolonged treatment.

Scanning electron micrographs of the TCC coatings formed for 15 seconds in the bath of 50 mg/l and 0.5 g/l CuSO_4 addition are shown in Figures 8.12 (a and b), where the bright particles were revealed as copper-rich deposits by the SEM/EDX analyses. The area fractions of copper deposits were measured by a height threshold in ImageJ software to be at ~ 3.3 and $8.1 \text{ area}\%$ respectively. In terms of the SEM/EDX analyses, Table 8.2 reveals a significant increase of coating components of zirconium and chromium on these particles after the treatment in the bath of 0.5 g/l CuSO_4 addition; however, the coating on the matrix appears to

be similar. After the prolonged conversion treatment for 300 seconds, TCC coatings formed in the solution of 50 mg/l CuSO_4 addition (Figure 8.13 (a)) revealed a relatively uniform coating surface with the presence of the copper-rich particles of several micrometres diameter. By contrast, the considerable coating cracks were observed around the clustered copper-rich particles in the bath of the 0.5 g/l CuSO_4 addition and the dimension of these particles was up to $\sim 10\ \mu\text{m}$ in Fig. 8.13 (b). The SEM/EDX point analyses of the coatings on the particle-free matrix in Table 8.3 revealed that the $\sim 0.12\ \text{wt.}\%$ copper and $2.05\ \text{wt.}\%$ zirconium exhibited in the case of the 50 mg/l CuSO_4 bath, and the $\sim 0.27\ \text{wt.}\%$ Cu and $1.02\ \text{wt.}\%$ Zr were investigated in the case of the 0.5 g/l CuSO_4 bath. In comparison, the coated Al in the as-received bath contained $\sim 2.64\ \text{wt.}\%$ Zr without copper component by the SEM/EDX analyses. This indicated the possible inhibition of zirconium deposits by the presence of the copper deposits, especially in the bath of the higher concentration of copper addition.

The transmission electron micrographs in Figure 8.14 show the cross-sectional microstructure of the TCC coatings on the matrix, consisting of an outer main layer over the inner layer of $\sim 5\ \text{nm}$ thickness. Table 8.4 of these coating thicknesses revealed the good similarity after treatment in all bath for 120 s, although the presence of the copper deposits probably produced a bigger thickness deviation. For the TCC coatings formed for 300 seconds, the coating thickness on the matrix was measured as 83 ± 4.23 , 70 ± 2.69 and $69 \pm 2.79\ \text{nm}$ for the as-received bath and the modified bath of 50 mg/l and 0.5 g/l CuSO_4 respectively. The decreased coating thickness in the modified bath was well consistent with the reduced concentration of zirconium by the SEM/EDX analyses.

8.2.6 Influence on transient formation of Cr (VI)

Raman spectra provide the fingerprint evidence of the corresponding molecules by means of the vibrational shift after their reaction of the laser phonons, and the Raman analysis depth is up to several micrometres [243, 244]. Figures 8.15 and 8.16 show Raman spectra of the TCC coated matrix and particles after treatment of 300 seconds in the bath containing 50 mg/l and 0.5 g/l CuSO_4 additions. The presence of copper deposits on the surface (Fig. 8.12 and 8.13) can enhance the intensity of Raman scattering, as known as the surface-enhanced Raman spectra (SERS) [199, 245]. Support of this fact is that the prominent Raman peaks are associated with copper species, especially on the copper-rich particles. In Fig. 8.15 (b), the

crystalline CuO corresponds to the major peaks at 280 and 616 cm^{-1} , with a shoulder at 328 cm^{-1} ; further, a broad peak at $\sim 1110 \text{ cm}^{-1}$ is the characteristic of the second harmonic of the B_g mode [199]. The complex Zr-/Cr-rich modules in the hydrated coating interfaced with the characteristic Raman scattering of Cu(II) oxide. Cu(II) oxide was featured at ~ 272 and $\sim 620 \text{ cm}^{-1}$ with a small shoulder at $\sim 313 \text{ cm}^{-1}$ in the coating on the matrix (Fig. 8.15 (a)); also the 290, 330 and 620 cm^{-1} peaks of CuO were observed in Fig. 8.16 (b), while the 300, 340 and 600 cm^{-1} Raman shifts were also assigned to the presence of CuO in Fig. 8.17. In addition, the cuprous oxide, Cu_2O , corresponded to the Raman shifts at 151, 282, 439 and 650 cm^{-1} [246] with a broad peak (500-550 cm^{-1}) associating to the T_{2g} mode [247]. The close vibrational shifts between 250-350 cm^{-1} and 600-650 cm^{-1} cannot separate the contribution of Cu_2O from the copper oxides analysis. The Cu(I) oxide was possibly formed due to the copper oxidation and corrosion, promoted by the chemical attacks of the halide ions and the dissolved oxygen [53, 54, 246, 248].

The second major Raman peaks in Figs. 8.15-8.17 were assigned to the oxides of Zr(VI) and Cr(III) components at the phonon shift range at 445-470 cm^{-1} [199, 204] and 520-541 cm^{-1} [158, 159] respectively. In addition, the presence of aluminium hydroxides and oxides corresponds to the Raman scattering of 690-706 cm^{-1} and 800-820 cm^{-1} [198, 249]. Raman shifts at 989 and 1000 cm^{-1} are in good agreement with the evidence of the sulphate component in the coating [201, 205]. Concerning the fingerprint stretching frequency of Cr(VI) oxides between 840-904 cm^{-1} [78, 156, 157], Cr(VI) oxides, in our results in Figs. 8.15 (b) and 8.16 (b), was revealed at 860 and 850 cm^{-1} respectively. Notably, the Cr(VI)-O Raman peaks were not detectable on the coating matrix, indicating the inhomogeneous distribution of Cr(VI) oxides on the surface. Furthermore, a broad and intense peak at 850 cm^{-1} was observed in the coating formed for 1200 seconds on Al-64 at.%Cu alloys in the as-received bath. These results are consistent with the hypothesis of the transient formation of Cr(VI) species around Cu-rich particles on AA2024-T3 alloys, where the dissolved oxygen was reduced to hydrogen peroxide to oxidize Cr(III) to Cr(VI). [159]

8.2.7 Influence on electrochemical behaviour

The influence of the modified bath of the copper sulphate additions on the corrosion protection of the coated alloys was compared with the situation in the as-received bath, where

the alloys were pre-treated by D30 chemical desmutting after alkaline etching as detailed in Chapter 6. Figure 8.18 compares the polarization characteristic of the TCC coatings formed for 300 and 600 s in the as-received and modified bath in 0.05 M NaCl solution at a scan rate of 1 mV/s. In the cathodic polarization region such as at $-0.6 V_{SCE}$, the current densities were measured to be $\sim 8.9 \times 10^{-8}$, 2.2×10^{-6} , 2×10^{-6} , 4.3×10^{-7} , 7×10^{-7} and 1×10^{-6} A/cm² for those in as-received bath for 300 s, in the modified bath of 0.5 g/l additives for 300 and 600 s, in the modified bath of 50 mg/l CuSO₄ for 300 and 600 s respectively. This revealed that the coatings formed in the bath of the greater concentration of CuSO₄ addition correspond to the poorer cathodic inhibition. The coatings after the prolonged treatment of 600 seconds in the bath of 0.5 g/l CuSO₄ showed the worst protection, where the cathodic polarization curve even displayed the right shift compared with the situation of the bare alloy control.

Moreover, the electrochemical impedance spectroscopy and the fitting results on the base of the equivalent circuit (Chapter 3) were employed to monitor the corrosion protection of TCC coatings in the bath with and without the copper addition. Figures 8.19 (a and b) show the impedance modulus and phase angle evolution with dependence on the frequency in the logarithm scale. The impedance modulus at 0.01 Hz in Fig. 8.19(a) displayed a significant downward shift when the coating was formed in the bath containing the higher concentration of copper sulphate (0.5 g/l), especially after the prolonged treatment of 600 seconds. The lowest corrosion resistance of this coated alloy is good agreement with the smallest phase angle (near $\sim -50^\circ$). Table 8.5 listed the EIS fitting results with the chi-squared error of less than 0.01. The electrolyte resistance between the reference and working electrodes was around 160 $\Omega \text{ cm}^2$ with good agreement with the electrolyte nature (0.05 M NaCl). The primary corrosion-protective property can be represented by the combination of coating resistance and charge-transfer resistance in the form of the total corrosion resistance. This total resistance on the bare alloy control was at the level of $\sim 1.1 \times 10^4 \Omega \text{ cm}^2$. By contrast, the total resistance of the coatings formed for 300 s in the bath containing 50 mg/l and 0.5 g/l CuSO₄ additive were fitted at the level of $\sim 6 \times 10^3$ and $3.5 \times 10^3 \Omega \text{ cm}^2$ respectively. In terms of the prolonged treatment up to 600 s, these total resistances were revealed at $\sim 7 \times 10^3$ and $\sim 5.5 \times 10^3 \Omega \text{ cm}^2$ respectively. Thus, the TCC coatings in the modified bath cannot provide the effective corrosion resistance, which was revealed to be lower than that of the bare alloys. In addition, the coatings formed in the bath containing 0.5 g/l copper component displayed a

larger capacitance of the coating/substrate interface, Q_{dl} , to provide the poorer corrosion protection[155].

8.3 Discussion

8.3.1 Influence of copper in alloys

The galvanic coupling of aluminium and the noble copper in the aluminium alloys is well known to give rise to the high rate of aluminium dissolution, where the copper particles serve as the cathodic sites to yield the fast oxygen reduction and/or hydrogen evolution. Consequently, the pH value of the solution/metal interface increases to produce the deposits of metal hydroxides, and then the mass-transport process across these deposits controls the proceeding rate of aluminium dissolution. Simultaneously, the amphoteric deposits in the form of aluminium hydroxides display the balance between the dissolution and deposition with dependence on the pH driving [147]. The Zr-/Cr-rich components possibly exhibit the similar pH-dependent balance of deposition and dissolution, where the solubility of zirconium oxide revealed a V-shape function with dependence on pH values ranging from pH 2 to pH 13[115].

The coating initiation on the AA2024-T351 alloys has been revealed to occur around the second-phase particles, attributed to the preferential cathodic reactions at these copper-rich particles (Chapter 5). In terms of the electropolished Al, the highly-ordered furrows were enriched with copper of ~5 nm thickness as evidenced by the characteristic TEM diffraction pattern of the θ' (Al_2Cu) phase. By contrast, the sputtering-deposited Al revealed no significance of copper on the substrate surface. The void defects on the surface by the AFM examination possibly play the role of the cathodic sites. The OCP of both substrates in the trivalent chromium bath displayed a similar evolution with treatment times, indicating no significant difference of their coating formation processes. The relatively longer period of the initial OCP fall on the sputtering-deposited Al may correlate with the slower growth kinetics compared to the situation on electropolished Al. This is related to the decreased rate of thinning the air-formed oxides by the reduced fluorine along the substrate as the RBS observation. By contrast, the copper presence on electropolished Al promotes the attraction of

fluorine to fast build up the appreciable electron tunnelling for the reaction of the bath and aluminium substrate, enhancing the kinetics of the coating imitation.

The absence of copper on the sputtering-Al substrate reduces the aluminium oxidation rate at $\sim 0.02 \text{ nm s}^{-1}$ in the period of 600 seconds; accordingly, TCC growth kinetics were impeded by two factors compared that on electropolished Al. Furthermore, the sputtering-deposited Al-24 at.%Cu, Al-40 at.%Cu and Al-64 at.%Cu substrates further revealed the increased growth kinetics and the decreased matrix dissolution rate with the higher copper concentration. Notably, a layer of the corrosion products beneath TCC coating was observed in the form of copper-/fluorine-rich layer [210] and this layer was thickened with the prolonged treatment. Further, the substrate of copper content up to ~ 40 at.%Cu displayed the thicker corrosion layer compared to the situation of Al-24 at.%Cu alloys after the conversion treatment for the same periods. By contrast, this corrosion layer was absent on the Al-64 at.%Cu alloys and the matrix oxidation was sufficiently impeded by reduced $\times 3$ compared to the coating growth rate on the surface. The copper concentration of ~ 40 at.% in alloys revealed to yield the incorporation of copper species into the alumina layer and coating region in the form of either nanoparticles [89] or soluble components [209]. Consequently, the localized detachment of the chromate conversion coating on AA2024 alloys was revealed to preferentially occur at these copper-enriched sites [88], which mechanism was also expected to display on the TCC coating formation on copper-rich sites.

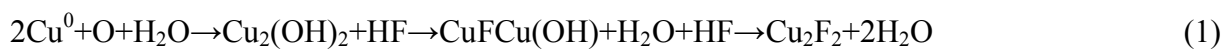
The TCC coating formed in the same period on electropolished and sputtering-deposited Al revealed a significant decrease of zirconium and an equivalent content of chromium with a Cr/Zr ratio of 0.75, which is approximately two times the Cr/Zr ratio of 0.47 on the electropolished Al. The alloying copper on the surface was suggested to play a catalytic role in this hydrolysis process of the zirconium hexafluoride ions to form fluoride-complex nodules of Na_3AlF_6 and K_3AlF_6 [82]. Thus, the absence of copper on the sputtering-Al substrate may inhibit this hydrolysis process to result in the reduced Zr-rich deposits in the coating. By contrast, the form of the chromium (III) component in the bath is the hydrated Cr^{3+} ions that deposit on the surface with a single dependence on the interfacial pH value. This also indicates that the chromium (III) species are stable and separate from the zirconium-containing ions in the bath so that their deposition processes are not correlated and dependent with the individual chemistry at the interface.

8.3.2 Influence of copper sulphate addition into the bath

The OCP evolution of electropolished Al during immersion in the bath containing an increased concentration of copper sulphate shifted to the more positive value, due to the copper deposits on the surface to reduce the area of aluminium contact. The cathodic copper deposits on the surface serve as the preferential initiation sites of TCC coatings, which are similar to the behaviour of the second phase particles in the coating formation process. Further, the population of cracks was increased in the coatings after the prolonged treatment, especially around these copper-rich deposits, hereby deteriorating the surface homogeneity. On the deposit-free matrix, the order of the coating thickness formed for 300 seconds in the bath was as follows, 0.5 g/l copper sulphate < 50 mg/l CuSO₄ < the as-received bath. The copper nucleation and saturation were controlled by the contact with aluminium substrate[199], and served as the cathode before the coating deposition. The increased concentration of copper sulphate addition in the bath promotes the deposition of these cathodic particles in the short period of conversion treatment, leading to the reduced kinetics of coating deposition on the remote matrix. In terms of the D30-treated alloy, these inhomogeneous coatings after immersion in the bath with the increased copper addition revealed the significantly reduced corrosion protection, which appeared even worse than that on the bare alloys. This is in excellent agreement with the role of the D30 pre-treatment (Chapter 6) in effectively reducing the copper-rich particles on the alloy surface to provide the enhanced corrosion protection.

8.3.3 Copper and Cr (VI) chemistry

Copper metal appears to be stable in the fluorine-containing solution compared to aluminium that can progressively corrode [58, 81, 84]. When the solution contains both the fluorine and dissolved oxygen, the copper dissolution was promoted, which reaction involves the oxygen reduction and the oxidation of Cu(0) and Cu(I) as follows.





Cu(II) fluoride (a product of reaction (3)) is not chemically stable on the base of hard-soft acid-base (HSAB) theory [57, 59] and then transforms to the copper hydroxide and oxide. Furthermore, the CuO film revealed an effective resistance against the chemical attack by dilute HF solution as evidenced by at a slower dissolution rate [55].

These reactions indicate the type of catalytic role of copper in an electrolyte containing fluorine and dissolved oxygen in the transformation process of Cu(0)/Cu(I)/Cu(II) components. In this sense, the formation of the transient Cr(VI) species detected around copper deposits was possibly promoted by such copper catalyst [159]. Furthermore, the catalytic role of manganese oxide was revealed to promote the formation of hydrogen peroxides in the naturally-aerated sea water to oxidize the Cr(III) to form Cr(VI) species [215]. Further, the effectiveness of hydrogen peroxides on oxidizing chromium (III) was evidenced by the fingerprint Raman shift [139]. Thus, the formation of hexavalent chromium species is influenced by such factors of the dissolved oxygen, sufficient fluorine and catalytic alloying elements.

8.4 Summary

1. The presence of the copper-rich layer in the form of θ' phase on electropolished Al promotes the TCC coating growth kinetics; on the sputtering-deposited Al, the ratio of coating growth relative to the matrix dissolution is ~ 3 in the period of 600 seconds.
2. The zirconium deposition kinetics were promoted by the presence of copper and the chromium (III) component was independent with the substrate; these two metal species in the bath are relatively independent and separate.
3. Cr(VI) oxides were revealed in the TCC coating formed in the naturally-aerated bath on the sputtering-deposited aluminium, further supporting the oxidation role of the dissolved oxygen in the Cr(III)/Cr(VI) transformation.

4. The coating growth kinetics were promoted on the alloys with increasing concentration of copper and the layer of corrosion products beneath the coating formed for 1200 seconds on the Al-40 at.%Cu alloys displayed the thickness of $\sim 33 \pm 2.6$ nm .
5. Copper-rich deposits from the bath containing copper sulphate serve as the preferential sites of coating initiation and give rise to the coating inhomogeneity and the resultant poorer corrosion protection.
6. The formation of the transient Cr(VI) species in the TCC coatings is influenced by factors such as the dissolved oxygen, sufficient fluorine and alloying elements.

Figure Captions 8.1-8.19

Figure 8.1 AFM topography of (a) the sputtering-deposited Al and (b) electropolished Al. The red arrows highlight void defects on the surface in depth of ~30 nm.

Figure 8.2 Open-circuit potential of electropolished (black line) and sputtering-deposited (green line) Al after the trivalent chromium treatment up to 1200 seconds at 40°C.

Figure 8.3 Transmission electron micrographs of (a) electropolished Al and (b) TCC coatings formed for 60 s of ~18 nm thick. The red arrows indicate the copper-enriched layer over the substrate.

Figure 8.4 Transmission electron micrographs of (a) sputtering-Al substrate and TCC coatings formed for (b) 60 s of ~7 nm thick, (c) 120 s of ~16 nm thick and (d) 300 s of ~42 nm thick.

Figure 8.5 TEM diffraction patterns of selected areas at the interface between TCC coatings formed for 60 s and substrate which contains: (a) electropolished Al and (b) sputtering Al. For the former case (a), the CuAl_2 θ' phase was demarcated with diffraction patterns as outlined by yellow arrows and numbers. The FCC aluminium was determined as outlined by red arrows and numbers. For the sputtering Al (b), the copper-free interface was observed.

Figure 8.6 RBS analyses of TCC coatings formed for 300 seconds on sputtering-deposited Al, where the red line represents the fitting results and the raw spectrum was in black.

Figure 8.7 Raman spectra with the 200 to 1200 cm^{-1} range for TCC coatings after treatment of 1200 seconds in naturally-aerated and deaerated SurTec solutions and the bare substrate as reference, where the substrate is sputtering-deposited aluminium of thickness of ~399 nm.

Figure 8.8 Variation of the thickness of the TCC coating and loss of matrix on sputtering Al and Al-2%Cu alloy with time of immersion in a dilute SurTec 650 at 40 °C.

Figure 8.9 Transmission electron micrographs of TCC coatings on (a, b) Al-24 at.%Cu alloy, (c,d) Al-40 at.%Cu alloy and (e, f) Al-64 at.%Cu alloy; the treatment in the SurTec 650 solution at 40 °C was for 300 seconds (a, c, e) and 1200 seconds (b, d, f).

Figure 8.10 Variation of the thickness of TCC coatings and loss of matrix on Al-24 at.%Cu, Al-40 at.%Cu and Al-64 at.%Cu alloy with time of immersion in a dilute SurTec 650 at 40 °C.

Figure 8.11 Open circuit potential evolution with dependence on the immersion time during the TCC coating formation on electropolished aluminium substrate for times up to 1800 seconds.

Figure 8.12. Scanning electron micrographs of TCC coatings formed for 15 seconds on electropolished aluminium substrate under the inlens signals, including (a) 50 mg/l CuSO₄ and (b) 0.5 g/l CuSO₄ addition into the SurTec 650 solutions. The Cu-rich particles coverage was ~ 3.3% and 8.1% respectively.

Figure 8.13 Scanning electron micrographs of TCC coatings formed for 300 seconds on electropolished aluminium substrate under the inlens signals, including (a) 50 mg/l CuSO₄ and (b) 0.5 g/l CuSO₄ addition into SurTec 650 solutions.

Figure 8.14. Transmission electron micrographs for the TCC coating formed on the aluminium substrate for (a-c) 120 s and (d-f) 300 s, consisting of the bath condition of (a,d) as-received, (b,e) 50 mg/l CuSO₄ and (c,f) 0.5 g/l CuSO₄

Figure 8.15 Raman spectra of TCC coatings formed for 300 s in the SurTec 650 solution with 50 mg/l CuSO₄ addition, containing the spectrum of TCC coatings on (a) matrix and (b) Cu-rich particles, where the neighboured ten points were used to smooth the raw data (red line).

Figure 8.16 Raman spectra of TCC coatings formed for 300 s in the SurTec 650 solution with 0.5 g/l CuSO₄ addition, containing the spectrum of TCC coatings on (a) matrix and (b) Cu-rich particles, where neighboured ten points were used to smooth the raw data (red line).

Figure 8.17 Raman spectra of the TCC coatings formed for 1200 s in the SurTec 650 solution on Al-64 at.%Cu alloys, where the neighboured ten points were used to smooth the raw data (red line). The specimens were dried in a cool-air stream soon after conversion coating treatment and the duration prior to Raman examination was less than 30 min.

Figure 8.18 Polarization curves for the TCC coating formed for 300 and 600 s in the bath with 50 mg/l and 0.5 g/l CuSO_4 addition and the TCC coating formed in the as-received bath and the bare alloys as a control. All alloys were pre-treated by D30 chemical desmutting after alkaline etching.

Figure 8.19 Impedance modulus- and phase angle-frequency evolution of TCC coatings formed for 300 and 600 s in the bath with 50 mg/l and 0.5 g/l CuSO_4 addition and TCC coating formed in the as-received bath and the bare alloy as a control. All alloys were pre-treated by D30 chemical desmutting after alkaline etching.

Table 8.1 Elemental concentrations ($\times 10^{15}$ atomic/cm²) determined by RBS analyses of coatings formed on sputtering aluminium for 60, 120 and 300 s.

	Zr	Cr	O _{RBS}	S	F	Al	Cr/Zr
60 s	2.52	1.87	46.73	0.32	3.21	25.33	0.75
120 s	7.51	5.88	68.70	0.98	9.80	28.10	0.78
300 s	27.74	20.63	171.84	3.54	35.40	50.70	0.75

Table 8.2 The average weight amount of components determined by SEM/EDX point analyses in TCC coatings formed for 15 s.

Solutions	Wt. %	O	F	Al	S	Cr	Cu	Zr
50 mg/l	Matrix	2.1	0.5	96.9	N/D	0.2	N/D	0.4
	Particles	14.4	1.8	72.5	0.3	4.0	1.4	5.6
0.5 g/l	Matrix	2.1	1.6	96.7	N/D	0.1	N/D	0.5
	Particles	15.8	3.1	34.1	0.3	3.0	35.4	8.3

Table 8.3 The average weight amount of components determined by SEM/EDX point analyses in TCC coatings formed for 300 s.

Solutions		Cu	Zr	Cr
As-received	Matrix	-	2.64	0.24
50 mg/l	Cu-rich particles	9.27	21.77	10.66
	Matrix	0.12	2.05	0.56
0.5 g/l	Cu-rich particles	82.31	3.64	1.63
	Matrix	0.27	1.02	0.26

Table 8.4 The average coating thickness (nm) from six measurements

Thickness / nm	As-received	50 mg/l	0.5 g/l
120 s	38±1.64	45±4.03	44±1.82
300 s	83±4.23	70±2.69	68±2.79

Table 8.5 Parameters of TCC coatings/alloy systems obtained from the best fitting of EIS data with the different equivalent circuits: R(QR) for bare alloy as reference; R(Q(R(QR))) for coated alloy. R_e , R_{po} , R_p represent the electrolyte resistance, the resistance of pores or defects through coatings and the charge transfer resistance respectively; two constant time phases CPE_{co} and CPE_{dl} represent the coating region and coating/substrate interfacial double layer region in the form of Q_{co} and Q_{dl} .

Specimens	$R_e / \Omega\text{cm}^2$	$R_{po} / \Omega\text{cm}^2$	$R_p / \text{k}\Omega\text{cm}^2$	$Q_{co} / (\times 10^{-6} \text{ s}^n / (\Omega \text{ cm}^2))$	n	$Q_{dl} / (\times 10^{-5} \text{ s}^n / (\Omega \text{ cm}^2))$	n
Bare alloy/D30	159	-	10.6	-	-	1.70	0.86
300 s-TCC/as-received	170	8230	205.2	2.80	0.96	0.89	0.83
300 s-TCC/50 mg/l	169	359	5.7	2.99	1	2.86	0.80
600 s-TCC/50 mg/l	167	2538	5.5	2.35	1	2.67	0.78
300 s-TCC/0.5 g/l	153	133	3.5	4.75	1	4.84	0.78
600 s-TCC/0.5 g/l	150	442	5.1	2.46	1	7.03	0.70

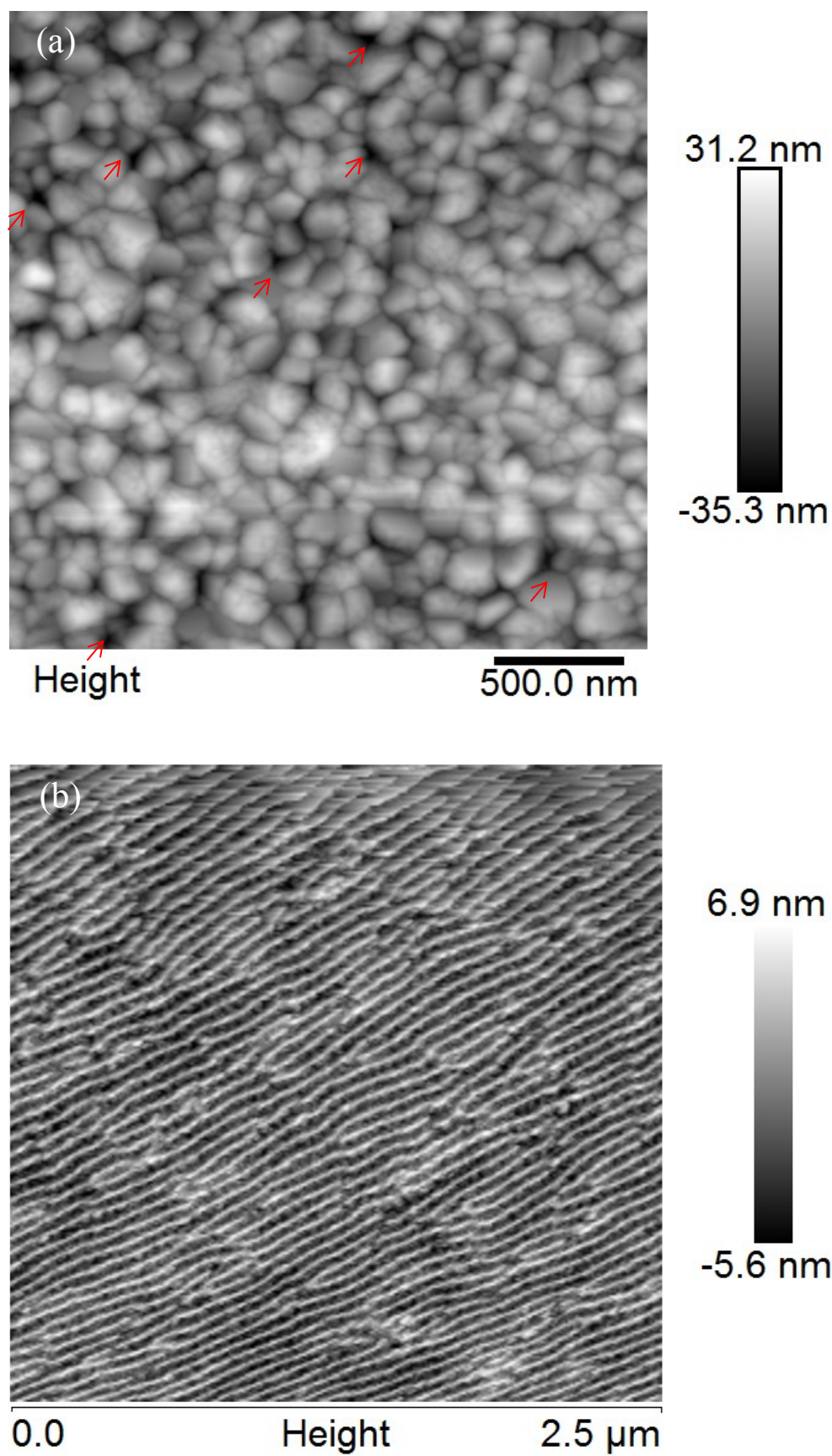


Figure 8. 1 AFM topography of (a) the sputtering-deposited Al and (b) electropolished Al. The red arrows highlight void defects on the surface in depth of ~ 30 nm.

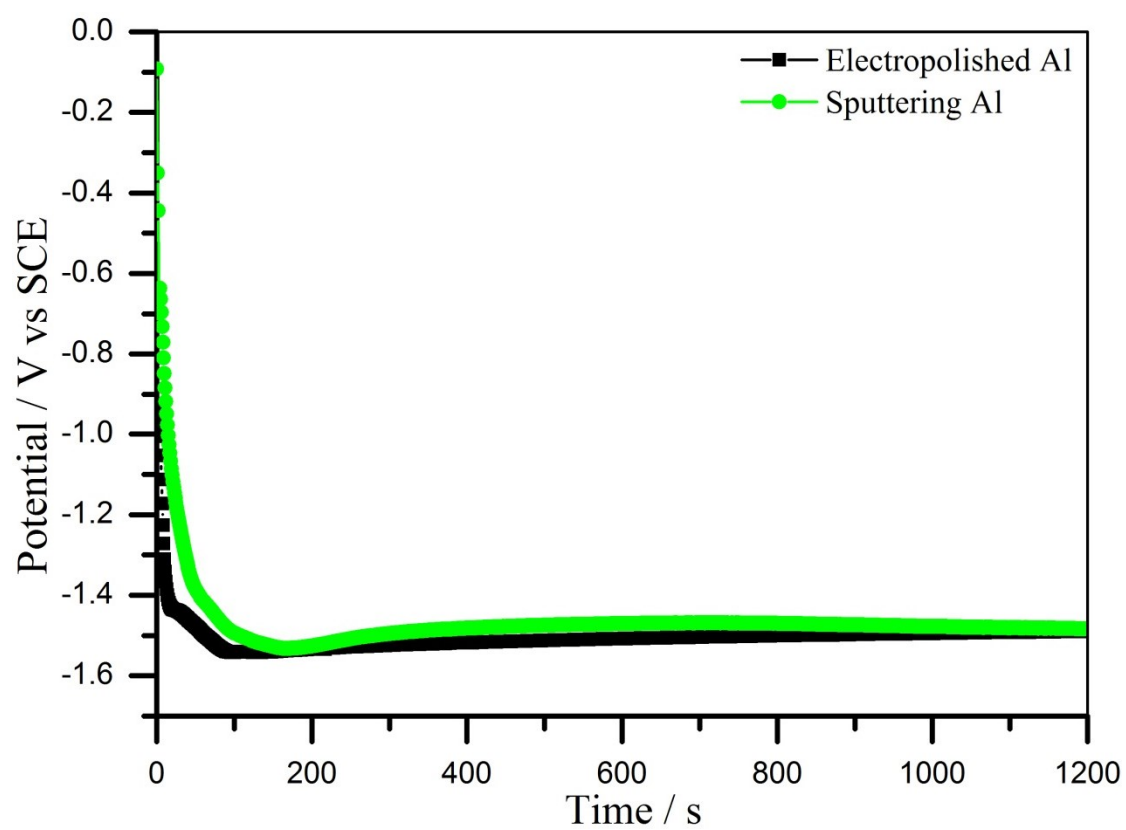


Figure 8. 2 Open-circuit potential of electropolished (black line) and sputtering-deposited (green line) Al after the trivalent chromium treatment up to 1200 seconds at 40 °C.

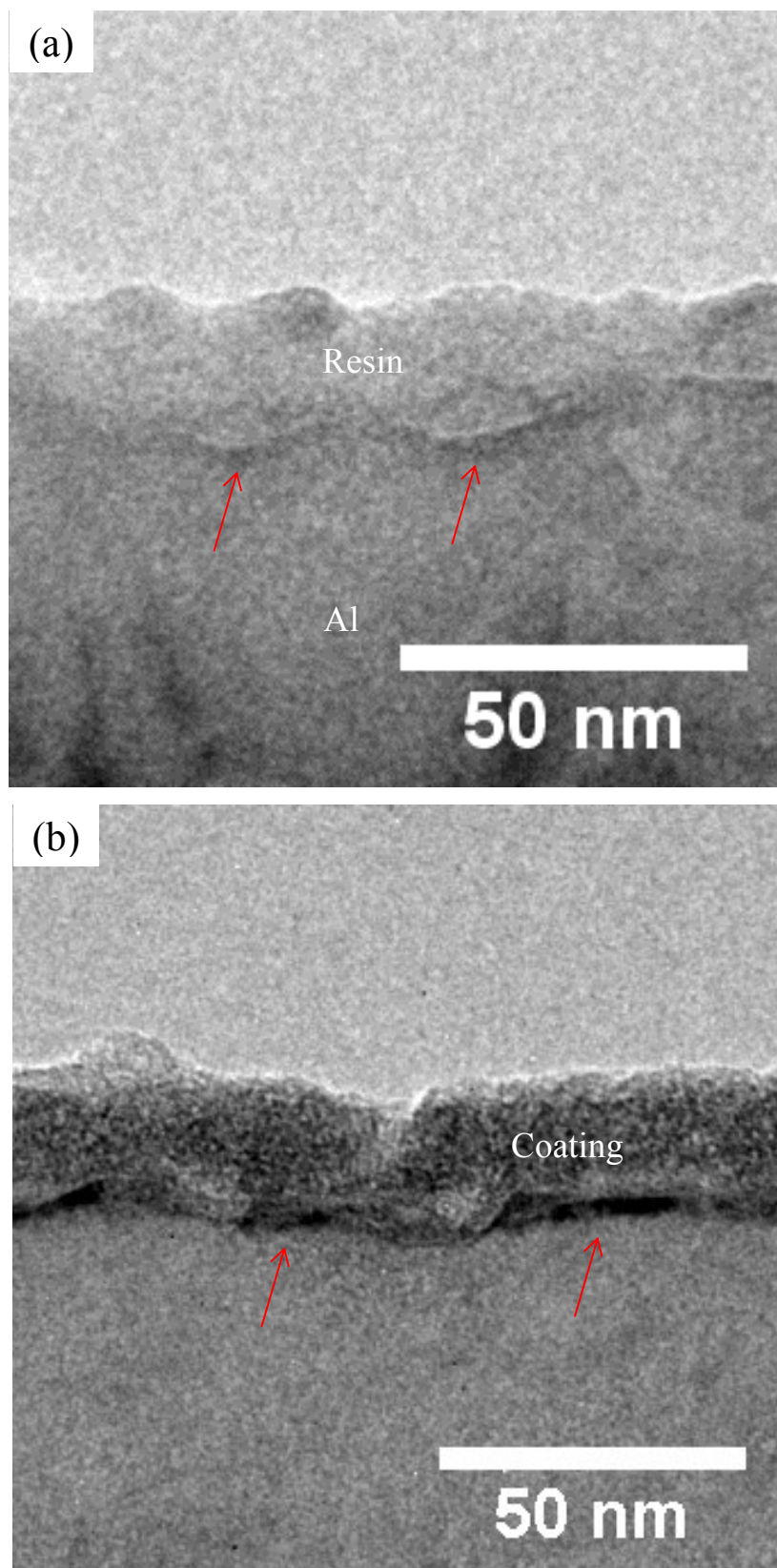


Figure 8. 3 Transmission electron micrographs of (a) electropolished Al and (b) TCC coatings formed for 60 s of ~18 nm thick. The red arrows indicate the copper-enriched layer over the substrate.

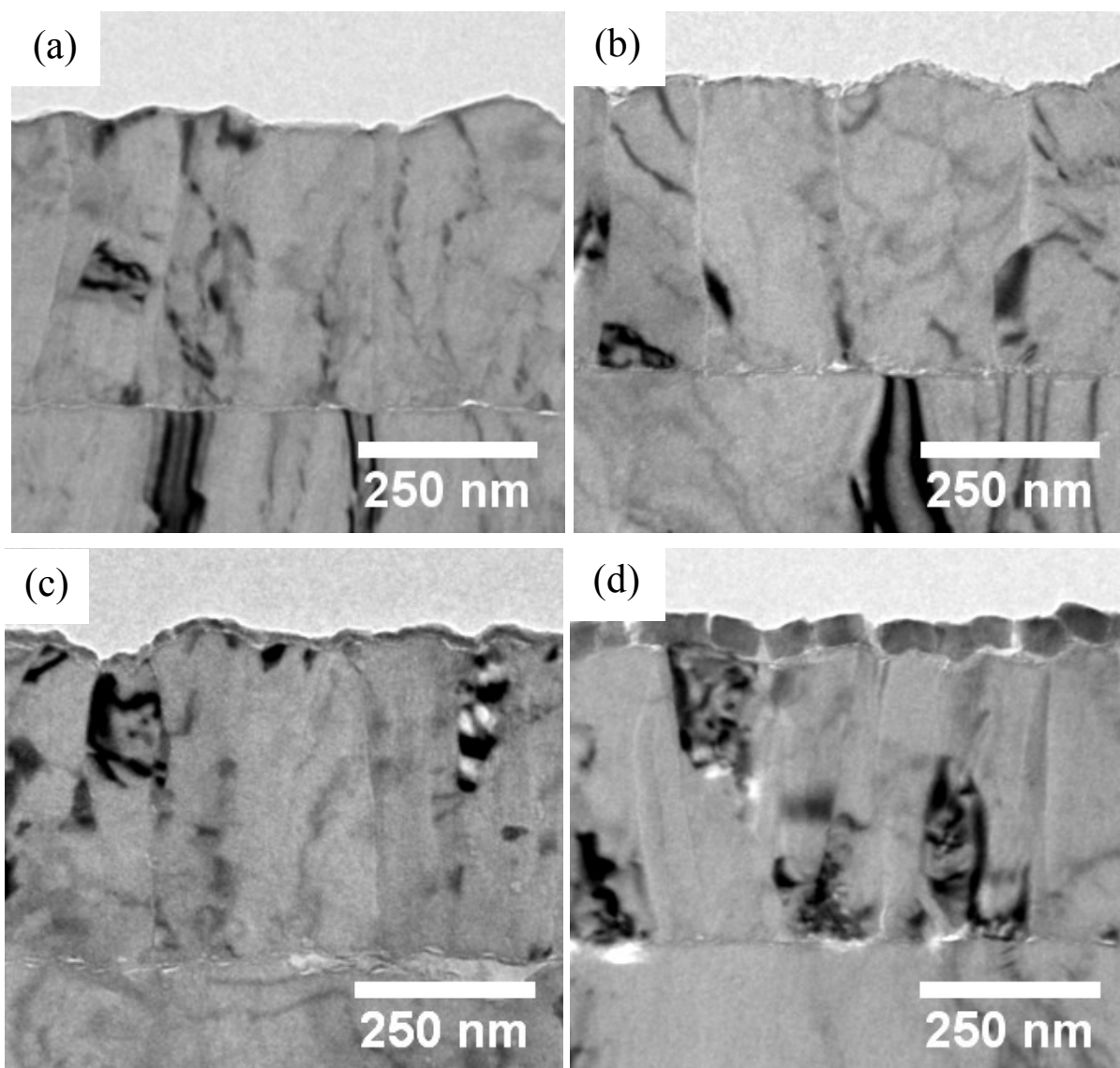


Figure 8. 4 Transmission electron micrographs of (a) sputtering-Al substrate and TCC coatings formed for (b) 60 s of ~7 nm thick, (c) 120 s of ~16 nm thick and (d) 300 s of ~42 nm thick.

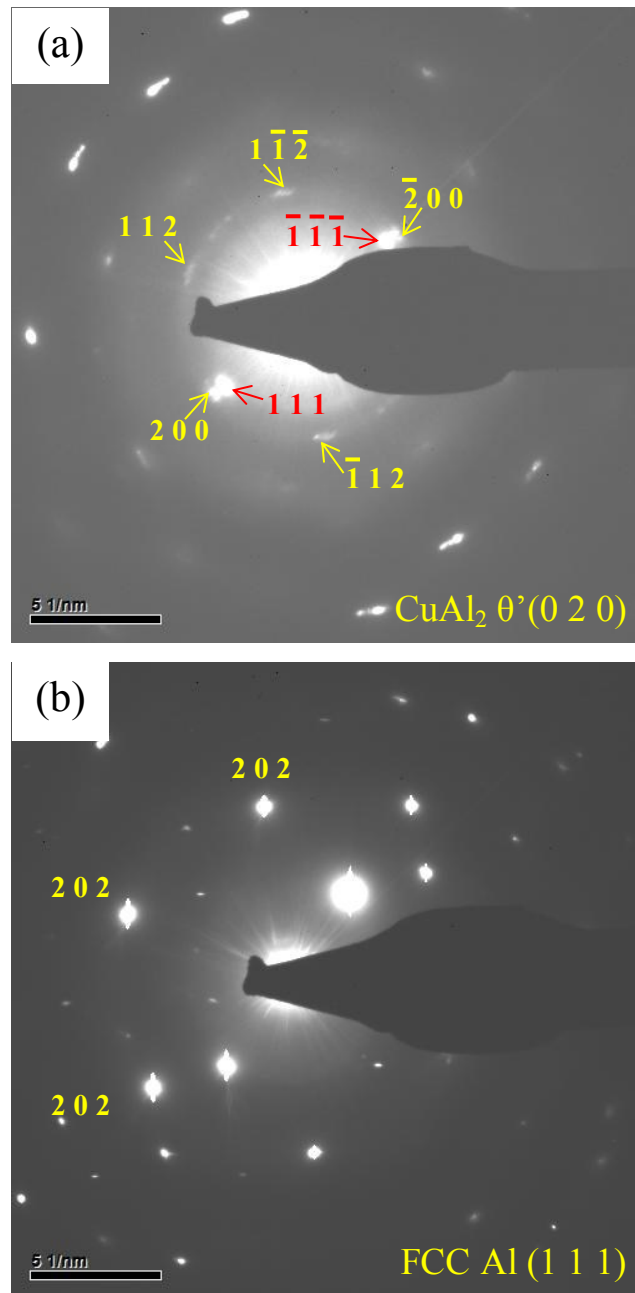


Figure 8. 5 TEM diffraction patterns of selected areas at the interface between TCC coatings formed for 60 s and substrate which contains: (a) electropolished Al and (b) sputtering Al. For the former case (a), the CuAl₂ θ' phase was demarcated with diffraction patterns as outlined by yellow arrows and numbers. The FCC aluminium was determined as outlined by red arrows and numbers. For the sputtering Al (b), the copper-free interface was observed.

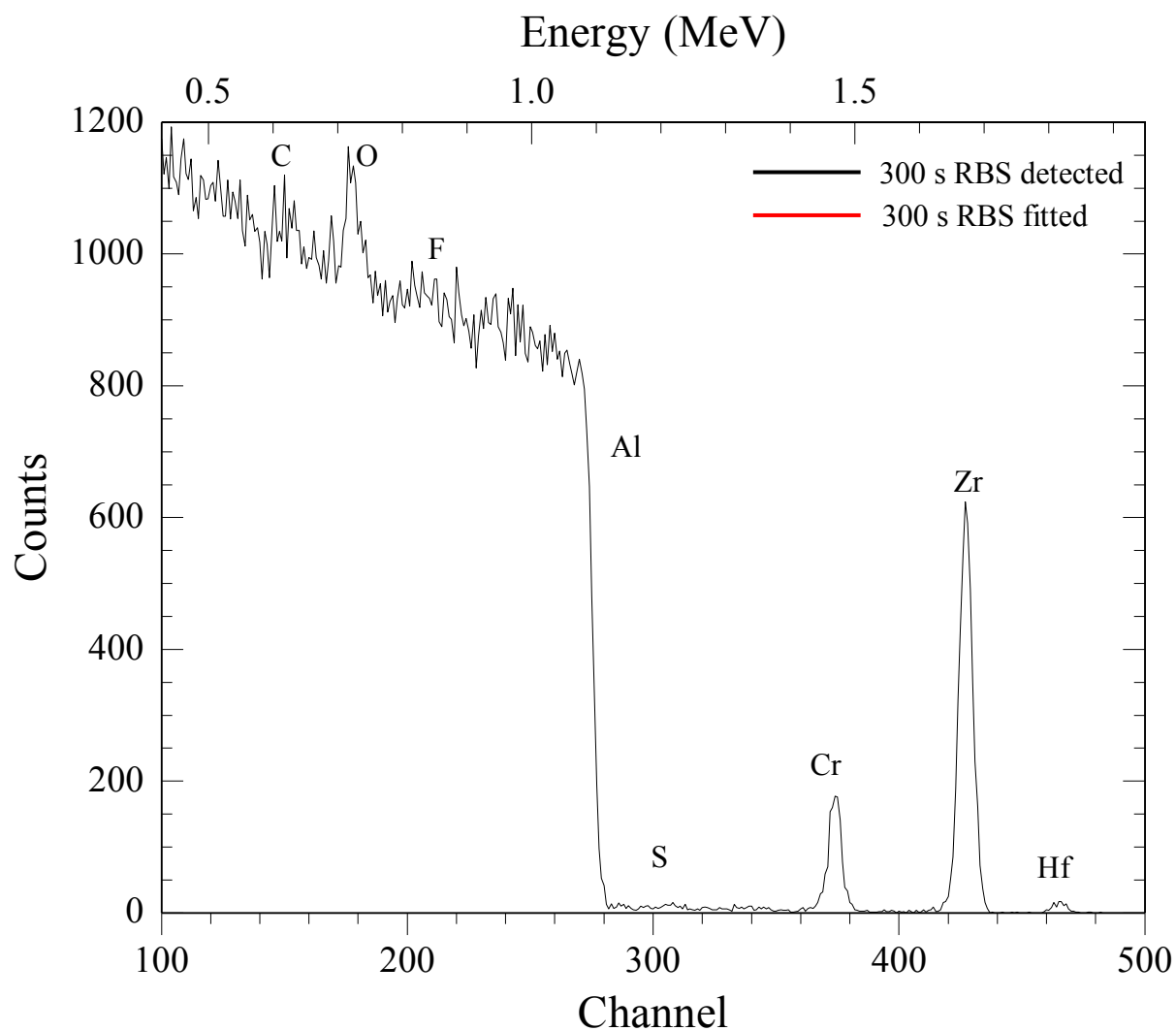


Figure 8. 6 RBS analyses of TCC coatings formed for 300 seconds on sputtering-deposited Al, where the red line represents the fitting results and the raw spectrum was in black.

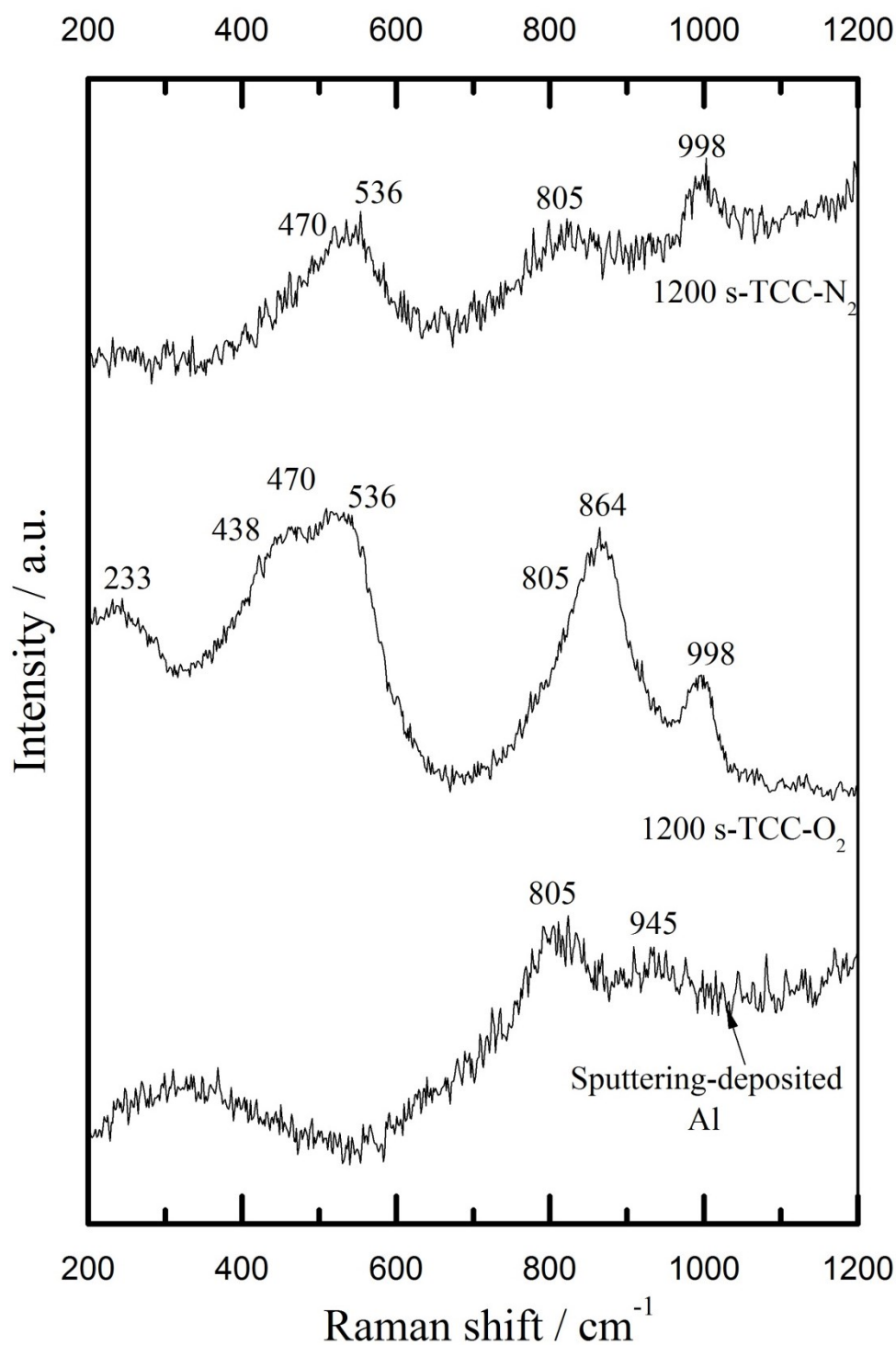


Figure 8. 7 Raman spectra with the 200 to 1200 cm^{-1} range for TCC coatings after treatment of 1200 seconds in naturally-aerated and deaerated SurTec solutions and the bare substrate as reference, where the substrate is sputtering-deposited aluminium of thickness of ~ 399 nm.

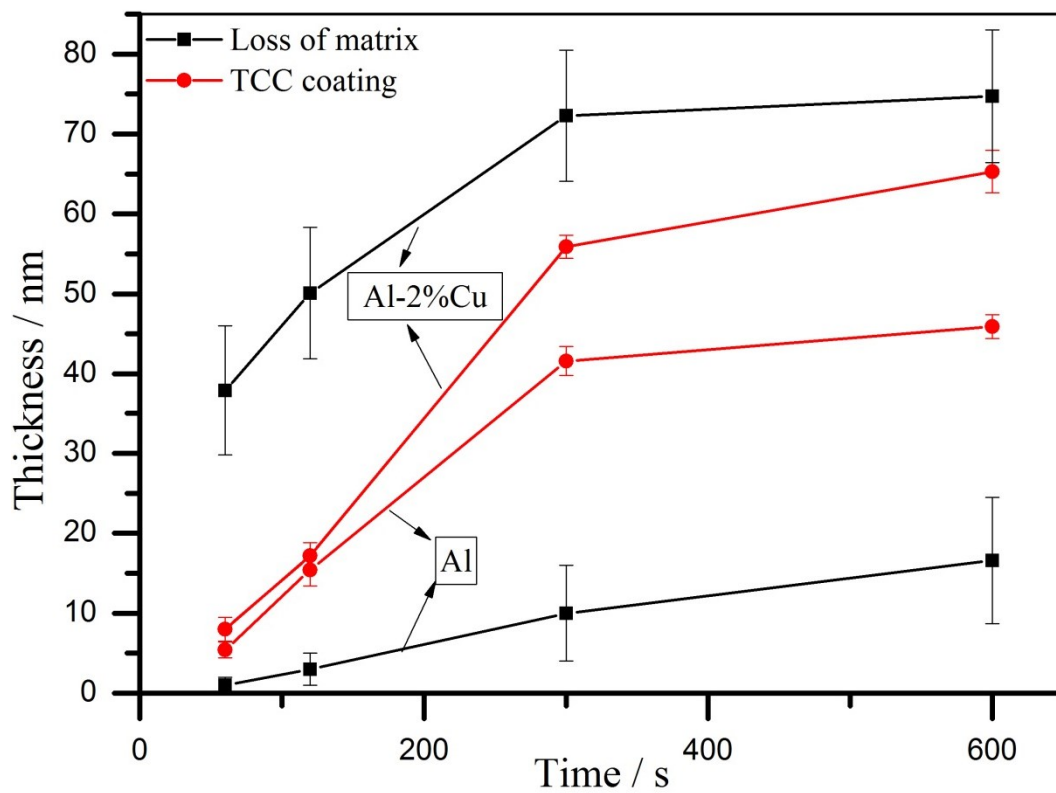


Figure 8. 8 Variation of the thickness of the TCC coating and loss of matrix on sputtering Al and Al-2%Cu alloy with time of immersion in a dilute SurTec 650 at 40 °C.

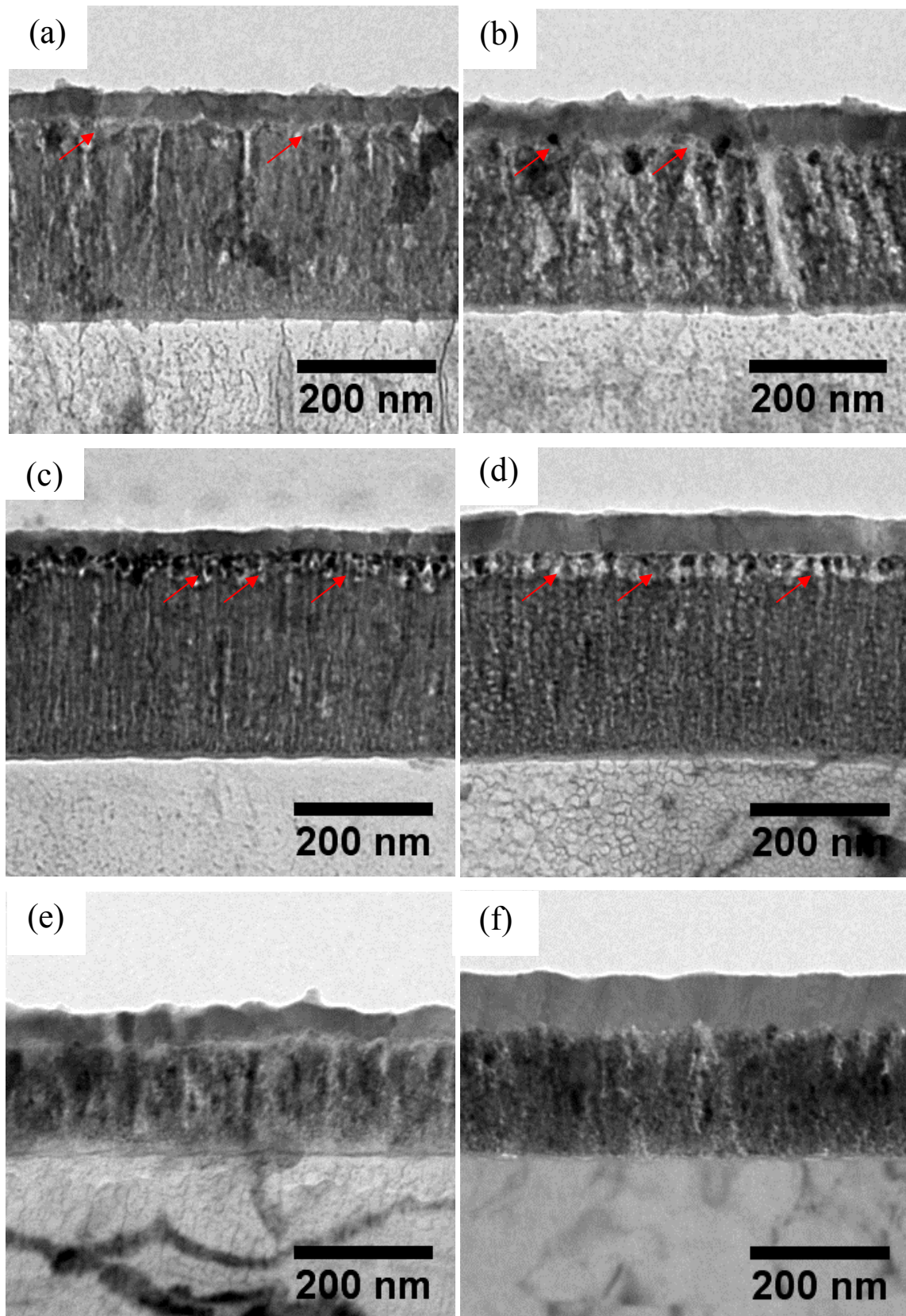


Figure 8.9 Transmission electron micrographs of TCC coatings on (a, b) Al-24 at.%Cu alloy, (c,d) Al-40 at.%Cu alloy and (e, f) Al-64 at.%Cu alloy; the treatment in the SurTec 650 solution at 40 °C was for 300 seconds (a, c, e) and 1200 seconds (b, d, f).

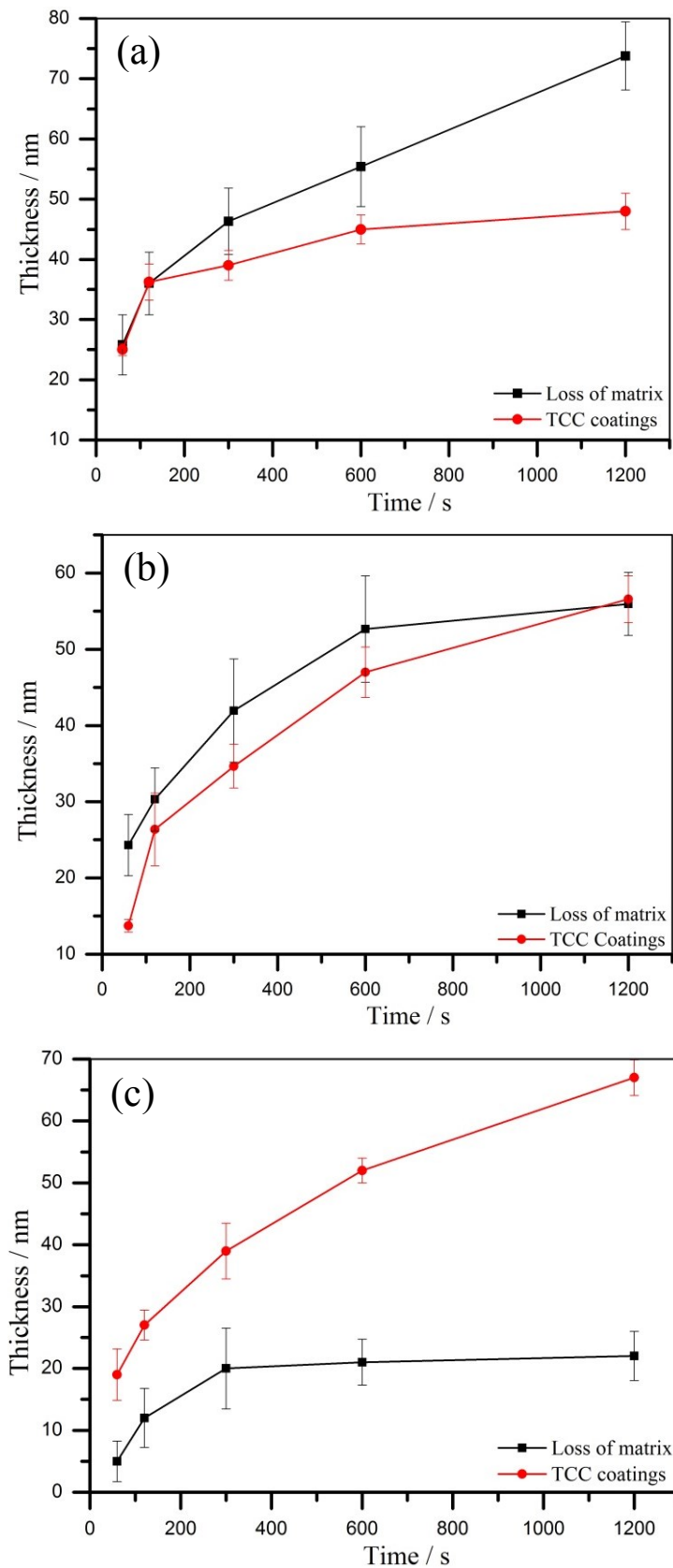


Figure 8. 10 Variation of the thickness of TCC coatings and loss of matrix on Al-24 at.%Cu, Al-40 at.%Cu and Al-64 at.%Cu alloy with time of immersion in a dilute SurTec 650 at 40 °C.

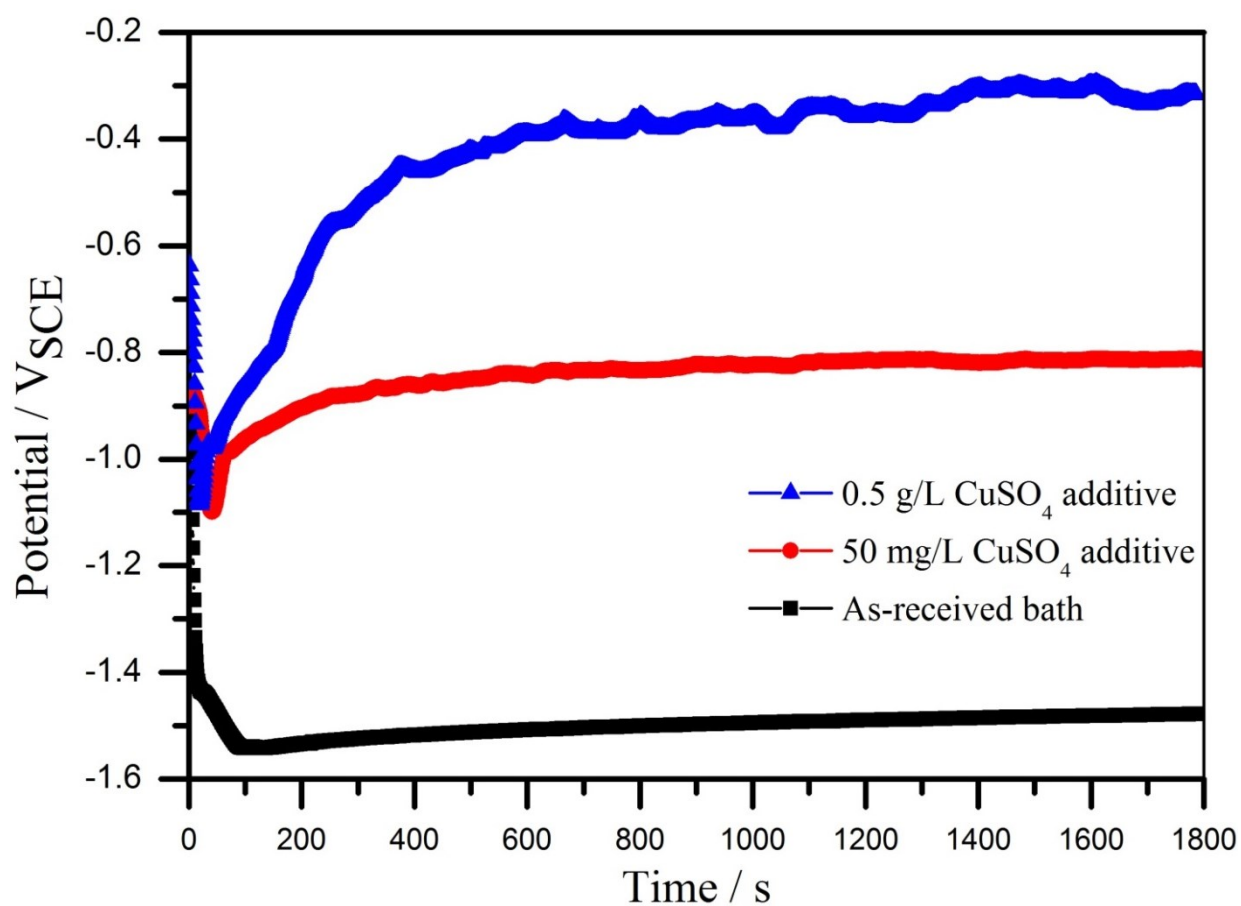


Figure 8. 11 Open circuit potential evolution with dependence on the immersion time during the TCC coating formation on electropolished aluminium substrate for times up to 1800 seconds.

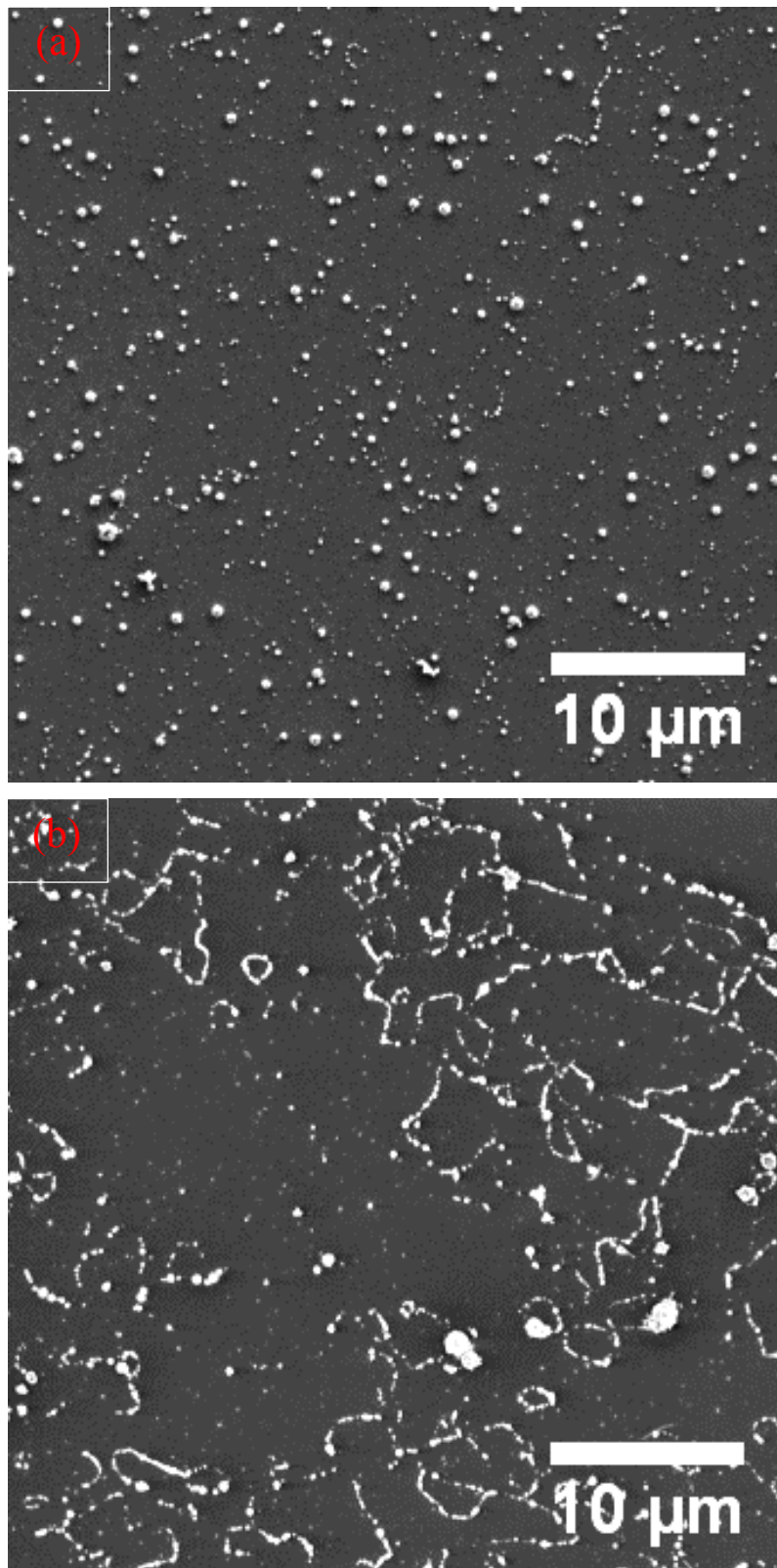


Figure 8. 12 Scanning electron micrographs of TCC coatings formed for 15 seconds on electropolished aluminium substrate under the inlens signals, including (a) 50 mg/l CuSO_4 and (b) 0.5 g/l CuSO_4 addition into the SurTec 650 solutions. The Cu-rich particles coverage was $\sim 3.3\%$ and 8.1% respectively.

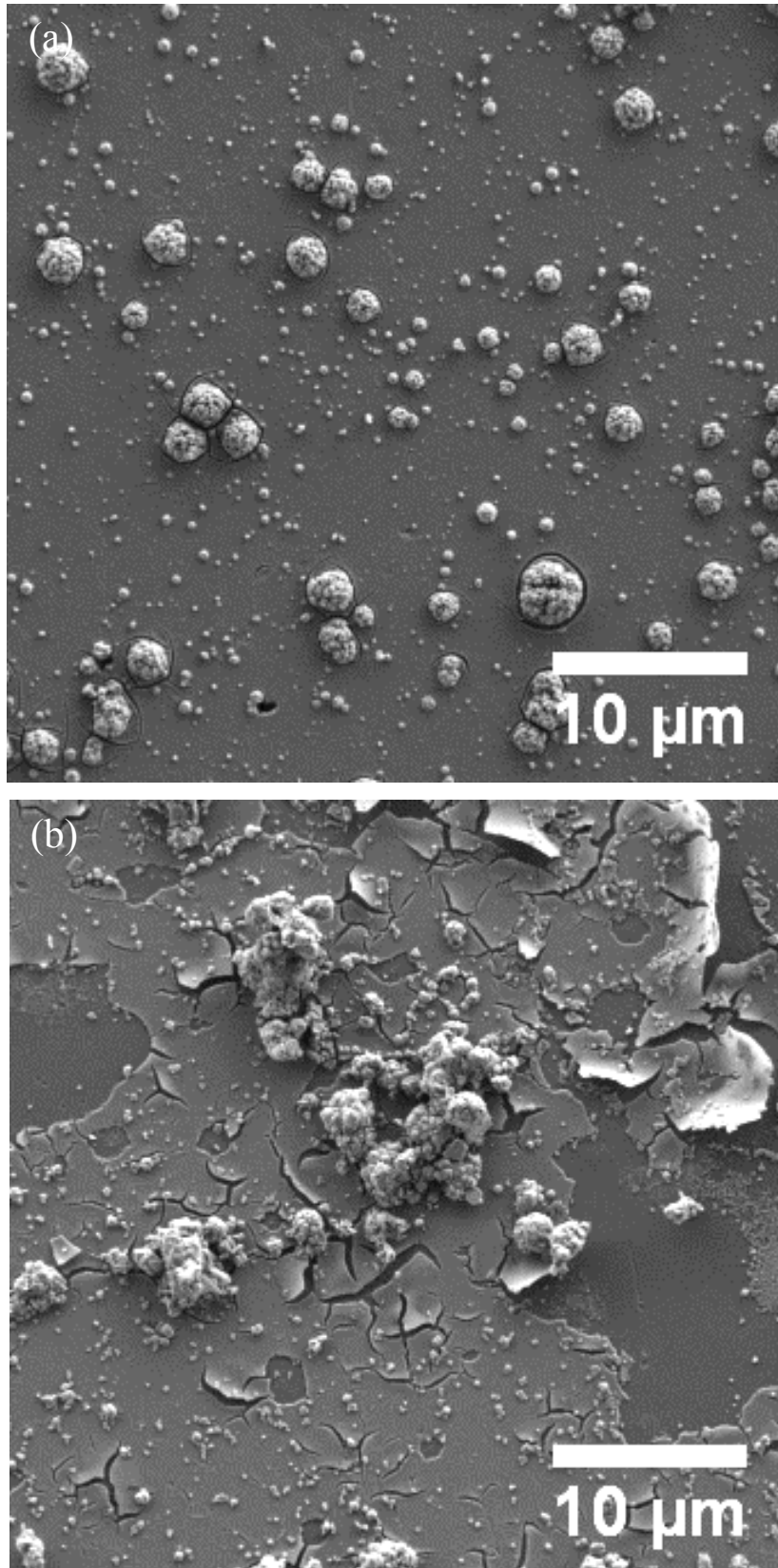


Figure 8. 13 Scanning electron micrographs of TCC coatings formed for 300 seconds on electropolished aluminium substrate under the inlens signals, including (a) 50 mg/l CuSO_4 and (b) 0.5 g/l CuSO_4 addition into SurTec 650 solutions.

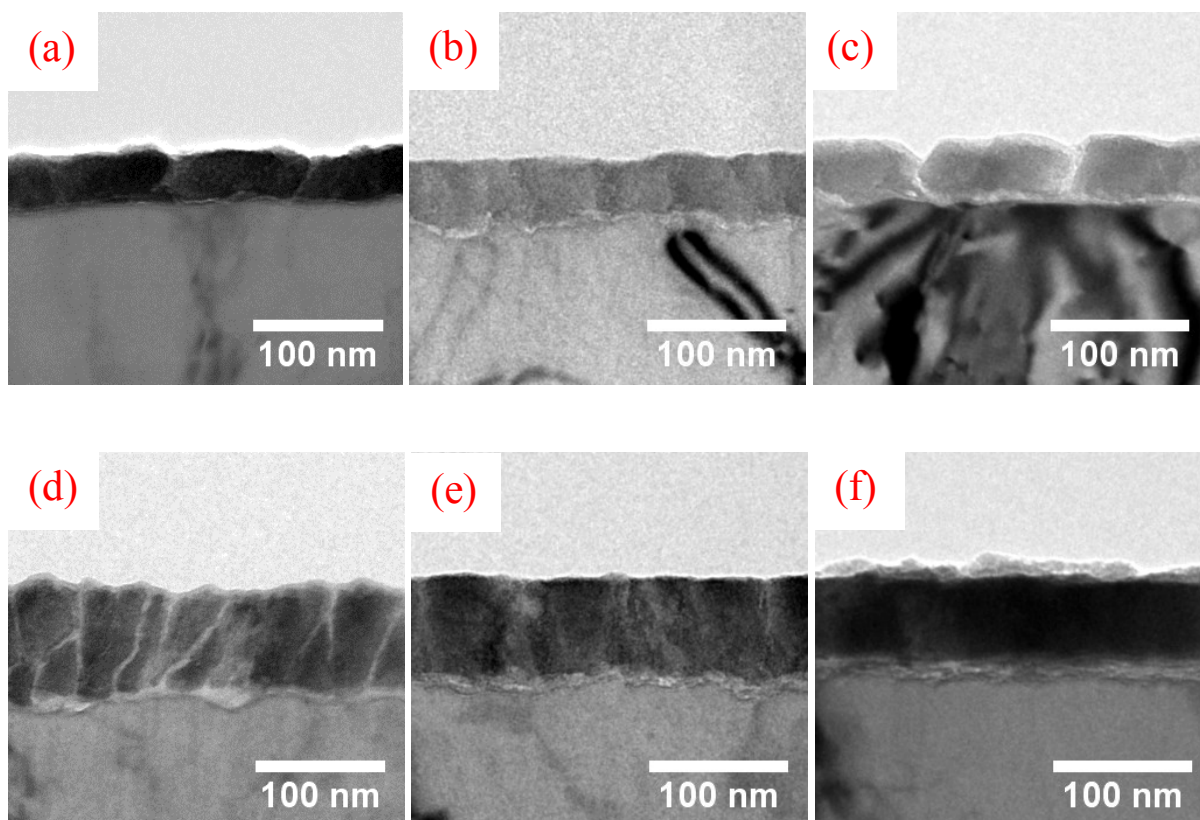


Figure 8. 14 Transmission electron micrographs for the TCC coating formed on the aluminium substrate for (a-c) 120 s and (d-f) 300 s, consisting of the bath condition of (a,d) as-received, (b,e) 50 mg/l CuSO_4 and (c,f) 0.5 g/l CuSO_4

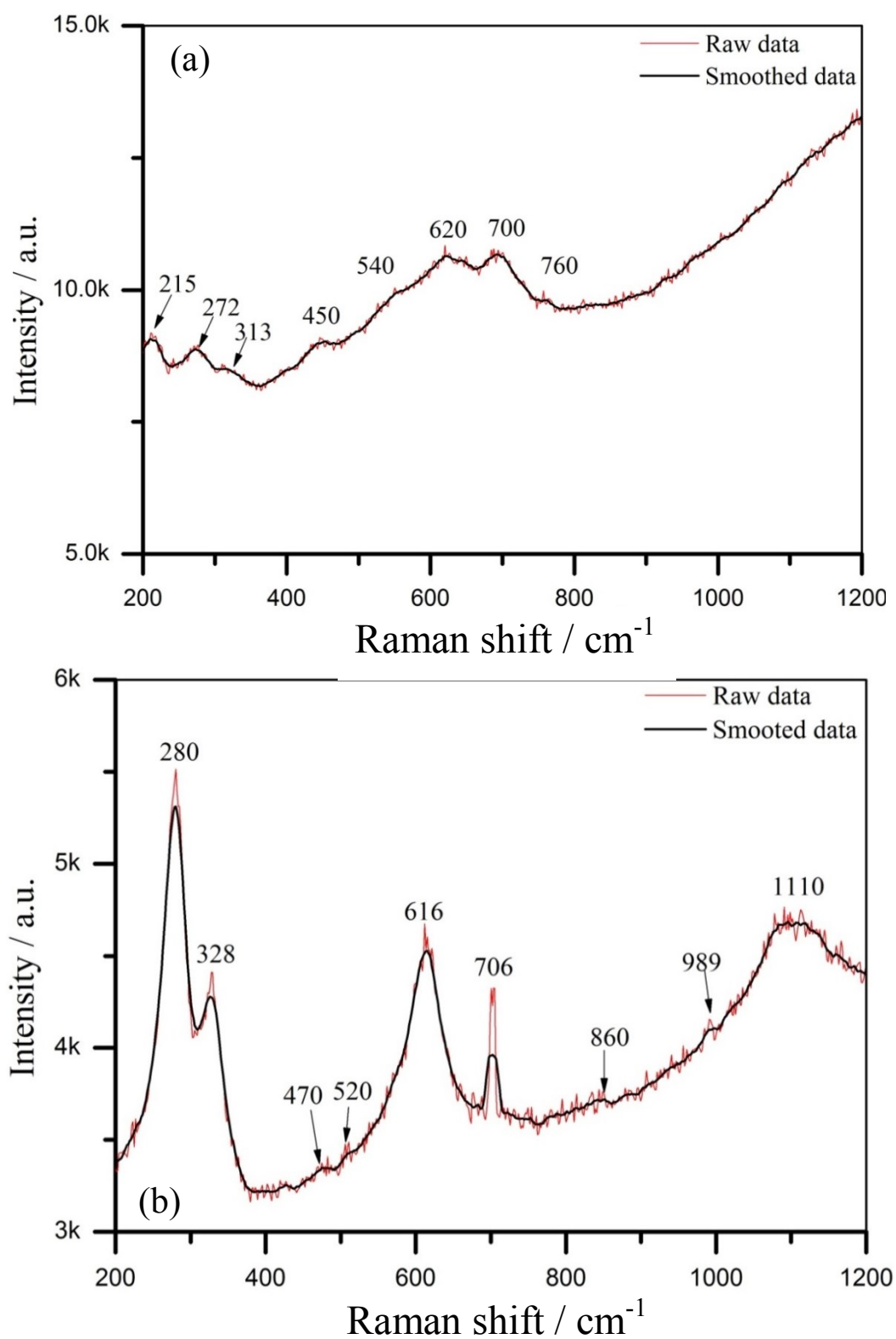


Figure 8. 15 Raman spectra of TCC coatings formed for 300 s in the SurTec 650 solution with 50 mg/l CuSO_4 addition, containing the spectrum of TCC coatings on (a) matrix and (b) Cu-rich particles, where the neighboured ten points were used to smooth the raw data (red line).

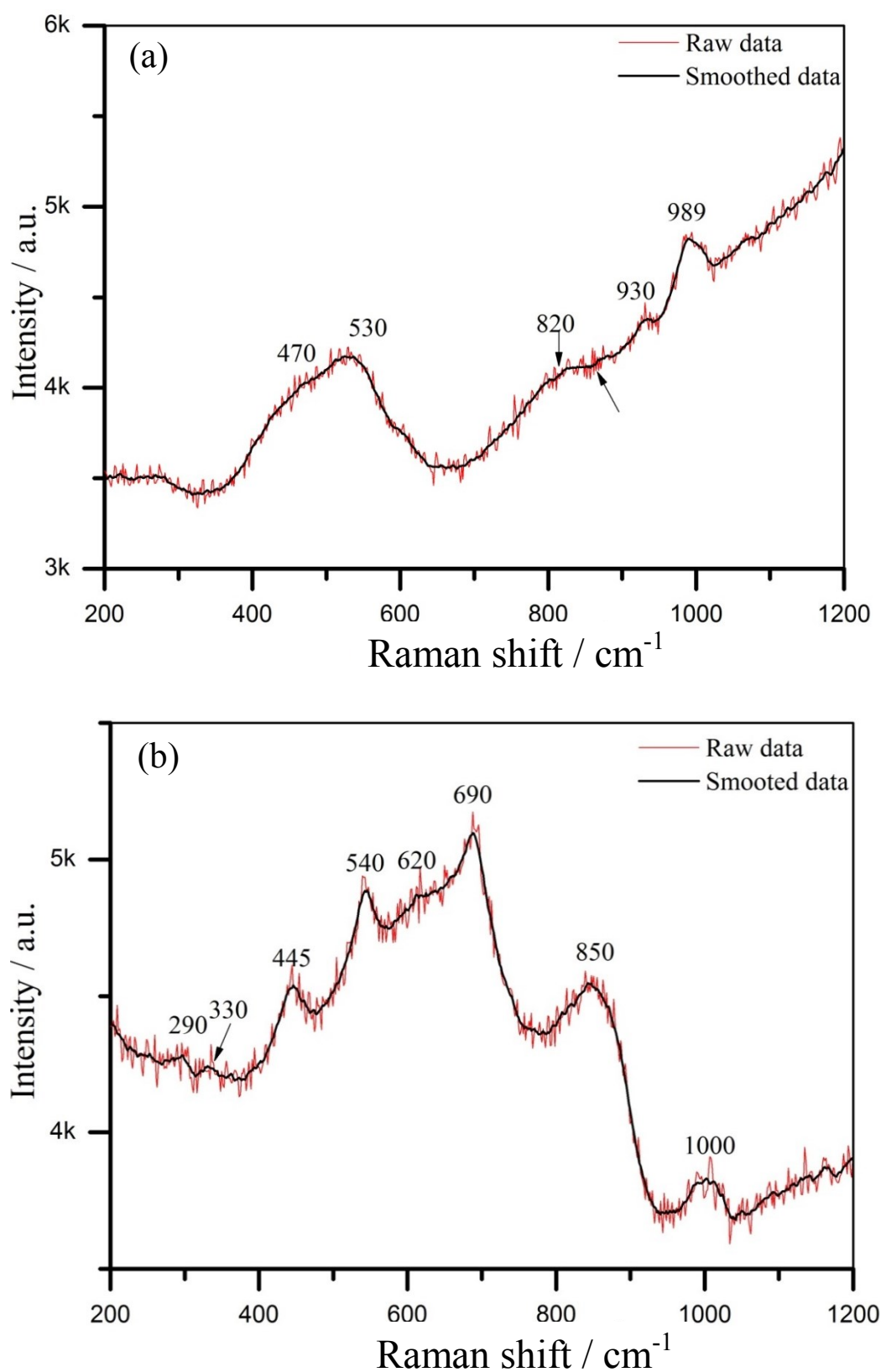


Figure 8. 16 Raman spectra of TCC coatings formed for 300 s in the SurTec 650 solution with 0.5 g/l CuSO_4 addition, containing the spectrum of TCC coatings on (a) matrix and (b) Cu-rich particles, where neighboured ten points were used to smooth the raw data (red line).

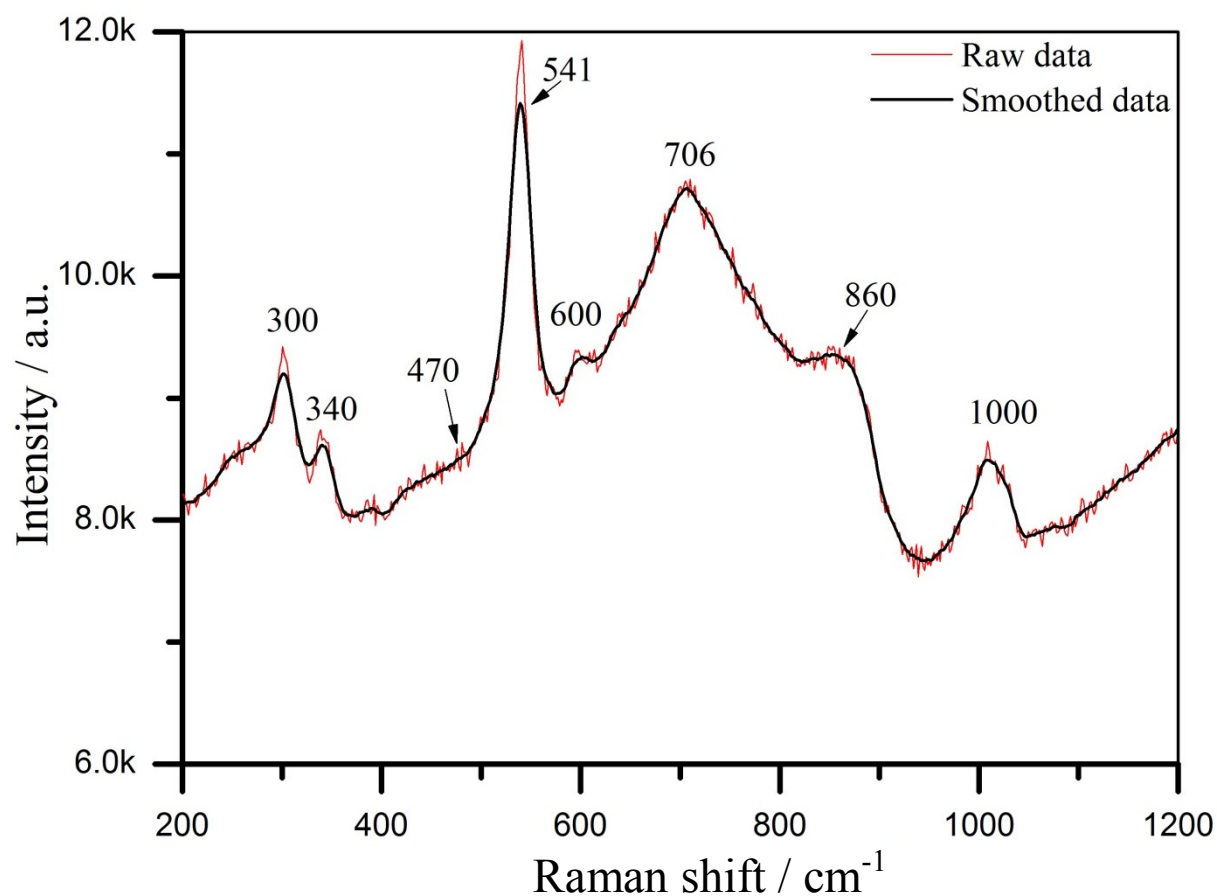


Figure 8. 17 Raman spectra of the TCC coatings formed for 1200 s in the SurTec 650 solution on Al-64 at.%Cu alloys, where the neighbored ten points were used to smooth the raw data (red line). The specimens were dried in a cool-air stream soon after conversion coating treatment and the duration prior to Raman examination was less than 30 min.

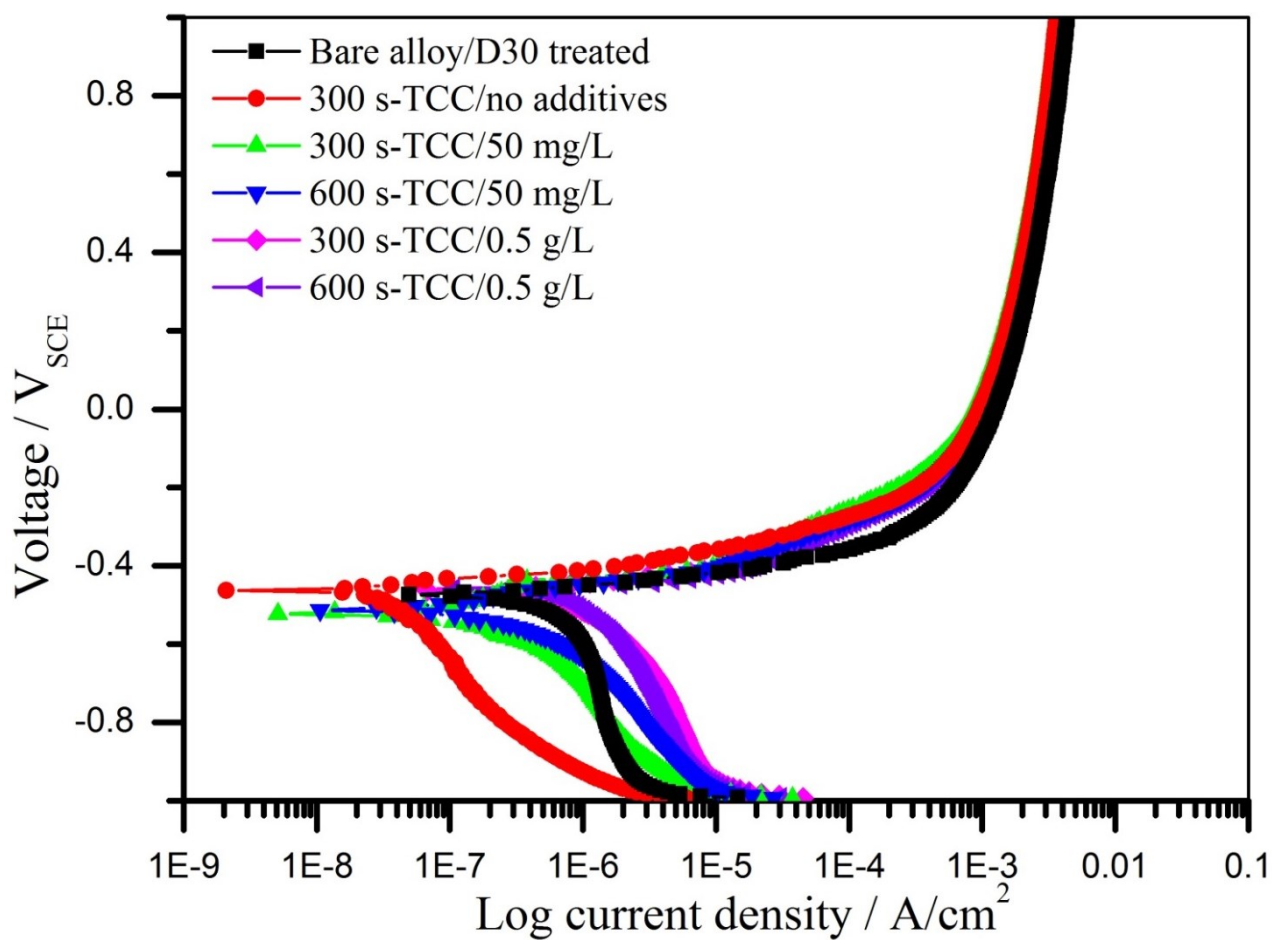


Figure 8. 18 Polarization curves for the TCC coating formed for 300 and 600 s in the bath with 50 mg/l and 0.5 g/l CuSO_4 addition and the TCC coating formed in the as-received bath and the bare alloys as a control. All alloys were pre-treated by D30 chemical desmutting after alkaline etching.

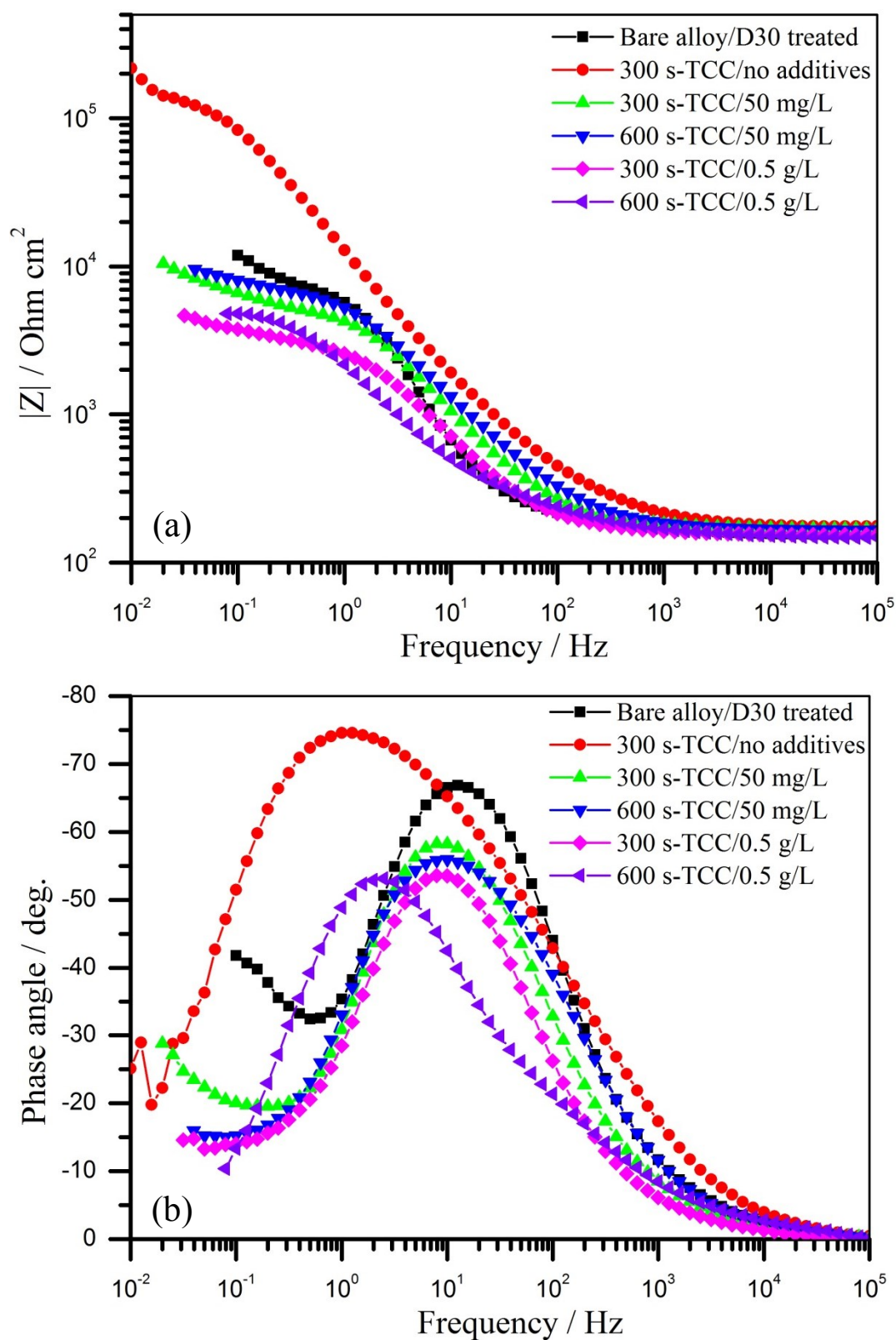


Figure 8. 19 Impedance modulus- and phase angle-frequency evolution of TCC coatings formed for 300 and 600 s in the bath with 50 mg/l and 0.5 g/l CuSO_4 addition and TCC coating formed in the as-received bath and the bare alloy as a control. All alloys were pre-treated by D30 chemical desmutting after alkaline etching.

Chapter 9 GENERAL SUMMARY AND CONCLUSIONS

This chapter summarizes the conclusions and presents the suggestions for future work. Concerning the former part, it consists of (i) TCC coatings on Al, (ii) TCC coatings on AA2024-T351 alloys, (iii) the influence of pre-treatments on TCC coatings, (iv) the influence of post-treatments on TCC coatings, and (v) the influence of copper on TCC coatings. In terms of future work, it includes (i) the effect of Cr(III) component on Cr(VI) examination, (ii) the influence of organic acid addition into the bath, (iii) the influence of sodium sulphite, (iv) the polymeric structure of the Zr-/Cr-based component, and (v) the coating growth kinetics by in-situ AFM.

9.1 Conclusions

9.1.1 TCC coatings on Al

1. The TCC coating formed on the superpure aluminium consists of two main layers. The outer layer, which constitutes most of the coating thickness, consists of AlF_3 , Al_2O_3 , AlO_xF , $\text{Cr}(\text{OH})_3$, CrF_3 , $\text{Cr}_2(\text{SO}_4)_3$, ZrO_2 and ZrF_4 species. The inner layer is aluminium-rich, with the presence of oxide and fluoride species.
2. The average rate of coating growth for treatment times of up to 300 s is $\sim 0.27 \text{ nm s}^{-1}$. Thereafter, the growth rate slows significantly, which is due to hindered transport of reactant and product species by the thickening coating layers or changes in the composition and thickness of the inner layer that affect the rate of electron tunnelling.
3. The coatings may partly detach from the aluminium substrate during rinsing with water shortly after their formation. Further, cracks develop in coatings formed after ~ 60 to 300 s. The cracks are probably initiated by stress in the coating related to drying of the coating.
4. Raman spectroscopy revealed qualitatively the presence of Cr(VI) species in the coating and provided evidence of the role of oxygen in Cr(VI) formation. The presence of CrF_3 interferes with the analysis of Cr(VI) species by XPS and with the analysis of Cr(III) oxide by Raman spectroscopy. With the assumption of a uniform distribution of Cr(VI) in the

coating, an upper limit of ~1 wt% of the coating weight was estimated for the amount of Cr(VI).

5. Raman spectroscopy is an effective tool to examine the presence and relative concentration change of the hexavalent chromium component across the TCC coatings. Air ageing for more than 24 hours can effectively decrease the hexavalent chromium in the TCC coatings, which preferentially reduce to form the Cr(III) film to protect the oxidation of the exposed aluminium by cracks.

6. The TCC coated Al in 0.1 M Na₂SO₄ and the mixture solution of 0.1 M NaCl and 0.1 M Na₂SO₄ revealed good consistency of the decreased trend of corrosion protection with the prolonged treatment, consistent with the development of cracks across coating.

7. The sodium sulphite addition in the water immersion post-treatment provides an eco-friendly surface chemistry with the absence of the Cr(VI) component by XPS analysis; however, the penetration of sulphite ions into the coating bottom may be limited and the fingerprint Raman evidence of Cr(VI) reservoir was examined.

9.1.2 TCC coatings on AA2024-T351 alloys

1. The TCC coating preferentially initiates around the second-phase particles and the S-phase particles play a dual role, one type being anodic dealloying with the fast coating formation and the other type with an intact morphology as similar as that on cathodic θ -/ α -phase particles.

2. The coating formed on AA2024-T351 alloy in a SurTec 650 bath usually consists of two layers, comprising a main layer containing chromium and zirconium species, with an atomic ratio of chromium to zirconium of $\sim 0.47 \pm 0.03$, and a thinner, underlying aluminium-rich layer. A thin layer of hydrated alumina may also form at the coating surface.

3. The coating growth on the alloy occurs at an average rate of ~ 0.23 nm/s during the first 120 s of treatment, and then decreases to ~ 0.04 nm/s. The coating thickness reaches ~ 50 nm

following a treatment of 600 s, which is roughly 50% of that achieved on aluminium in the same time.

4. Hydroxide, oxide, fluoride and sulphate species are present in the coating. Zirconium is mainly present as oxide, while chromium is present mainly as hydroxide. Small amounts of fluoride are associated with both metals, while sulphate is associated with chromium.

5. The enhanced local corrosion with the feature of substrate recession along the copper-rich layer in the coatings formed for 120 s correlates with the fluorine enrichment and the chemical attack promotes the local dissolution of aluminium and copper.

6. XPS data indicated the presence of Cr(VI) species in the coating. Using RBS data, the total amount of Cr(VI) was estimated to be ~0.1 to 1% of the coating weight. The formation of the Cr(VI) is associated with the generation of H_2O_2 by reduction of oxygen.

7. TCC coating primarily provides the cathodic barrier against corrosion and the long-term corrosion protection by the TCC coatings formed for 300 s was revealed by the electrochemical noise analyses to be as long as ~60 hour in 3.5 wt.% NaCl solution.

9.1.3 Influence of pre-treatments

1. Surface pre-treatment by the D30 deoxidation can effectively remove the protruded particles generated by the alkaline etching and provide a cleaned surface beneath a thinner oxide film. This cleaned surface promotes the formation of the more uniform coatings.

2. An $\sim \times 5$ increased initiation rate on the D30 treated substrate is related to the thinner oxides on the matrix. The subsequent logarithmic kinetics correlates with the inhibition of mass transport through the mutual blocking pores in the intact coating.

3. The TCC coatings on the D30-treated alloy consist of the concentrated fluorinated compounds of zirconium and chromium, with the decreased contents of copper and aluminium by XPS analyses, revealing a more stable composition.

4. A significant improvement of corrosion protection was revealed on the D30-treated alloy after conversion treatment of 300 seconds in the SurTec 650 solution followed by water immersion for 120 seconds and air ageing for 24 h.
5. The concentrated nitric acid plays a limited role in removing the surface particles on the polished alloys and the protruded particles on the etched alloys. This leads to the poor corrosion protection by the successive TCC coatings.

9.1.4 Influence of coating post-treatments

1. Rising temperature of the water bath from 20 °C to 40 °C can improve the cross-sectional morphology and distribution of the coating components. This imparts good consistency to the improvement of the corrosion resistances of the coating.
2. The influence of pH variation of water bath on the coating thickness is a complex function of the rates of hydration and condensation, and the deionized water bath (40 °C, pH=5) can provide the best barrier inhibition of the coated alloy with an appreciable coating thickness.
3. The best TCC coating process on the alloys after alkaline etching and nitric acid desmutting consists of the conversion treatment for 600 seconds and the immediate water treatment (40 °C, pH=5) for 120 seconds and water rinsing and the air aging for 24 h. The charge-transfer resistance of this coating reveals a ~50-fold increase.
4. The sodium sulphite addition in the water bath of 50 and 100 g/l can destroy the coating microstructure to reduce the corrosion protection. The effect of the post-treatment in the sodium sulphite solution is influenced by the factors of solution concentration and pH value.

9.1.5 Influence of copper concentration in Al-Cu alloys

1. The presence of the copper-rich layer in the form of θ' phase on electropolished Al promotes the TCC coating growth kinetics; on the sputtering-deposited Al, the ratio of coating growth relative to the matrix dissolution is ~3 in the period of 600 seconds.

2. The zirconium deposition kinetics were promoted by the presence of copper and the chromium (III) component was independent with the substrate; these two metal species in the bath are relatively independent and separate.
3. Cr(VI) oxides were revealed in the TCC coating formed in the naturally-aerated bath on the sputtering-deposited aluminium, further supporting the oxidation role of the dissolved oxygen in the Cr(III)/Cr(VI) transformation.
4. The coating growth kinetics were promoted on the alloys with increasing concentration of copper and the layer of corrosion products beneath the coating formed for 1200 seconds on the Al-40 at.%Cu alloys displayed the thickness of $\sim 33 \pm 2.6$ nm .
5. Copper-rich deposits from the bath containing copper sulphate serve as the preferential sites of coating initiation and give rise to the coating inhomogeneity and the resultant poorer corrosion protection.
6. The formation of the transient Cr(VI) species in the TCC coatings is influenced by factors such as the dissolved oxygen, sufficient fluorine and alloying elements.

9.2 Suggestions for Future Work

9.2.1 Effect of Cr(III) component on Cr(VI) examination

TCC coatings comprise trivalent chromium species in types of CrF_3 , $\text{Cr}_2(\text{SO}_4)_3$ and $\text{Cr}(\text{OH})_3$ by XPS analyses. However, the binding energy of CrF_3 at 580.03 eV revealed the overlapping region of Cr(VI) oxides (579.58 eV). By omitting the peak of CrF_3 in the Cr 2p_{3/2} photoelectron region, the concentration of Cr(VI) oxides displayed a significant increase on the electropolished Al (Chapter 4) and pre-treated AA2024-T351 alloys (Chapter 5). In comparison, Raman spectroscopy is a powerful tool to distinguish the presence of Cr(VI)- and Cr(III)-containing modules by the fingerprint Raman shift at 840-904 cm^{-1} and at 520-580 cm^{-1} respectively [159]. Furthermore, the Raman shifts of individual Cr(III) species have been revealed in Chapter 4.

Thus, the effect of CrF_3 and $\text{Cr}_2(\text{SO}_4)_3$ solutions on the Cr(VI) formation can be effectively examined by the Raman spectra. Here, the sputtering-deposited aluminium was used to avoid the effect of copper on the Cr(III)/Cr(VI) formation as suggested in Chapter 8. These specimens were immersed in the trivalent chromium bath, containing either 0.01 M CrF_3 , or 0.01 M $\text{Cr}_2(\text{SO}_4)_3$, dried in a cool-air stream, and soon tested by Raman spectroscopy. For the coating preparation, the solution pH value was adjusted to ~ 3.9 and temperature was maintained at $40\text{ }^\circ\text{C}$ in a water-heat bath.

This work is to investigate whether or not the single Cr(III) component can transform to Cr(VI) species on the aluminium surface. If Cr(VI) species were revealed by the Raman spectra in the coatings formed in both solutions, the Cr(III)/Cr(VI) transformation process is not influenced by the anions of either fluorine or sulphate, but is only determined by the interfacial chemistry at the solution/aluminium interface.

9.2.2 Influence of organic acid addition into the bath

Concerning the presence of Cr(VI) species, the addition of organic acid is promising to fix metallic chromium (III) species by a polymeric bond to reduce the transformation kinetics that has been revealed in the sea water by Nakayama et al [215]. They also provided an order of reducing ability of organic acids as follows, ascorbic acid > hydroxylamine > humic acid > formaldehyde. In terms of this concern in the TCC coatings, the organic acid addition into the SurTec 650 solution can impede the Cr(III)/Cr(VI) transformation with high possibility to provide the eco-friendly and corrosion-protection TCC process.

In addition, the presence of the organic acid in the Zr-based bath has revealed the preferential nucleation of this polymer film around the intermetallic particles, attributed to the promoting condensation reaction of organic polymer. Consequently, zirconium-based conversion coatings appeared a limited coating thickness, even though the treatment period was prolonged up to 600 seconds. [107, 114] This indicates that surface pre-treatments to sufficiently clean the particles play an important role in the formation of polymer TCC coatings with an appreciable thickness.

In this case, AA2024-T351 alloys were pre-treated by alkaline etching and D30 desmutting. Subsequently, specimens were treated in the modified SurTec 650 solution for 300 and 600 seconds, followed by the immersion in the water bath for 120 s, water rinsing and drying in a cool-air stream. The modified SurTec 650 solution was prepared with the addition of the polymer acid and then stirred and stored in the lab for 24 hours before the use. The coating formation, growth kinetics, structure, composition and corrosion protection can be investigated by the electron microscopy, ion beam analysis and electrochemical examinations.

9.2.3 Influence of sodium sulphite

The sulphite ions of concentrations of 10, 50 and 100 g/l have revealed an effectiveness to reduce the near-surface Cr (VI) species by the immersion post-treatment in a sodium sulphite solution of TCC coatings. However, Raman spectra at $\sim 860\text{ cm}^{-1}$ in these coatings indicate the presence of Cr(VI) oxides, which may exist in the inner coating layer. This indicates the limitation of the post-treatment in the sodium sulphite solution to reduce Cr(VI) components in the coating. Further, the resultant corrosion protection of coated specimens displayed a significant decrease of the corrosion resistance, which possibly relates to the concentration and pH value of the sodium sulphite solution. In the future, the parameters of the post-treatment bath will be further studies in the respects of Cr(VI) component by XPS and Raman spectra, corrosion protection by EIS and morphologies and coating composition by electron microscopy and ion beam analysis.

Besides, the addition of this sulphite component into the bath may completely solve this concern of Cr(VI) component during the coating formation. The physisorption of the sulphite anions on steel [250] and aluminium alloys [251] revealed a good cathodic inhibition, which was attributed to its toleration of a wide range of concentration of chloride and sulphate ions up to 0.1 M. This revealed the promising improvement of the SurTec 650 bath with the addition of sodium sulphite or sodium metabisulfite. Electropolished aluminium was immersed in this modified bath for 1200 seconds, followed by water rinsing and drying in a cool-air stream. These coated specimens were soon examined by Raman spectroscopy to reveal whether this modification does work or not.

9.2.4 Polymeric structure of the Zr-/Cr-based component

Xia et al. [78] employed the Fourier transform infrared (FTIR) and Raman spectra to examine the fingerprint scattering shift of trivalent and hexavalent chromium components in chromate conversion coatings. Their results revealed the potential polymeric structure of Cr(III)-O-Cr(VI) bonding. Support of this fact is that Cr(VI) oxides were observed with the vibrational shift due to the mixture of trivalent chromium component that was absent at the special Raman shift at $520\text{--}540\text{ cm}^{-1}$. For TCC coatings, the comparative study of the composition of TCC coatings on the electropolished and the sputtering-deposited Al in Chapter 8 suggested that their deposition was only dependent on the individual pH chemistry. In addition, the TEM/EDX maps of cross-sections displayed the overlapping possibility of zirconium and chromium in the outer coating layer.

Thus, the structure of Zr-/Cr-based TCC coating can be examined by the similar methods of Xia. Specimens of hydroxides of zirconium and chromium were prepared in the individual solution by adding sodium hydroxide. The precipitation was collected by methods of Xia who employed suction filtration and cleaned the precipitation by nano-pure water of volume as much as 50 ml. These specimens were used for a control of Raman shift to compare the Raman spectra of TCC coatings. The polymeric structure of TCC coating is deemed on whether their Raman shifts were influence in a mixture of zirconium hydroxide into trivalent chromium solution or a mixture of chromium (III) hydroxide into zirconium hydroxide solution.

9.2.5 Coating growth kinetics by in-situ AFM

Concerning the vacuum influence on the hydrated TCC coating during examination by transmission electron microscopy [150], the atomic force microscopy by tapping mode can record the in-situ coating thickness between detached and coated areas. Further, the matrix dissolution was also can assessed by AFM measurement between detached and uncoated areas. Figure 9.1 illustrates this AFM measurement of TCC coatings, where the uncoated, detached and coated areas were outlined by I, II and III symbols.

TCC coatings on Al have been revealed to easily detach after the air ageing for 24 hours and water rinsing treatment in Chapter 4. Thus, this boundary between detached and coated areas was examined by AFM tapping mode to investigate the in-depth thickness of coatings. In terms of the matrix dissolution, the prior lacquer was used to impede coating formation, and then this lacquer-covered area was removed either by the stripping or by the acetone dissolution and was used for uncoated areas (named I). The height difference between uncoated and detached areas can be recorded by AFM to represent the matrix dissolution.

Figure Captions:

Figure 9.1 Illustration of in-situ AFM examination of the uncoated, detached and coated areas, which were represented by I, II and III symbols.

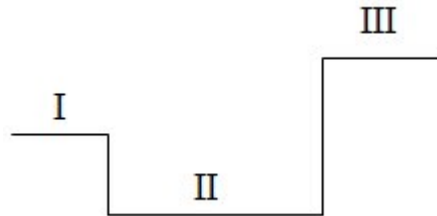


Figure 9. 1 Illustration of in-situ AFM examination of the uncoated, detached and coated areas, which were represented by I, II and III symbols.

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