DOI: 10.14750/ME.2018.011

ANTAL KERPELY DOCTORAL SCHOOL OF MATERIALS SCIENCE & TECHNOLOGY

Study of Zr4/Cr3 Based Conversion Coatings on Aluminium Alloys

A dissertation submitted in partial fulfillment of the requirements for the degree of
Doctor of Philosophy in the subject of Material Science and Technology

by

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Hungary, 2018

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ABSTRACT

The aluminium and its alloys are used mostly for several industrial applications. Aluminium exhibits desirable mechanical properties resulting from addition of elements like Si, Cu, Mg etc. Some of the aluminium alloys exhibits good corrosion resistance property under normal atmospheric conditions. Protecting the surface of metals with a coating will improve its life expectancy. The hexavalent chromium coating is used till date because of a better corrosion resistance property. However, its toxic nature leads to immediate replacement with an ecofriendly coating. The Zr4/Cr3 based conversion coating has shown promising results that could possibly replace hexavalent chromate coatings. SurTec 650 RTU from SurTec ltd. is one of most leading zirconium based trivalent chromate solutions among potential alternatives. Therefore, this dissertation is focused on understanding the coating structure, influence of alloying elements in substrate during conversion process, effect of ageing and growth kinetics of the coating. The coating over three aluminium alloys namely AA6082-T651, AA2024-T351 and AA7075-T651 was selected for investigations because of the variation in alloying elements. The investigation was conducted by depth profiling of coated samples using secondary neutral mass spectroscopy and glow discharge optical emission spectroscopy. As a result, the structure of the coating was revealed by using high vacuum exposure. The influence of alloying elements in the substrate during conversion process was identified. The elemental level changes that occur in coating during ageing process was discussed. At last, the complete growth cycle of this conversion coating over an aluminium alloy was explained.

ACKNOWLEDGEMENT

My success in this doctoral school was made possible by the combined effort of number of people.

First and foremost, I would like to thank to my supervisor Prof. Dr. Pál Bárczy. His continuous encouragement and focused guidance towards innovative research had given me the excitement and spirit to complete this Ph.D. course with the framed time limit. His support and patience had provided me sufficient guidance to solve various scientific problems throughout my works. I was awarded course completion certificate earlier than the mentioned time frame. It would have been impossible without his advising and mentoring. I learned a lot from his vast experience in research and teaching field. Apart from my Ph.D. works he also gave me a wide knowledge and handful experience in space industrial environment by providing me an opportunity to work for Admatis Ltd. as part time job over duration of my course. I am grateful to his support and acceptance of work.

I would also like to thank Dr. Béla Márton Somosvári for his valuable contribution and support in several experimental works. He provided me professional guidance and generous advice at several stages of work. His advice and encouragement has given me a strength and patience to overcome all work pressure. He was so helpful and provided me completed guidance to survive in Hungary which is not my home country.

Many thanks to Admatis team and Tamás Bárczy, managing director of Admatis Ltd. for providing me a comfortable work space in Admatis Ltd. His valuable contribution and generosity had provided me a strength and financial support to complete the course. My part time job experience in Admatis Ltd. has given me a wide knowledge and hands on experience in several surface treatment and space qualification techniques, which would be highly helpful in my career. I would also like to acknowledge that most pictures in this thesis report was a contribution from the Admatis Ltd.

I was fortunate to work with Dr. Kálmán Vad and Dr. Attila Csík, who had patiently analysed the coatings over several alloys using SNMS at MTA Atomki, Hungary. They are the extreme reliable source of practical scientific knowledge. Their constant support and patience has helped me to publish a scientific paper in the journal of applied surface science.

I am also very grateful to Dr. Török Tamás for his valuable contribution in the GD-OES measurements. We exchanged several emails and books over the course of a year that made

sense in understanding the behaviour of coating at various points in my research work. I gained a lot information from his vast chemistry knowledge and scientific curiosity. His constant support and trust in my work capabilities had given me self-confidence and encouragement to publish several journal papers. His inspiration and positive opinions about my work over the duration of this Ph.D. course helped me to achieve desired results since the very beginning.

I would also like to thank Dr. Olivér Bánhidi and Dr. Péter Baumli for their contribution and support during various experiments that was carried out at the University of Miskolc related to this thesis work. Special thanks to Dr. György Kaptay, who is solely responsible for streaming my Ph.D. work towards scientific community. I was also greatly benefited by his arts of doing science class that has providing me a clear knowledge and importance of publishing in high impact factor journals.

Finally, I would like to that Dr. Tamás Szabó, Dr. Gabriella Zsoldos, and Ágnes Solczi for helping me to get the financial support from the university for attending various scientific conferences and my publication activities. I am also grateful to my friend Nikolett Görcsös, manager of E6 hostel who made my stay comfortable that give me piece of mind to focus only on my work.

Eventually, these achievements and success would be highly impossible without support, blessings and understanding of my parents Mrs. Malarvizhi and Mr. Thirupathi.

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LIST OF ABBREVIATION

ADMATIS	ADvance MATerials In Space
AA	Aluminium Alloy
A. U	Arbitrary Unit
ASTM	American Society for Testing and Materials
AFM	Atomic Force Microscope
AMU	Atomic Mass Unit
CPS	Counts Per Second
CCC	Chromate Conversion Coating
Cr6 / Cr^{6+} / Cr6+/ Cr (VI)	Hexavalent chromium
Cr3 / Cr^{3+} /Cr3+/ Cr (III)	Trivalent chromium
ESA	European Space Agency
EDS	Energy Dispersive X-ray Spectroscopy
GD-OES	Glow Discharge Optical Emission Spectroscopy
ISRO	Indian Space Research Organisation
ICP-OES	Inductively Coupled Plasma – Optical Emission Spectroscopy
NRA	Nuclear Reaction Analysis
NAVIAR	U.S Navy Naval Air System
NASA	National Aeronautics and Space Administration
OSHA	Occupational Safety and Health Administration
RBS	Rutherford Back Scattering
REACH	Registration, Evaluation, Authorisation and Restriction of Chemical
RoSH	Restriction of Hazardous Substance
SNMS	Secondary Neutral Mass Spectroscopy
TEERM	Technology Evaluation for Environmental Risk Mitigation
TEM	Transmission Electron Microscope
TCP or TCC	Trivalent Chromate Process or Trivalent Chromium Coating
Zr4 / Zr^{4+} / Zr4+/ Zr (IV)	Zirconium
Zr4/Cr3	Zirconium/chromium-based conversion coating

1 INTRODUCTION

Aluminium alloys like AA6082, AA2024 and AA7075 are widely used in aircraft and space construction metallic components due to their lightweight and mechanical properties [1]. It is necessary to protect metal surfaces with a coating that provides good resistance against corrosion and adhesion to top coats. Hexavalent chromium-based conversion coating is widely used for aluminium alloys. However its toxic, hazardous and carcinogenic nature of hex chrome compounds has led to an urgent need to find eco-friendly replacements, as mandated by various directives of the European Union [2]. Among potential alternative treatments, Zr4/Cr3 based conversion coating has shown promise [3]. This conversion coating is nowadays widely used for the protection of aluminium alloys [4]. The developments published, related to this conversion coating shown successful results in corrosion protection behaviour over aluminium alloys and provided good adhesion for paints.

This conversion bath usually consists of zirconium fluorides and trivalent chromium salts. The formation mechanism of this coating over AA2024 alloy has been studied for several years, it is now known that this process involves dissolution and redepositing of ions from the substrate as well as from the chromium bath with interfacial pH variation during the coating process [5][6]. Investigation on the growth of coating over AA2024 indicate that this coating consists of two layers, an outer layer containing a greater number of Zr and Cr species and inner layer rich of oxides and fluorides of aluminium [7][8].

In one study the impacts of ageing using AA2024 alloy as a substrate were studied and it was suggested that coating become more hydrophobic at elevated temperature [9]. While there are studies on the formation of coating over AA7075, research on the effect of high vacuum and ageing related to Zr4/Cr3 based conversion coating over AA6082 and AA7075 alloys is limited.

The structure of coating has not been studied or reported so far. A TEM image of coating over AA2024 shows that the coating is porous in nature [10]. However, not much is known about the impact of vacuum or influence of sample preparation. Published investigations about coating thickness measurements mentioned that under vacuum, coating undergoes severe dehydration.

Besides, the study about coating growth kinetics over super pure aluminium using AFM and TEM indicated that coating growth has three states: an active period up to 30 s, linear state lasting for 600 s and changes to limited growth after 1200 s [11]. The study was done on pure aluminium; thus the influence of alloying elements is not well defined. To discover, we have coated AA6082 alloy sample under various immersion time to predict growth kinetics of conversion coating inside the bath.

An investigation about formation of coating over AA2024 reveals that the coating has several cracks and detachment over the substrate. The coating over copper rich particles shows some change in formation as mentioned in literature [12]. This indicates that alloying elements have major contribution to the formation of the coating [13]. However, not many studies have been carried out previously to understand the influence of substrate composition in the formation of Zr4/Cr3 conversion coating. The effect of alloying elements in aluminium substrate was not investigated in the published papers related to this conversion coating.

1.1. Objectives

After detailed study of the most recent literatures, we have concluded to focus only on certain knowledge gaps. Our main interests were to identify the structure of the coating which was never described perfectly. Because of its vivid environmental sensitivity (time, temperature, pressure, humidity etc) and thin layering, the structure transforms continuously under laboratory environment from day to day. Furthermore, the vacuum environment inside the structure investigating devices like TEM and SEM also generates further structural changes. The most sensitive depth profiling techniques such as SNMS and GD-OES was applied in this research work. There are four main aims to achieve, relating to the four activities listed below.

1. To study the role and contribution of alloying elements in the aluminium substrate during conversion process.
2. To understand the elemental structure changes that occur during ageing process, on the basis of investigations with SNMS apparatus.
3. To study the effect of high vacuum on the structure of this Zr4/ Cr3 based conversion coating over aluminium alloy.
4. To study the growth kinetics of Zr4/Cr3 conversion coating over AA6082

2 SUMMARY OF PUBLISHED ARTICLES

The conversion coating is the oldest method for protecting metal surfaces from external environment. The research about trivalent chromium coating started in early 1990's when hexavalent chromium is found to be toxic and hazardous to human [14]. The necessity for replacements was initiated in 2006 when the air exposure of chromium is regulated to a permissive limit of 5µg/m^3 by Occupational Safety and Health Administration (OSHA) [15]. Since then the research institutes and industries were focused towards an alternative replacement for coating that contains non-hexavalent chromium and also exhibits equally good corrosion protection for aluminium alloys.

2.1 Alternatives for non-chromate conversion coating

In the late 1990's Henkel Corp. developed a new cobalt-based conversion coating that has showed some significant result in adhesion toward paint, but it does not provide good corrosion protection in salt spray chamber. The published report about an overview of chemistry, formation, and corrosion protection of inorganic vanadates conversion coating over aluminium alloys shows slight corrosion inhibition in near neutral solution. However there is an increasing pitting potential and decrease in oxygen reduction reaction rate on AA2024 alloy [16].

The protective coating based on cerate, molybdite and other rare earth components over aluminium substrate through an environment friendly process was evaluated under electrochemical techniques concluded that these coatings provides adequate corrosion protection but not equivalent to hexavalent chromate conversion coating [17]. This initiates the research towards cerium-based conversion coatings and published results revealed it to be an effective method to resist localized corrosion of aluminium borate whisker reinforced AA6061 composite. The increased $CeCl_3$ concentration in coating bath had shown to have a significant influence in corrosion behaviour and surface morphologies over coated samples [18]. Despite of these, this coating also produces adverse health effects even though it is not a cancer-causing agent to mammals like hex chrome.

Later, a published report about an overview of non-hexavalent chromate conversion coatings that could provide good adhesion and corrosion resistance for aluminium and its alloy. It has been concluded that the manganese-based oxides produced by heptavalent manganese-based system could be closely matched with actual hexavalent chromate conversion coating in terms of actual chemistry and performance. However, this coating does not provide any significant adhesion toward paints [19]. The similar research conducted by ESA at 2008, comparing the traditional hexavalent chromium from Alodine®1200 based on Henkel Corp. with other chromium free coating available in the market validated that most of non-chromate conversion coatings like Iridite NCP (fluorotitanate based), Nabutan STI/310 (Fluorotitanic based), Alodine 5700 (Organometallic zirconate complex based) cannot replace the hex chrome coating in particular for space applications [14].

Among rest of the potential alternatives, trivalent chromium coating has shown promising results which gained wide acceptance from several industries, recently as replacement for hex chrome coating. This coating was first developed by Agarwala and his team on an aluminium alloy by the immersion of samples in an aqueous solution containing $Cr_2(SO_4)_3$ and Na_2SiF_6. Later, this coating has showed significant improvement in corrosion protection and adhesion properties by the addition of zirconium/titanium ions which was developed and patented by NAVIAR [20].Based on this NAVIAR solution, several fluoro zirconate coatings have been developed and are sold commercially. Among those Henkel Corp. is one of the leading coating industries that has developed Alodine®5200, which exhibited less corrosion protection on AA2024 but stable under 48 h in neutral salt spray chamber. The coatings using this solution can be applied over metals by immersion, spray, and wipe etc. The chemical structure, formation mechanism of this coating was less known.

In this sense, Liangliang Li did his thesis work on studying corrosion behaviour and formation mechanism of trivalent chromium coating from Henkel Corp. in Michigan State University, USA at 2013 [5]. His publication revealed that the formation of TCC coatings is driven by increase in interfacial pH caused by the dissolution of oxide layer. The coatings consist of $ZrO_2/Cr(OH)_3$ over layer and a K and F rich fluoroaluminate interfacial layer. The thickness of coating in vacuum is approximately 50 nm on AA2024 and 70 nm on AA7075. He also stated that true coating thickness may vary due to influence of vacuum in measurements.

Further, he also revealed that the corrosion protection mechanism involves reducing the oxygen reduction kinetics and partially blocking the mass transfer of dissolved O_2 and ions to the metal. The insulating electrons transfer through the nonconductive $ZrO_2/Cr(OH)_3$ layer proving active corrosion inhibition. The various experimental results like full immersion test in salt water, humid atmosphere test, moist SO_2 and thin layer mist test of this Henkel Corp. based TCC showed some corrosion protection for AA2024, AA7075 alloys. Interestingly, he also figured out that the variation in curing time and temperature of coating somehow influences the corrosion protection behaviour. In addition, he predicted that these factors could possibly determine the structure of coating. As a result, testing the coatings at various curing time and temperature, he hypothesized the coating with less cracks and detachments from metal has better corrosion resistance.Neglecting numerous other publications related to improvement on corrosion resistance property of TCC coating over aluminium alloys that claims better corrosion resistance, seems to be a non equivalent replacement to traditional hexavalent chromate conversion coating [21].

In earlier literatures, there are some publications about self-healing nature of Cr6 coating. One of the unique capabilities of hexavalent chromium conversion coating is that it has self-healing nature. Self-healing is the predominate feature of the chromate conversion coating. The word self-healing indicates that, whenever the substrate metal exposed, due to scratch or defect on the CCC, it is protected by the nearby Cr6 species that is leached from the coating [22]. The self-healing involves three steps: the release of Cr6 into corrosive environment, transport of Cr6 through aqueous phase to a non-coated or damaged area and reduction of soluble chromate to insoluble and protective chromium hydroxide. The investigation about self-healing nature of Alodine®5600 based trivalent chromate coating over AA2024 alloys showed that after static exposure in dilute Harrison solution, the Cr species were detected in the exposed electrolyte suggesting that TCC coating is capable of releasing Cr into the solution and there is no traces of Zr ions.

The recent report on trivalent chromium-based conversion coating named TEERM by the collaboration of NASA and ESA testing several commercial available solutions like Metalast TCP HF, SurTec 650 , Bonderite M/NT 65000 and MAPSIL SILICO showed that SurTec 650 provided better corrosion resistance than traditional hexavalent chromate conversion coating [23]. Since then several industries and research institutes have conducted more intense research to understand the formation, corrosion protection behaviour of this zirconium-based trivalent conversion coating from SurTec Ltd. over aluminium alloys.

In this regard, Jiantao Qi and his team started their thesis work on zirconium based trivalent chromium conversion coating using SurTec 650 at the University of Manchester, UK. His work about the formation mechanism, influences of water immersion after conversion coating procedure and corrosion inhibition over AA2024 covered most of the characteristics features of conversion coating. The published article about the composition of coating over pure aluminium alloy indicate that coating consist of two main layers. The outer layer constitutes most of coating thickness consisting of ALF_3, Al_2O_3, $Cr(OH)_3$, CrF_3, $Cr_2(SO_4)_3$, ZrO_2 and ZrF_4 species. The inner layer is aluminium rich with presence of oxide and fluoride species. The inner coating provides the main corrosion protection [7]. His published work about the formation mechanism of coating reveals the reason behind the two layers. The Zr and Cr rich outer layer is response to an increase in pH of solution due to the reduction of oxygen and hydrogen evolution. The aluminium rich inner layer is predicted to be following reaction

$$2\mathrm{Al} \rightarrow 2\mathrm{Al}^{3+} + 6\mathrm{e}$$

$$2\mathrm{Al}^{3+} + 3\mathrm{O}^{2-} \rightarrow \mathrm{Al}_2\mathrm{O}_3$$

$$\mathrm{Al}_2\mathrm{O}_3 + 6\mathrm{HF} \rightarrow 2\mathrm{AlF}_3 + 3\mathrm{H}_2\mathrm{O}$$

Over all the formation process on the alloy consist of the initial surface activation and preferential coating initiation on the cathodic phase particles [10].

His work about the post water immersion concludes that corrosion protection behaviour of this zirconium based trivalent chromium conversion coating is marginally improved by immersion coated sample in water bath around 40˚C at pH 5. The post water treatment significantly reduces F rich constituents and an increase extend of oxides/hydroxides [24].The same team from University of Manchester also included the study about corrosion behaviour of coating over AA2024. The corrosion observed on the surface is divided into two types of attack sites, including localised corrosion and cooperative corrosion. The cooperative corrosion events were characterised by domes of corrosion product with ring of corrosion product and intergranular grain boundary attack [25][26].

Interestingly, a comparison of studies about the formation of coating over pure aluminium using TEM, AFM and GD-OES by Manchester group clearly indicated variation in thickness prediction using AFM and TEM. The results obtained using AFM showed higher coating thickness in comparison to values obtained from TEM. This research was conducted by unique method, specimen of electro polished aluminium sample prior to conversion coating were decorated by stop off lacquer dots to inhibit coating deposition. After conversion coating that lacquer dots were removed to produce the uncoated spot along some detached area. This investigation reveals that coating growth consist of three different states activation period, linear growth and limited growth over pure aluminium alloy [11]. Further, high vacuum environment in the microscope revealed a coating shrinkage. It is predicted from results that the coating undergoes severe dehydration causes shrinkage in vacuum.

3 BACKGROUND INFORMATION

3.1 Aluminium and its alloys

Aluminium is one of the most available metals used for several industrial applications. The aluminium exceeding 99.9% purity was first available in the early 1920's produced by the Hoopes electrolytic process [27]. The emerging industrial developments demanded a unique quality of aluminium by the homogenous mixture of alloying elements. Within few decades the Wright brothers gave birth to an entirely new industry which grew in partnership with aluminium industry related to the development of structure reliable air frames components, engines and ultimately for missile, fuel cells and satellite components. Now a days, aluminium and its alloys are included in several applications like cooking utensils, mirror frames etc. [28].

The aluminium is classified in to several types based on mixtures of alloying elements. Aluminium alloys usually have a four-digit designation. The first digit designates purity or alloy type. The second digit indicates modification of the alloy. The series of aluminium alloys are listed below [29]

1. 1xxx-aluminium (at least 99% pure)
2. 2xxx-aluminium-copper alloy
3. 3xxx-aluminium-manganese alloy
4. 4xxx-aluminium-silicon alloy
5. 5xxx-aluminium-magnesium alloy
6. 6xxx-aluminium-magnesium-silicon alloy
7. 7xxx-aluminium-zinc alloy
8. 8xxx-aluminium-lithium-tin, characterizing miscellaneous composition

Some of these alloys are heat treatable that can be hardened by controlled cycle of heating and cooling.

The four-digit designation of aluminium alloys is usually accompanied by any of the following four letters: F, O, W and T. The extension of F stands for fabrication, O for annealed, W for solution heat treated and T for heated treated to stable temper condition other than O or F.

- T3- solution heat treated, cold worked and naturally aged,
- T4-sloution heat treated and naturally aged
- T6-solution heat treated and artificially aged

- T7-solution heat treated and over aged
- T8-solution heat treated, cold worked and artificially aged.

For example: 2024-T3 is an aluminium-copper alloy, fourth in the 2xxx series, which is solution, cold worked and naturally aged.

AA2024-T351[30]

This is one of the aluminium alloys which has poor corrosion resistance property. Generally, it is used in application requiring high strength to weight ratio and good fatigue resistance application. The machinability is quite average and weldable only through friction welding. T351 tempered has an ultimate tensile strength of 470 MPa and yield strength of 280 MPa. It has elongation of 20%

AA7075-T651[31]

This alloy has significantly better corrosion resistance than the 2xxx alloys. T651 tempered 7075 alloy has an ultimate tensile strength of 570 MPa and yield Strength of 500 MPa. It also has failure elongation of 3-9% but these properties can change depending on the forms of material used.

AA6082-T651 [32]

This alloy has good corrosion resistance compared to other alloys because of this it is used in many commercial applications. It also has high strength and low ductility. The density is 2.71 g/cm^3, Young's modulus 71 GPa, yield straight 280 MPa and thermal expansion is around 23.1 m-K

3.1.1 Application

Alloy	**Application of alloys used in this thesis** [33]
AA2024	For high strength application like aircraft and spacecraft structure, truck wheels, pistons, recreation equipment's and rivets
AA7075	For aircraft and other applications requiring highest strength. Alclad 7075 combines the strength and advantages of AA7075 with corrosion resisting properties of commercially pre aluminium-clad surface. Further, this AA7075 is also used in satellites for clamping hardware's as shown in Figure 1

AA6082	Good formability, weldability, corrosion resistance and strength in T- tempers. Used for chemical equipment's, rail roads, general sheet metal, hospital and medical equipments, building products, fasteners, architectural application, Used in pipe railings, trucks and trailers, highway signs, marine applications, recreational vehicles, machine parts, satellite radiators

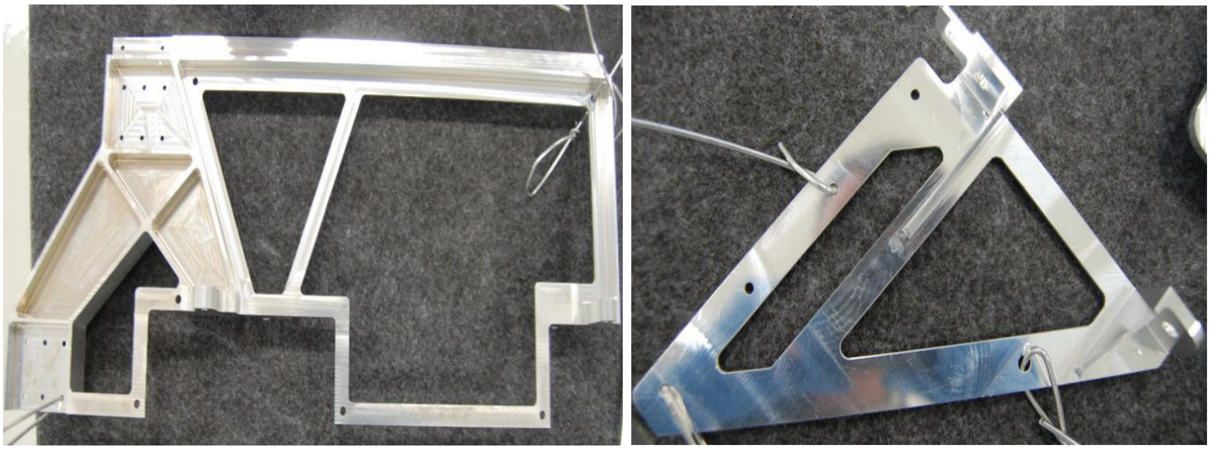


Figure 1. Sentinel-2, satellite hardware's manufactured using aluminium alloys (left: AA6082 and right: AA7075)

3.2 Coatings

Coatings are liquid, paste or powder layers that are applied to the surface of any materials by various methods and equipment's of given thickness. The typical coating systems as shown in Figure 2 forms an adherent film on the surface of the substrate [34]. The process of formation of this type of protective film can occur either physically or chemically. The physical film formation is often associated with drying procedure where there is an evaporation of organic solvents or water. Chemical film formation is often involving chemical reaction between the components. The chemical film formation is also referred as surface treatment process.

The surface treatment process can be divided into two main groups related to process technology and the chemical nature of the involved compounds [35].

- Electrochemical and chemical plating
- Physical vapour deposition
- Chemical vapour deposition
- Ion implantation
- Organic coating (Paints)

- Hot dipping galvanising
- Coating based on diffusion process

These coatings must fulfil many requirements. They must protect the substrate against corrosion, weathering, and mechanical damage. It is also used for decorative purposes in automotive and household applications.

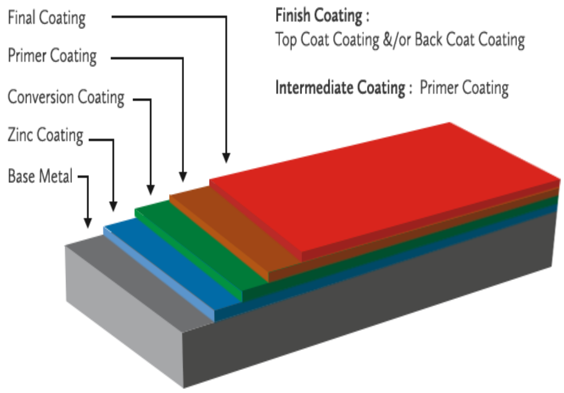


Figure 2. Schematic representation of a coating system used for industrial and general purposes

3.3 Selection of coating

The main task of any coating is to protect the underlying substrates from corrosive atmosphere. The coating must isolate metal from contact with the external surrounding. The selection of coating metal and its thickness is fundamentally decided by the service life of the required coatings [36]. The selection and application of maintenance coating is more complicated than its initial procedures. Climatic condition, chemical exposure, available time, budged, health, safety and the grade of surface preparation does influence on the planning of optimum coating section [37].

Oil/gas industries, faces an escalating number of challenges in terms of corrosion protection. In the Danish part of the North Sea many oil fields have reached an age at which the oil reserves are limited. In this case, the produced liquids consist primarily of sea water with small content of oil. The large content of sea water results in corrosion of production facilities and may entail to complete shutdown of production facilities. Corrosion in oil production plants can be controlled by upgrading to more corrosion resistance material like stainless steel or nickel alloys or the corrosive environment can be treated with corrosion inhibitors like epoxy coatings.

However, for the commercial applications like automobile, household and space traditional conversion coatings are more reasonable due to price and life expectancy of metals. Among several metallic coatings chromate-based conversion is still popular surface treatment method mostly for their unmatched corrosion resistance mainly on components coated by zinc, cadmium, aluminium and its alloy product [38].

3.4 Conversion coating

Conversion coating can be characterized as a chemical process where the surface of metal dissolves and reacts with the surrounding solution to form a new surface film that consists of a non-soluble metal compounds. This conversion process can be driven by external current or purely by chemical method [35]. The most widely used conversion coating in aerospace industries is the chromate conversion coating under trade name Alodine from Henkel Corp. or SurTec 650 from SurTec Corp. [5]. Chromate conversion coating means chromating the surface of metal substrate that provides good corrosion resistance, durability and exhibits stable electrical conductivity [39]. The chromate conversion coating can be divided into two types hexavalent (Cr6) and trivalent (Cr3) chromate conversion coating. This chromate conversion coating enhances the adhesion of paint and provides the metallic surface with good decorative finishes. Mostly conversion process is used mainly for aluminium and its alloys. However, it is also used to coat zinc, steel, magnesium, cadmium, copper, tin, silver and other metallic substrates. The conversion coatings are most frequently applied by immersion or spraying.

Hexavalent chromate conversion coating bath consist of solutions containing hexavalent chromium, fluorides and other components. The coating process results in the formation of an amorphous protective coating composed of the substrate complex chromium components from the processing bath. The hexavalent chromium coating as shown in Figure 3 provides stable corrosion protection on aluminium alloys lasting for 1400 h in neutral salt spray test according to ASTM B117 [14]. Because of this strong and major reason, it has been used in several industrial applications like wheel rims, roof sacks, fasteners etc.

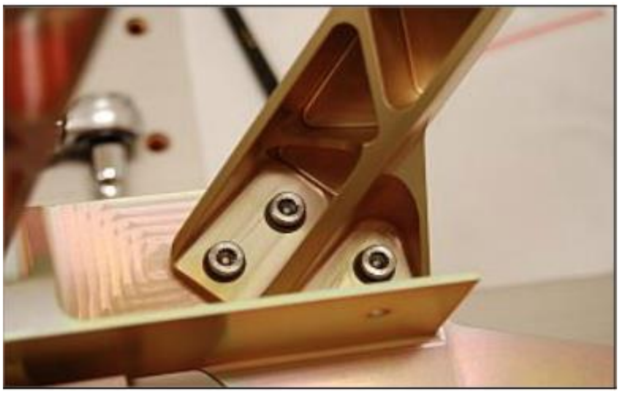


Figure 3. Hexavalent chromium coated AA6082 sentinel-2 diffusor screen by conversion process

3.4.1 Environmental and safety concerns

The proven carcinogenicity, mutagenicity and toxicity of Cr6 compounds had led to strong limitation in its usage. This component has been prohibited for electronic and various other industrial applications by REACH and RoSH regulation. Published investigations proves that hexavalent chromium species dissolves in the human perspiration [40].

It has been assumed that individual Cr6 and Cr3 species is not harmful, however in the presence of biological reducing agents the Cr6 reacts forming metastable reactive Cr5/Cr4 species and other components damaging the DNA molecules. The mechanism of toxicity is also discussed in some reports, stating that the precomplexes with Cr6 are very reactive and could penetrate through cell membrane. Highly reactive Cr6 can be stabilized in human body by common hydrocarboxylic acid group [41].

Relating to the issues mentioned above ‘‘The EU regulations No. 348/2013 from 4/17/2013, affecting the appendix XIV of the regulation of European Parliament and Council number 1907/2006 about registration, evaluation, authorization and limitation of chemical substances, production of inorganic compounds with Cr6 such as chromium trioxide, ammonium dichromate and other is required to be authorized by European chemical agency, this authorization is charged. Further the production of these components is considered illegal after certain date’’ [2][38].

In current days, there are several ongoing researches carried out both in industry and scientific community for an ecofriendly replacement. Among potential alternatives, Zr4/Cr3 showed some success. Due to restrictions, Cr6 usage in automobile industries had been replaced by Zr4 based Cr3 conversion coatings. Hexavalent chromating is no longer used in electrical engineering industries. However, it still being used in military and aerospace industrial application for aluminium alloys. The recent publications by NASA, ESA, ISRO and small scale industries like Tiger, Admatis etc. showed zirconium based trivalent chromium conversion coating can be used for space application [42].

3.5 Zr4/Cr3 based conversion coating

Recent developments are focused on Zr4/Cr3 based conversion coating due to its better performance in comparison to the traditional hexavalent chromate coating [5]. The NAVIAR has developed a zirconium based trivalent chromium coating that exhibits corrosion protection lasting for more than two weeks in a neutral salt spray chamber [43]. This coating is based on SURTEC 650, one of the leading commercially available non chromated conversion coatings in the market. Several research papers were published based on this SurTec 650 RTU Zr4/Cr3 conversion coating solution from various industries and research institutes. This coating bath generally consists of zirconium and trivalent chromium fluoride salts [44].

The coating formed over metal substrate as shown in Figure 4 consists of two main layers. The outer layer which constitutes most of the coating thickness consist of AlF_3, Al_2O_3, Cr $(OH)_3$, CrF_3, ZrO_2 ,$Cr_2(SO)_4$ and ZrF_4.The inner layer is aluminium rich with the presence of oxide and fluoride species [7].

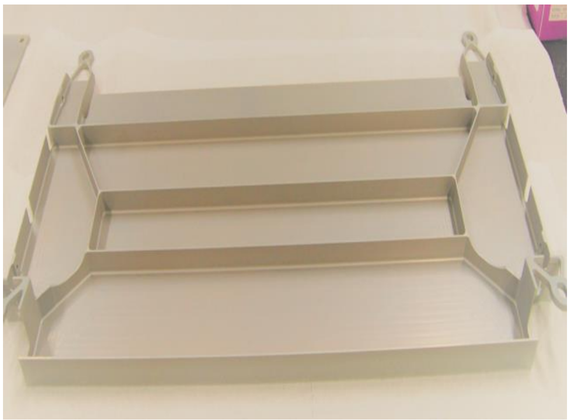


Figure 4. Zirconium based trivalent chromium conversion coated telescopic baffle of sentinel-2

3.6 Metal Surface Pretreatments

The most common reason for pretreatment of material before surface finishing process is to prepare the surfaces for subsequent surface modification [35]. This procedure is applicable to all the surface treatment process. The initial pretreatments, as listed in Figure 5 are to remove organic and inorganic contamination from the surface of the material. In case of metals the pretreatments are normally based on immersion or spray cleaning with alkaline and acid formulations. Considering conversion coating the surface treatments usually comprises of etching and desmutting.

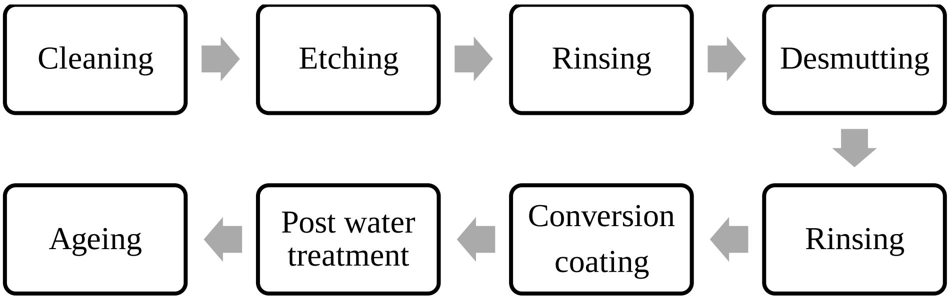


Figure 5. Steps involved in the process of conversion coating

Understanding the mechanics of each procedure for certain substrate can help us in guiding the selection of an appropriate chemicals to implement in the conversion process. Certain industrial application like electronics and high-level space vacuum implementation required complicated technical cleaning procedure far above than the normal requirements for industrial use.

3.6.1 Cleaning

Cleaning is a process of removing soil or any contamination from surface of samples before conversion process. The selection process for cleaning procedures involves several factors. The size and shape of the work piece establish the cleaning procedure, equipments size and handling techniques involved.

- The nature of contamination
- The substrate to be cleaned
- The degree of cleanliness required
- Cost consideration and total surface area to be cleaned
- Surface requirements of subsequent operation such as paint or plating.

Apart from these, selections of cleaning process also involve consideration of subsequent operations to be performed. Abrasive blasting produces the lowest degree of cleanliness. Solvent, solvent vapour degreasing, emulsion soak, alkaline soak, alkaline electro cleaning, alkaline plus acid cleaning and ultrasonic cleaning procedures makes surface cleaner [45].

3.6.2 Ultrasonic cleaning

Ultrasonic cleaning makes use of cavitation in an aqueous solution for better cleaning effectiveness. This is the most appropriate method used in industries that eliminates the need for the use of stronger and harmful solvents for cleaning.

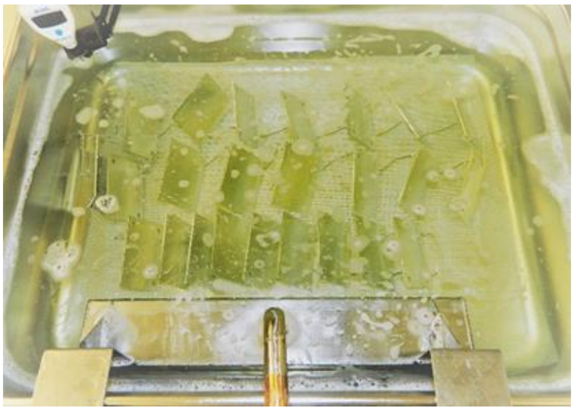


Figure 6. Surface of sample cleaned by ultrasonic cleaning

The ultrasonic cleaning uses high frequency sound wave in the cleaning liquid solution. These sound waves generate low and high-pressure zones throughout the liquids. In the zones of negative pressure, there is a decrease in boiling points and formation of microscopic vacuum bubbles. The sound waves that move in this same zone becomes positive pressure there by causing the bubbles to implode. This is basic principle that ultrasonic cleaning works on and it is known as cavitation. Over all, the pressure and temperature loosen contaminants and perform the actual scrubbing of ultrasonic cleaning process. In ultrasonic bath, the energy is usually produced by transducer as shown in Figure 6 which converts electrical energy to mechanical energy. The number and position of immersible transducers are determined by the actual size and configuration of the parts, size of the batch and size of the tank [46] .

3.6.3 Electropolishing

In certain cases, cleaning also includes electropolishing due to high surface roughness of material. Electropolishing is an electrochemical process that involves in removal of metal impurities including carbon, silica and frees other free particles from the surface of metals.

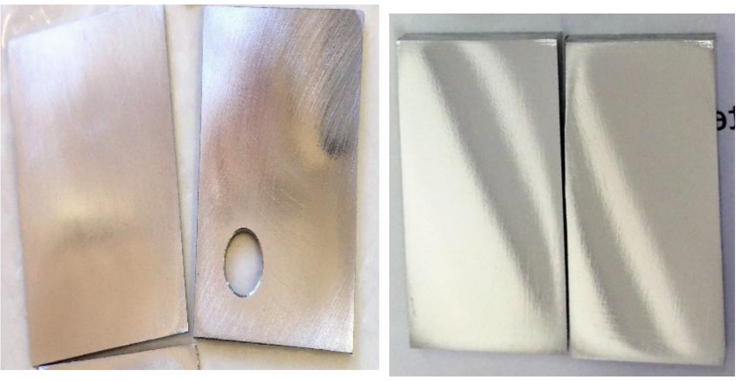


Figure 7.Metal surface of AA6082 aluminium alloys before (left) and after (right) electropolishing

In electropolishing anodic dissolution removes the surface materials. The process of removing the surface of material begins with the high points with the microscopic surface texture. By removing these points, the electropolishing process will improve the surface finishing leaving a smoother and more reflective surface as shown in Figure 7. The basic criterion for electropolishing is the difference in current density across surfaces. The current density is observed to be greater at the high points and lesser at the low points within the surface profile. The rate of electropolishing is directly proportional to the current density [47]. The increased current density at the raised points force the metal to dissolve faster at that points thus tends to level the surface of the metal. In general, after the process of electropolishing the metals will be neutralized, rinsed, cleaned and dried.

The goal of this process is to devoid of burrs or cervices that attract traps contamination. This process also improves the near surface chemistry of the material and promotes the formation of an improved corrosion resistant surface layer. This type of cleaning procedure is involved in metal finishing industrial applications such as stainless steel surgical devices, copper semiconductors etc. In the scientific research electropolishing is commonly used in sample preparation techniques, so that mechanical deformation of surface layers is not observed under scanning microscopic devices.

3.6.4 Etching

Aluminium when exposed to normal atmospheric condition is highly resistant to change and degradation due to the presence of thin and protective layer of aluminium oxide over the surface [27]. When surface of metal is exposed to atmospheric oxygen it forms aluminium oxide through the oxidation process. It is necessary to remove oxide layer before any surface treatment procedure termed as etching. It is usually done with either alkaline or acid solutions [48]. The etching process is usually used an intermediate step in the conversion process. The advantage of etching is that in addition to removal of oxide layer it also eliminates surface scratches, nicks and other imperfections. Alkaline is mostly used for industrial applications. An alkaline etching, etches the surface alloy depending on the alkalinity of the solution and the immersion time. In case of aluminium metal, this method removes the surface oxide layer leaving behind more noble metals such as copper.

Alkaline Etching

Alkaline etching can be carried out in several solutions, but the cheapest and simplest form is alkaline solution based on caustic soda. When aluminium is immersed in hot caustic soda the surface is progressively dissolved to form a finish, that is microscopically roughened with development of small pits or depression [33]. Usually the alkaline etching solution is modified with nitrates, fluorides, wetting agents etc. to achieve required etching action.

Disadvantage

In certain types of aluminium alloy a dark grey deposit would be formed on the surface as shown in Figure 8 after etching in alkaline solution. This is because of the silicon and copper content of the alloy [33]. So alkaline etching is not recommended in certain type of alloys, for example AA2024. It also requires desmutting especially for the aluminium alloys. Thus, increases the overall cost of coating procedure.

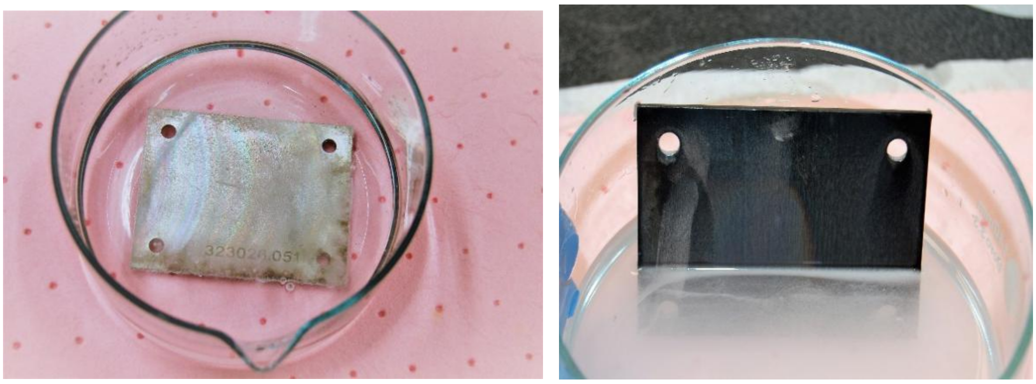


Figure 8. Alkaline etching of AA7075 using NaOH solution at room temperature (left), etched sample with residues over surface after removal of oxide layer (right)

Acid Etching

Acid etching is also an effective way of etching aluminium alloy. Due to its greater cost, acid etching is not so frequently used in industries .Acid treatment is effective in certain types of aluminium alloys that has high copper and zinc constituents [45]. Most commonly used acids for etching are hydrochloric, hydrofluoric, nitric, phosphoric, chromic, and sulphuric acids.

The combination of these acids with the mixture of other salts are often used for specific applications [49]. The acid etching is often used alone but sometimes it may either precede or followed by alkaline etching. In most of the case acid etching solution especially those containing fluorides are excellent for smut and scale removal. After acid etching and rinsing the samples are ready for further processing which is one of the main advantage of acid etching process.

3.6.5 Desmutting

The elimination of oxide layer from aluminium alloys leave residues over surface of metal. Thus, alloy surface must be reconstructed for proper adhesion of conversion coating. The acidic desmutting that might include several acid baths including sulfuric acid, nitric acid and hydrofluoric acid. The sulfuric acid is less aggressive than other two acids, so it might require high operating parameters. The bath can be used as mixtures with combination of halogens which determines the surface reactivity and deoxidizing rate.

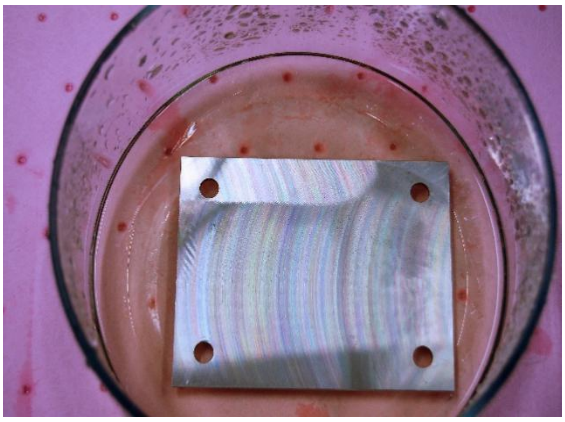


Figure 9. Desmutting of etched AA7075 alloy using H_2SO_4 at room temperature

3.6.6 Post water immersion

The post water immersion means the coated samples are immersed in deionized water for few seconds at desired temperature and pH to achieve the better coating morphology and corrosion protection. The post water treatment in the deionized water bath can replace normal rinsing process it is expected to play a similar role in stabilizing the coatings. In case of the Zr4/Cr3 based conversion coating the post water treatment as shown in Figure 10 makes considerable shrinkage in coating that makes coating better in corrosion protection.

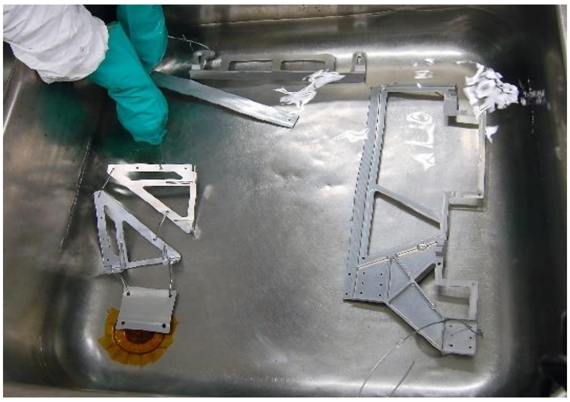


Figure 10. Post water immersion procedure for Zr4 based chromium conversion coated AA6082 sentinel-2 hardware's

3.6.7 Ageing

The ageing is one of the most crucial steps in the conversion coating procedure. The ageing process means samples are dried for certain time to obtain the proper coating structure. The effects of ageing have not been studied in detail. This is a whole new process under which the trivalent chromium coating system shows some changes in physical properties of coating after certain time period. The water contact angle of the test shows some significant change occurs during ageing process. It has been predicted that coating undergoes dehydration during this process.

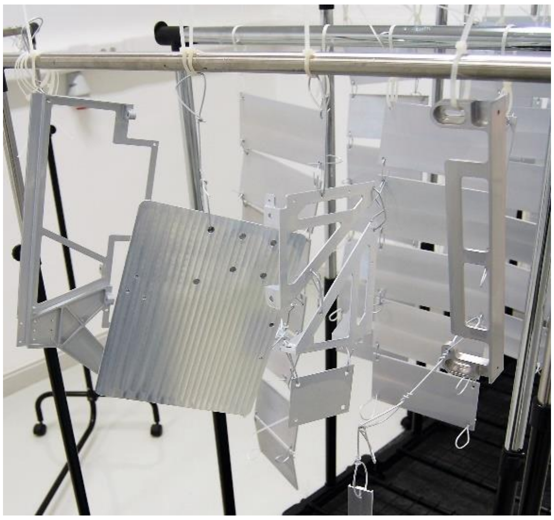


Figure 11. Ageing process for Zr4 based Cr3 coating over AA6082, Sentinel – 2 hardware

3.7 SurTec 650 RTU

3.7.1 Properties of SurTec 650 RTU

SurTec 650 RTU is a hexavalent chromium free solution used for passivation of aluminium and its alloys. The alloys can be coated either by spray or wipe process. The viscosity of solution is adjusted by manufactures for better and longer moistening. The final coating that is formed can bare excellent corrosion protection that is comparable to hexavalent passivation. This coating procedure generally requires pre-treatments. The end products result in an iridescent, faintly blue to tan and visible layer. This zirconium based trivalent coating formed over aluminium alloys using this SurTec 650 RTU can withstand heat up to 100˚C with minimum loss in corrosion resistance [44].

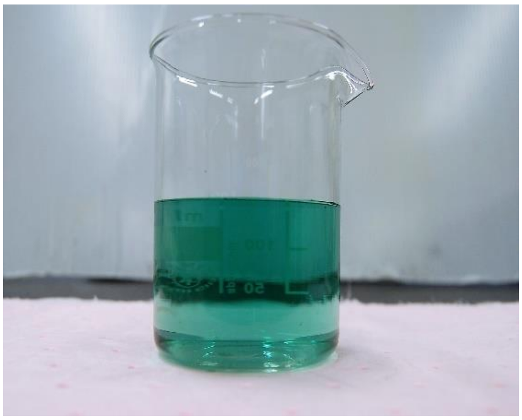


Figure 12. SurTec 650 RTU solution

3.7.2 Physical and chemical properties of SurTec 650 RTU

State	liquid
Color	Pale green
Odour	Barely perceptible odour
Solubility in water	Miscible
Boiling point/range	100˚C
Melting point/range	0˚C
Relative density	1.003 g/ml
pH	3.3

3.7.3 Composition of SurTec 650 RTU

The acidic aqueous solution of this chemical comprises of several salts per litre of water. Usually about 3 to 22 grams of water soluble basic trivalent chromium salts and preferable from 3 to 12 grams of other chromium salts. This solution also contains 6 to 8 grams of an alkali hexaflurozirconate. Further, it also includes 1 to 10 grams of water soluble thickener. The preferred chromium components are incorporated in the solution in form of $Cr_2(SO_4)_3$,

$(NH_4)Cr(SO_4)_2$ or $KCr(SO_4)_2$ and mixture of these compounds. The SurTec 650 RTU is composed based on the US patent 6,375,761 B1 that is attached in appendix.

3.8 Sol-gel Science

Definitions

A colloid is a micro-heterogeneous systems containing at least two phases a dispersion media and a dispersed phase. The wide range of solid-liquid and/or liquid-liquid mixtures is described as collides. Under colloidal science, a sol termed as a colloidal suspension of a solid particles in liquid. An aerosol is a colloidal suspension of particles in a gas and an emulsion is a suspension of liquid droplets in another liquid [50]. As interpretation from various definitions, gel can be considered as a state that consist of continuous solid and fluid phase of a colloidal dimension.

In general, the sol (or solution) evolves gradually towards the formation of gel like network containing both liquid and solid phase [51]. According to the basics of gel, if one molecule reaches macroscopic dimensions so that it extends throughout the solution, the substance is said to be gel. The time or degree of reaction at which the last bond is formed that completes this giant molecule is known as gel point. Thus, gel can also be defined as a substance that contains a continuous solid skeleton enclosing a continue liquid phase. The formation of gel can also occur via particulate sols, when attractive dispersion forces cause them to stick together in such a way as to form a network. The gel can have several types of bond, so it cannot be characterised by its bond for example, polymeric gel is covalently linked, gelatine gels were formed by entanglement of chains and particulate gels are established by Van der Waals forces. The gel is classified into five different types such as colloidal, metaloxane polymer, metal complex, coordinating and crosslinking's polymers and insight polymerizable complex [52].

Sol-Gel Process

There are several examples in literature for sol gel process under preparation of metal oxides and other materials. In these methods, the reactants undergo chemical reactions that convert from sol into solid particles with diameter of 1-100 nm. In colloidal science, this process is defined as drying where sol react with each other to form a continuous macromolecule gel that entraps both solvents and reactants [53]. For example, preparation of alumina is a popular research that has numerous publications. Neglecting the methods of preparation, this reaction is a multistep process that involves the transformation of the aluminium alkoxide to aluminium hydroxide with dehydration of AlO(OH) in the sol-gel process [54].

4 EXPERIMENTAL SECTIONS

4.1 Sample preparation

Table 1. Elemental composition of investigated alloys

Wt. %	Zn	V	Ti	Sn	Si	Pb	Ni	Mn	Mg	Ga	Fe	Cu	Cr	Bi	Al
AA6082	0.01	0.01	0.01	0.007	1.09	0.003	0.005	0.17	0.99	0.008	0.237	0.092	0.008	0.002	96.7
AA7075	5.87	0.009	0.03	0.002	0.07	0.001	0.004	0.011	2.55	0.014	0.009	1.85	0.19	0.005	89.3
AA2024	0.06	0.004	0.05	0.006	0.09	0.003	0.005	0.55	1.63	0.01	0.18	4.86	0.01	0.004	92.7

The elemental composition of metal samples was determined by ICP-OES as mentioned in Table 1. The samples were obtained as 10x10 mm sheets with 4 mm thickness. The received specimens were initially cleaned with detergent and rinsed with isopropyl alcohol, ethanol, and acetone for few seconds. Mechanical polishing modified the surface of samples up to 800 grid finishes and then it was electro polished using Struers electrolyte A2 I and II 50 v/v% at 20 V for 60 s around 25^{o}C followed by rinsing using DI water, ethanol and drying in cool air stream. The degreased samples were etched with 5 v/v% of NaOH for 180 s and desmutted with H_2SO_4 solution of 17 v/v% for 180 s. Both pre-treatments were carried out at room temperature. The samples were thoroughly rinsed using deionised water after each pre-treatment.

Zr4/Cr3 conversion parameters:

1. Sample Preparation: Elemental analysis of Zr4/Cr3 based conversion coating	
Alloy used	Etched and desmutted AA6082
Solution	SurTec 650
pH	3.8
Temperature	40 ˚C

Immersion time	600 s
Rinsing	Deionised water at room temperature
Drying	24 h before measurement
Instrument used	SNMS

2. Sample Preparation: Coating structure by exposure to vacuum	
Alloy used	Etched and desmutted AA6082
Solution	SurTec 650
pH	3.8
Temperature	40 ˚C
Immersion time	180 s
Rinsing	Deionised water at room temperature
Drying	24 h before measurement
Vacuum exposure	2 h at 10^{-7} mbar
Instrument used	GD-OES and SNMS
The coating over AA6082 exhibits high coating thickness compared to other two alloys, so this alloy was opted to study the structure.	

3. Sample Preparation: Effect of alloying elements in substrate during conversion process	
Alloy used	Etched and desmutted AA6082 and AA2024
Solution	SurTec 650
pH	3.8
Temperature	40 ˚C
Immersion time	300 s
Rinsing	Deionised water at room temperature
Drying	24 h before measurement
Instrument used	GD-OES

4. Sample Preparation: Ageing effect

Alloy used	Etched and desmutted AA6082 and AA7075
Solution	SurTec 650
pH	3.8
Temperature	40 ˚C
Immersion time	180 s
Rinsing	Deionised water at room temperature
Drying	24 h before measurement labelled as ‘‘Fresh’’
	168 h before measurement labelled as ‘‘Aged’’
Instrument used	SNMS
Some of the experimental results proved that ageing improves the corrosion resistance property of coating over AA7075 [55], so the coating over AA6082 and AA7075 alloys was studied to understand the elemental level changes during ageing process.	

5. Sample Preparation: Growth Kinetics of the coating	
Alloy used	Etched and desmutted AA6082
Solution	SurTec 650
pH	3.8
Temperature	40 ˚C
Immersion timings	60, 300, 600, 720, 1440, 1920, 2280 s
Rinsing	Deionised water, room temperature
Drying	24 h before measurement
Instrument used	GD-OES
As mentioned in Table 2 (pg.no 45), AA6082 has high coating thickness compared to other alloys so this alloy was opted to study the growth kinetics	

4.2 Secondary Neutral Mass Spectroscopy (SNMS)

Elemental depth profile of coatings on various substrates was performed by an INA-X (SPECS GmbH Berlin) type SNMS system at ATOMKI in Debrecen, Hungary. SNMS is a unique thin film analysis method utilizing post ionisation. The post ionisation medium increases the probability of ionization of neutral particles sputtered from the sample surface. The INX-A device uses Electron Cyclotron Wave Resonance (ECWR) plasma as ion source and post ionization medium with sputtering energies of a few 100 eV. The system is equipped with a quadrupole type mass spectrometer up to 340 AMU for detecting elements. Basically, samples were bombarded and post ionized using an inductively coupled low pressure radio frequency Ar discharge. The Ar ions were extracted from the plasma to sputter the sample surface with a high frequency negative bias on the sample. Energy dispersive ion optics then identified residual ions. The bombarding energy of Ar ions over coated sample was around 350 eV with plasma pressure of 1.5 mbar. The elemental composition of the coating was determined using sensitivity factors of the constituents. The sputtering time was converted in to a depth by calibration of sputtering rates with a profilometer and taking in to account sputtering yield changes during profiling with changes in the layer density [56]. The depth scale was fixed by accepting the nominal surface roughness of the sample before and after measurements.

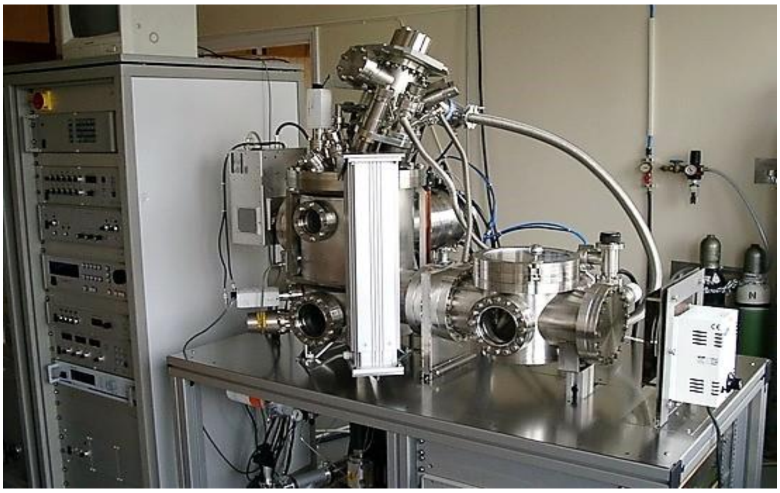


Figure 13. SNMS devices at ATOMKI, Debrecen- Hungary

Almost all ions from the chromating bath and the substrate are somehow involved in the formation of layer. For this analysis, we concluded that oxygen, aluminium, chromium, and zirconium are the main building element of the layer because there was no peak for alloying elements like zinc, magnesium, silicon, iron, copper, and manganese were observed.

Features of the SNMS method with electron gas post ionization

- Simple and reliable quantification
- High sensitivity
- High depth resolution in the nm region
- Time efficient depth profile analysis.

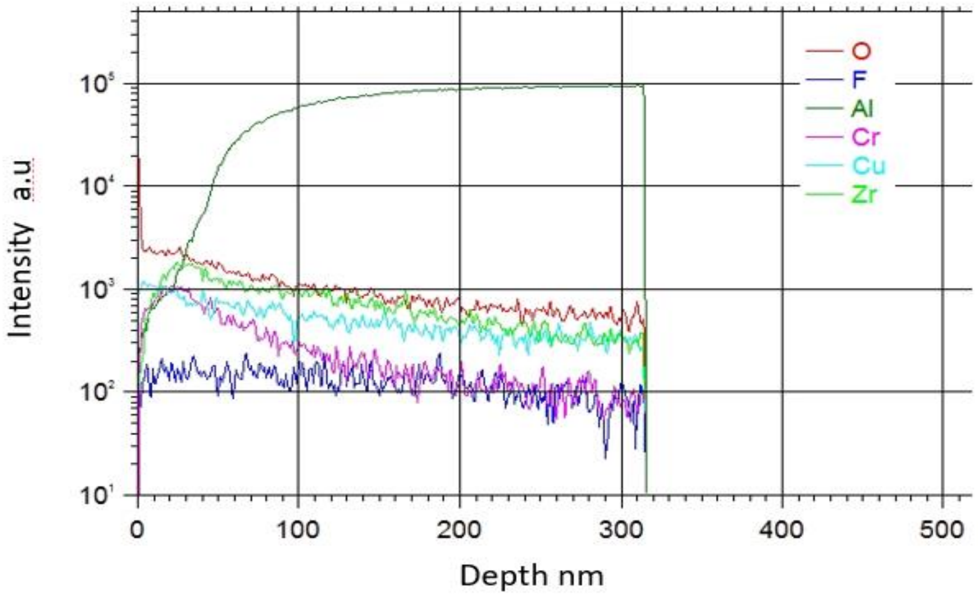


Figure 14. Raw data from SNMS obtained by depth profiling of coating over AA7075

4.3 Glow Discharge Optical Emission Spectroscopy (GD-OES)

The GD-OES is a sophisticated technique for analysing thin film owing to its unique combination of fast sputtering rate, high depth resolution, excellent sensitivity and multielemental capability. In this technique, cathodic sputtering is used to remove layer by layer from the surface of sample. The glow discharge source is filled with an argon gas under low pressure (0.5 to 10 hPa). The atoms removed from the surface undergoes inelastic collusion, the electrons transfer their kinetic energy to argon atoms that cause them to dissociate into argon cations and further electron, this mixture is called plasma [57]. The characteristic spectrum emitted by the excited atoms is measured by spectrometer. The intensity is recorded as function of time. Based on sputtering depth on the measured sample measured using surface profilometer the sputtering time is transformed in to quantitative content depth profile.

Figure 15. GD-OES device at University of Miskolc, Miskolc- Hungary

The elemental analysis was done by GD-profile instrument with copper anode of 4 mm diameter. With a flushing time of 30 s, a pre-integration time of 30 s, a background of 5 s, a pressure of 635 Pa, a power of 35, a module of 7.2 and a phase of 4 V. The emission line used for this analysis were 396.157 nm for Al, 324.759 nm for Cu, 383.834 nm for Mg, 339.230 nm for Zr, 452.439 nm for Cr, and 130.223 nm for O. The obtained results were analysed neglecting the effects of contamination, surface roughness, variation in sputtering rate of each element. All numerical values that represents the coating thickness have been consider with ~ ± 20 nm.

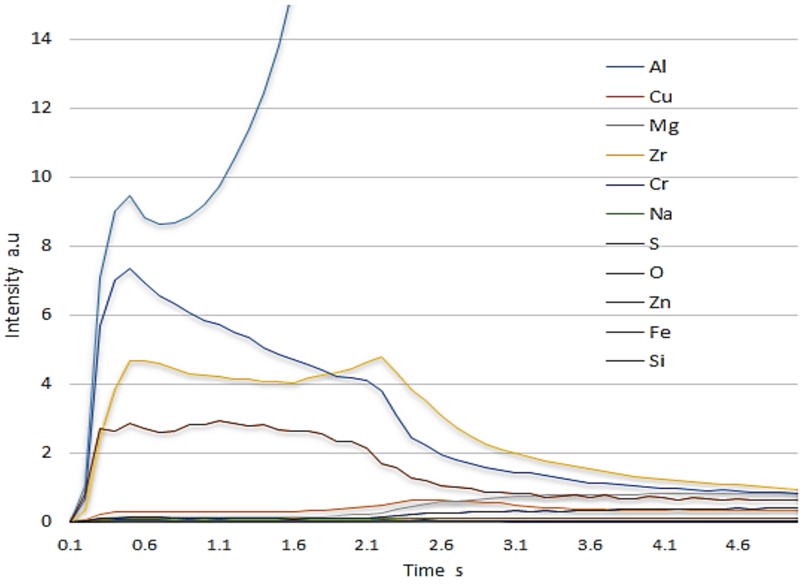


Figure 16. Raw data obtained from GD-OES by depth profiling of coating over AA2024

5 RESULTS AND DISCUSSION

5.1 Elemental analysis of coated sample using SNMS

Almost all the ions that is suspected to be present in the coating region were investigated by the SNMS. Figure 17 represents intensity vs atomic mass of elements detected from the coating. The graph indicates ions from both the coating and the substrate. The intensity on the y axis represents an approximate quantity of the ions in arbitrary unit. The carbon (12.0), oxygen (15.9), sodium (22.9), aluminium (26.9), silicon (28.0), sulphur (32), chromium (51.9), manganese (54.9), copper (63.5), zirconium (91) ions that were identified from the coated AA6082. This graph also indicates the concentration of Zr could be higher compared to Cr in the coating. Neglecting the ions from the substrate, we have concluded that zirconium, chromium, oxygen and aluminium are the major ions that exists in coating. The presence of carbon is possibly due to contamination from the vacuum chamber or mass spectrometer of SNMS device.

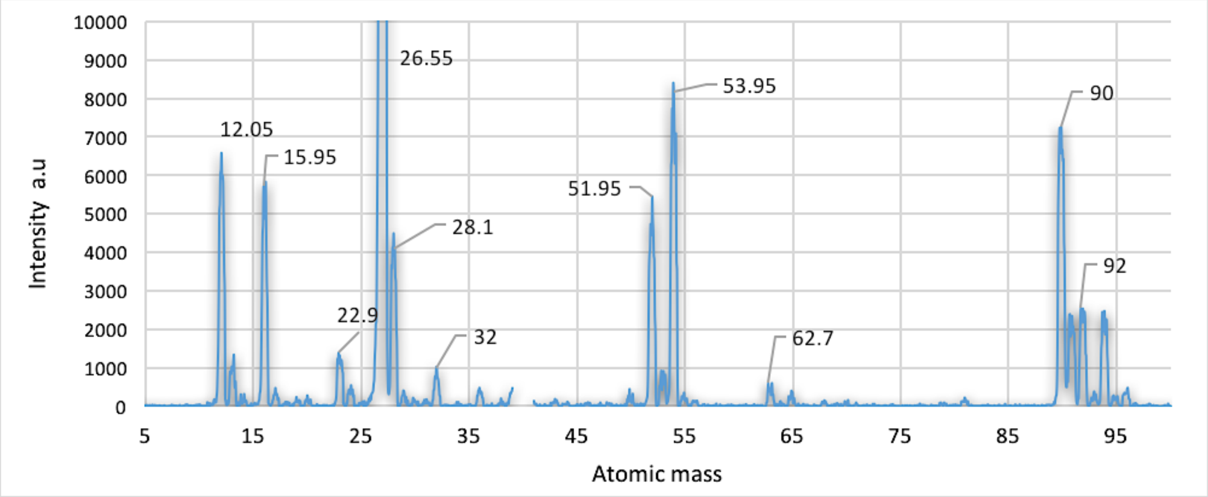


Figure 17. Elemental analysis of coated AA6082 using SNMS

However, some published journal papers states that fluoride ions does influence the formation mechanism of this coating over aluminium alloy [10]. In this analysis, we couldn't identify the presence of fluorides both in the substrate and the coating region. The presence of oxygen indicates that most ions in the coating exist in form of oxides. The Figure 17 also indicates that the ions such as potassium and calcium cannot be identified by the SNMS due to usage of argon gas for sputtering of ions from the coating inside the vacuum chamber.

5.2 SNMS depth profile analysis

A typical layer structure of a coated AA6082 alloy is shown in Figure 18. The intensity was measured in arbitrary unit indicating the relative number of detected atoms. As seen in Figure 18, the oxygen content tends to decrease, but it is retained inside the layer. The aluminium curve indicates a different behaviour. On the surface, its value is minimum, but after leaving the layer, a sharp increase is observed up to a maximum, with no further change beyond a depth of 200 nm. The zirconium and chromium curves shows elongated peaks at 30–80 nm depths, with a slow transient towards increasing depths. We interpret these curves up to their peaks to represent the coating area, while the deeper part of the curve is believed to be a phantom segment caused due to surface roughness. The SNMS figures also confirms the absence of a sharp transition between the substrate and the coating. We interpret that the ~0.34 μm surface roughness of the coated samples decreases the depth resolution, thus elongating interfacial regions in the curves.

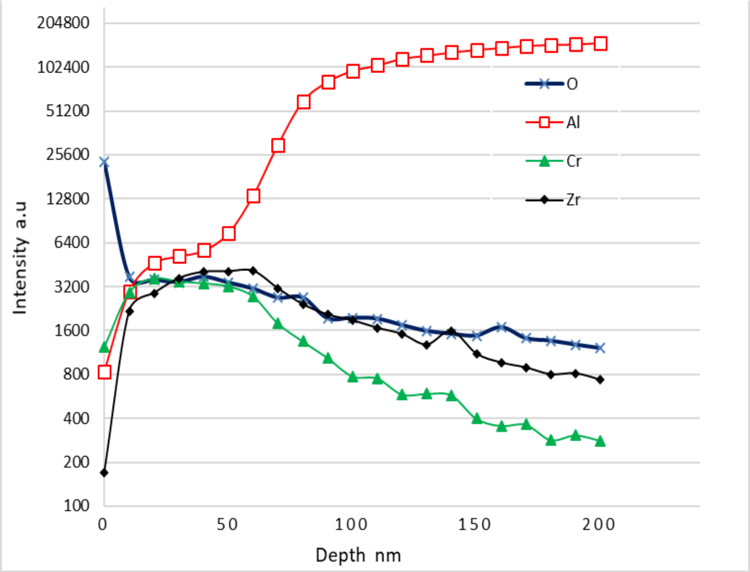


Figure 18. Typical SNMS atomic distribution in coated AA6082 alloy

5.3 GD-OES depth profile analysis

The Figure 19 shows elemental analysis of coating over AA6082 alloy for 600 s immersion time. The first peak in graph indicates the point where the sputtering of coating begins, and second peak represents interface between the coating and the substrate. In this report thickness of the coating was considered as the distance between the two peaks. It is obvious, that our interpretation is approximate since after the second peak around 300 nm there is a decreasing tendency for Zr, Cr and O curves with slight increase in alloying elements such as Mg, Cu. So, we can conclude that the coating thickness of this sample is around 300 nm. It is also observable from the Figure 19 that there is no sharp transition zone possible due to limitation in accuracy of measurement device.

The legend indicates the list of elements used for coating analysis using GD-OES. The ions that does not show any significant variation before second peak is considered as not available in the coating region. The intensity values on Y axis are an arbitrary unit which does not represent the exact elemental composition of coating. Instead of that, shapes of curve are analyzed to detect changes in coating composition. Both the Zr and Cr curve exhibited similar shapes. Because of the slight Cr content in substrates, only Zr distribution curves is considered for the analysis of coating and thickness measurements.

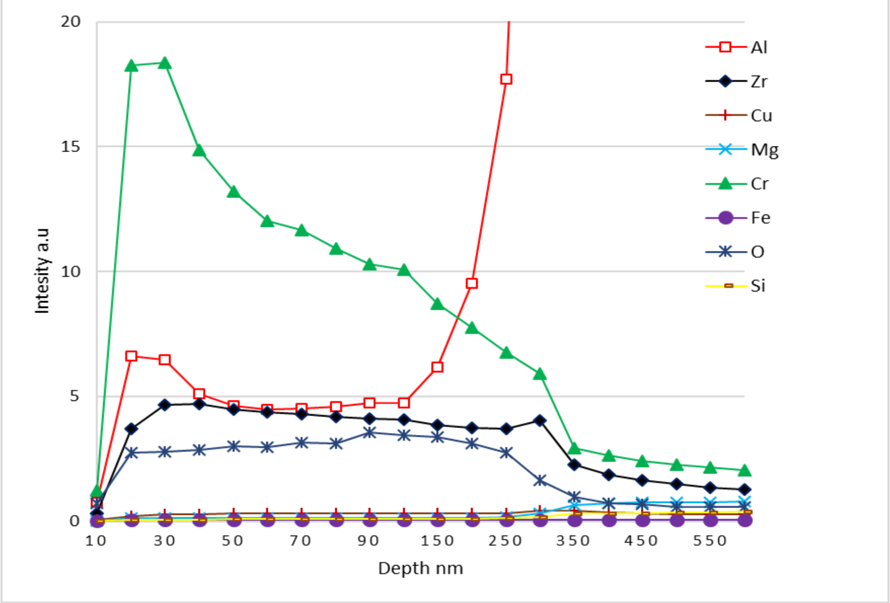


Figure 19. Typical GD-OES atomic distribution in coated AA6082 alloy

5.4 Structure of coating

Figure 20 represents the concentration distributions of Al, Cr, Zr and O ions as a function of sputtering time at fresh state over an AA6082 sample. The Cr and Zr curves have peaks, whereas the O and Al curves show monotonous decreasing or increasing trends. The concentration distribution for another AA6082 sample analysed after high vacuum treatment is shown in Figure 21. Comparing these figures, the O curve does not significantly change, but the Al and Cr curves radically decrease after high vacuum exposure. Interestingly, Zr ions completely disappear from the layer. In addition, layer shrinkage is also apparent after comparing both the figures.

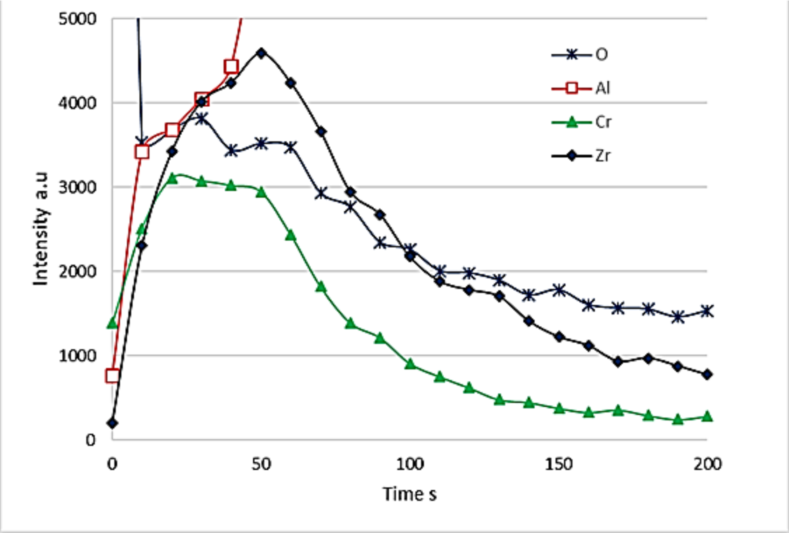


Figure 20. Atomic distribution in a coated AA6082 from SNMS prior to vacuum exposure (sol-gel structure)

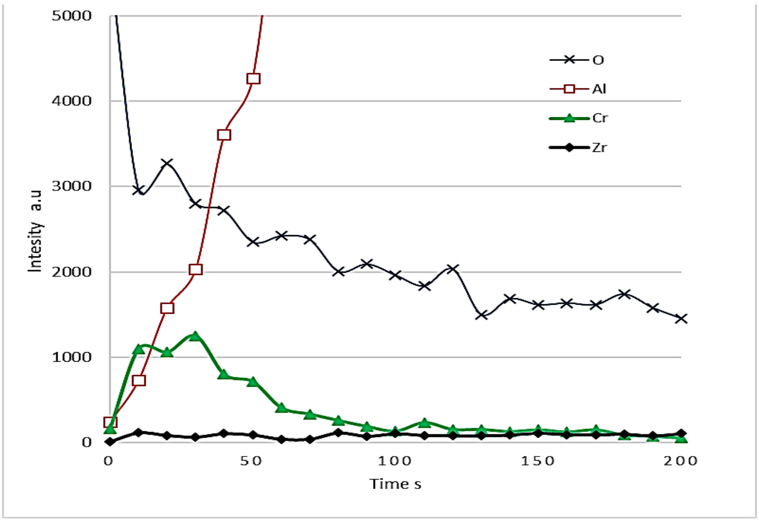


Figure 21. Atomic distribution in a coated AA6082 from SNMS after high vacuum treatment (gel structure)

To interpret these phenomena, we assume that the coating has a two-phase structure. The first phase is the -Al-O-Cr- molecular chain, building a gel-like network. The second is a low-viscosity sol phase, composed of mostly Zr with a few Cr ions from the coating bath and some Al ions from the substrate. This second phase proved to be removable from the network under high vacuum. The layering process seems to follow interesting kinetics. Electron interchange toward Cr ions begins with Al ions near the surface of the substrate, leading to molecular chain growth. Some Al ions from the solute can travel through the filtering network and dissipate in the sol phase. The nature of this sol phase is not fully understood. We assume that the Zr ions are surrounded by hydroxides in a cluster-like behaviour, in which some of the Cr and Al ions are in sol state. In summary, the conversion coating has a two-phase sol-gel structure that is observed after exposure to vacuum. A similar sol-gel effect has been observed from the depth profiling using GD-OES of coated samples that were exposed to high vacuum as explained below.

The Figure 22 shows the distribution of ions in coating that is formed over AA6082 alloy coated for 180 s. The graph represents that O, Cr, and Zr curves has high intensity up to 3 s after which there is a decrement, whereas the aluminium curves has less intensity for first few seconds after which it plummets in to higher. It is also significant from this graph that other alloying elements were not present in the coating region. Interestingly, the same coating over another sample is exposed to high vacuum reveals that there is a slight decrement in Cr, O and Al curves with complete disappearance of the Zr in the coating as shown in Figure 23. Comparing Figure 22 and Figure 23, the disappearance of second peak is probably due to the tremendous shrinkage in the coating after vacuum exposure [58].

We interpret these phenomenal changes by assuming that coating has two different phases as mentioned earlier from SNMS curves. The first is the -Al-Cr-O- phase that is in gel form. The second phase is in low viscosity sol form that mostly consists of Zr ions with smaller amount of Cr and Al ions. This second phase can be removed from the coating by exposure to high vacuum. Based on these results from GD-OES and SNMS curves, we predict a simplified atomic model of Zr4/Cr3 based conversion process in the coating bath.

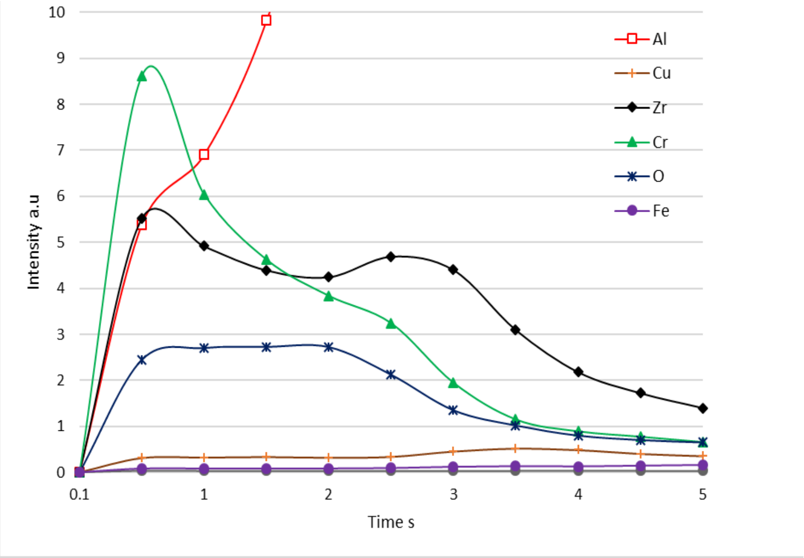


Figure 22. Atomic distribution in a coated AA6082 from GD-OES prior to vacuum exposure (sol-gel structure)

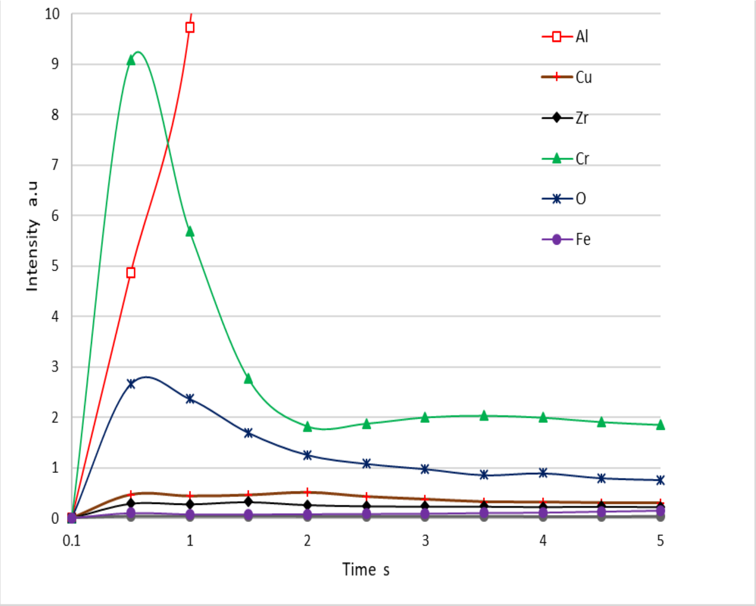


Figure 23. Atomic distribution in a coated AA6082 from GD-OES after high vacuum treatment (gel structure)

5.5 Simplified atomic model

After pre-treatment, the samples were immersed in to the coating bath. Almost all the ions from the substrate and the coating bath is somehow involved in the coating formation process. However, Cr$^{3+,}$ Zr^{4+} ions in the coating bath and Al^{3+} ions from the substrate does a major contribution in the ion exchange process. The slight change in temperature and an appropriate variation in interfacial pH due to the dissolution of aluminium from the metal into Al^{3+} ions as shown in Figure 24 initiates the formation mechanism of coating. This is because Al^{3+} ions are stable in aqueous solution in slightly acidic and slightly alkaline media but not in neutral or nearly neutral media from aluminium Pourbaix diagram [49]. The Zr^{4+} and Cr^{3+} ions already exist inside the coating bath reacts with aluminium ions converts the surface of aluminium alloys into a complex mixture of all the three ions in various forms such as oxides, hydroxides, sulphates, and fluorides [7]. The layering kinetics starts near the surface of aluminium by formation of molecular chain of complex mixture Al, Cr and O components. The Zr^{4+} ions are mostly kept its sol state throughout the conversion process and it is assumed to be surrounded by hydroxides having a cluster like behaviour. Interestingly, some parts of Al filtering through the molecular oxide chain film and dissipated into sol phase. Finally, the detailed information about various chemical reactions that involve in the complete formation mechanism of coating over AA2024 could be obtained from literature [7]. In summary, it is stated that the formation mechanism of Zr4/Cr3 based conversion coating is highly depending on the standard electrode potential of that alloying elements in the substrate. The dissolution of aluminium in to the coating bath determines the formation mechanism of coating and its growth. This dissolution process is decelerated or promoted by the alloying elements in the substrate resulting in layer formation. Figure 24, also represents that the dissolution of aluminium ions is more for AA6082 compared to AA2024

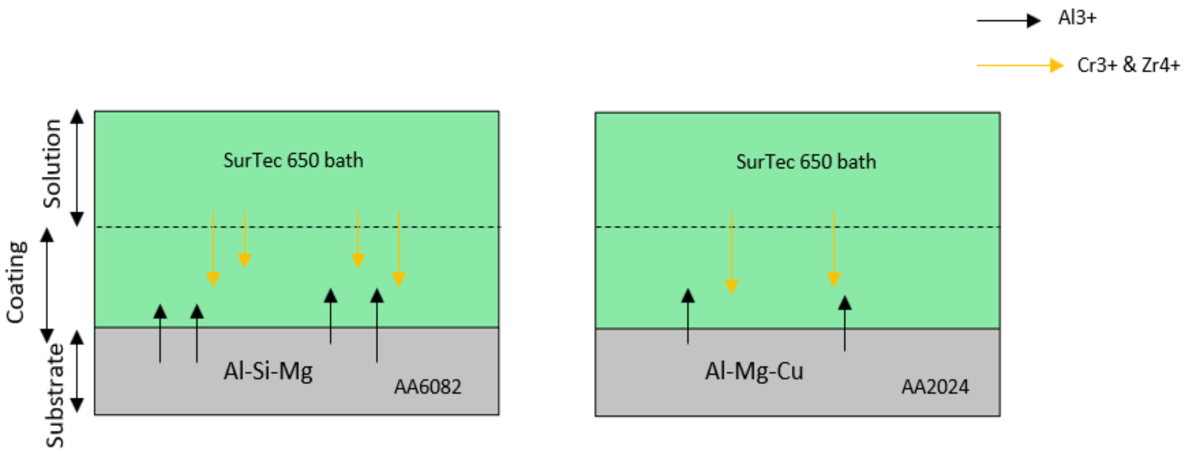


Figure 24. Simplified sketch of conversion process inside coating bath

5.6 Effect of alloying elements in the substrate during conversion process.

To study the effect of alloying elements during the conversion coating a series of coated samples were examined by GD-OES under same experimental parameter. The Figure 26 shows the distribution of aluminium and zirconium in coatings over AA6082 and AA2024 alloys after immersion in to the SurTec 650 bath for 300 s. The graph indicates that under same immersion time, aluminium dissolution is less, and the layer is thinner with less zirconium for AA2024 compared to AA6082. Since AA2024 is highly alloyed by copper ions, we predict that it disturbs the dissolution rate of Al ions. Whereas in case of AA6082, the dissolution rate is high which is the root cause for thicker coating growth under various immersion times. Over all, the dissolution process depends up on the standard reduction potential of ions that is evident from the literature [59].

$$\mathrm{Si} + 6\mathrm{OH}^- \leftrightarrow \mathrm{SiO}_3^{2-} + 4\mathrm{e}^- + 3\mathrm{H}_2\mathrm{O} \qquad \in^0 = -1.697\ \mathrm{V}$$

$$\mathrm{Al} \leftrightarrow \mathrm{Al}^{3+} + 3\mathrm{e}^- \qquad \in^0 = -\,1.662\ \mathrm{V}$$

$$\mathrm{Mg} \leftrightarrow \mathrm{Mg}^{2+} + 2\mathrm{e}^- \qquad \in^0 = -2.37\ \mathrm{V}$$

$$\mathrm{Cu} \leftrightarrow \mathrm{Cu}^{2+} + 2\mathrm{e}^- \qquad \in^0 = +0.159\ \mathrm{V}$$

$$\mathrm{Zn} \leftrightarrow \mathrm{Zn}^{2+} + 2\mathrm{e}^- \qquad \in^0 = -0.762\ \mathrm{V}$$

The Si and Al ions have higher values in comparison to Cu ions. Thus Si ions gives priority for the dissolution of aluminium more inside the solution compared to Cu ions. This causes the variation in coating thickness formation over two alloys as shown in Table 2. The Figure 25 represents the variation in coating thickness under various immersion time for three different aluminium alloys. This graph also indicates that highly alloyed substrate has low coating thickness under various immersion times compared to low alloyed substrate.

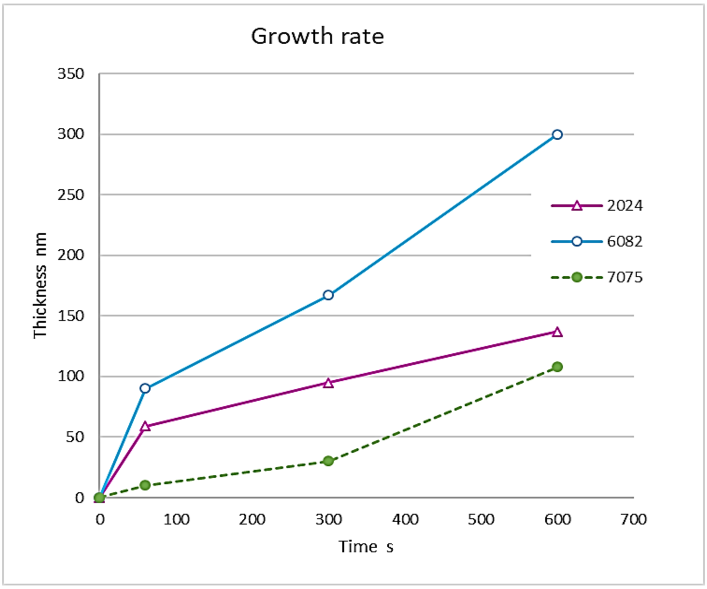
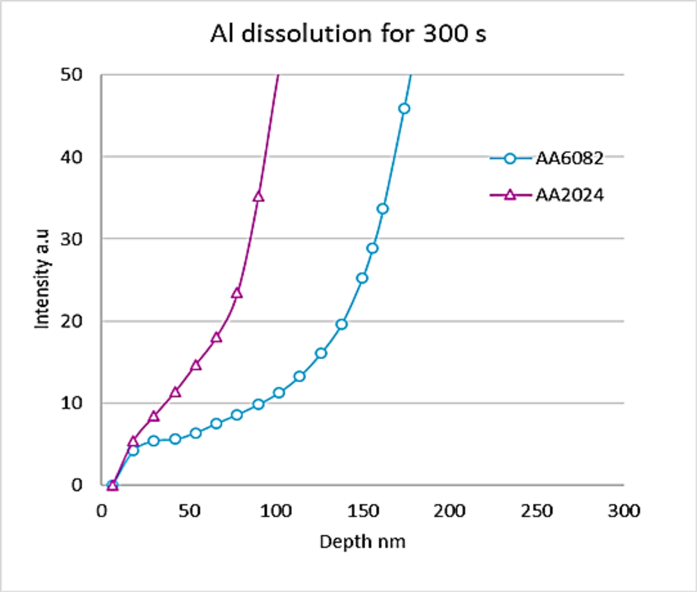


Figure 25 : Variation in thickness of coating under various immersion time.



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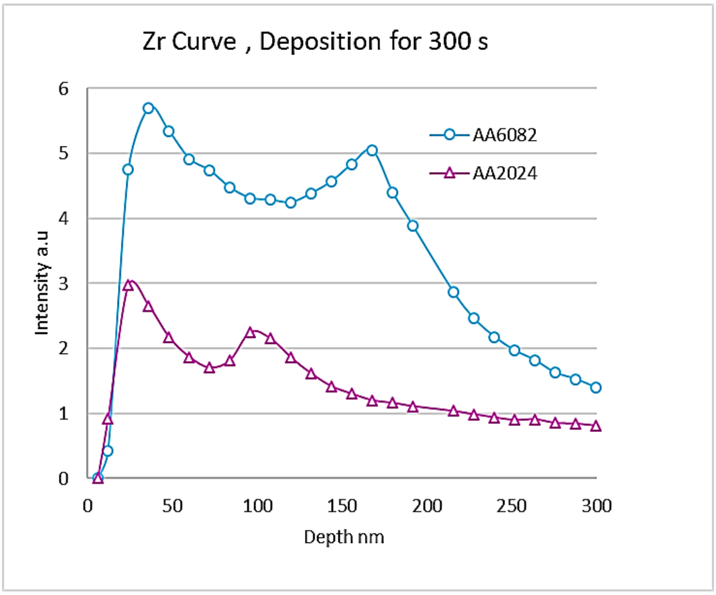

Figure 26. Aluminium dissolution and Zr deposition in coating over AA6082 and AA2024 alloys after 300s immersion time

Table 2. Coating thickness variation (nm) for two different alloys

	0 s	**60 s**	**300 s**	**600 s**
AA2024	0	59	95	137
AA6082	0	90	167	300

Table 2 indicates the variation in thickness of coating of AA6082 and AA2024 alloy with increase in immersion time. It is evident, from this table that the thickness of coating increases with immersion time. From these results, our hypothesis is that the layer formation seems to be highly dependent on the quantity of alloying elements in the underlying substrate over which the coating is formed. The high alloyed substrate seems to have low coating thickness compared to low alloyed substrate. The aluminium dissolution determines the coating thickness.

5.7 Ageing

The effects of ageing have not been studied in detail previously , but there are certain literature claiming that ageing plays a major role in conversion coating behaviour [5]. The ageing process means drying the coating for a certain period of time to achieve the proper structure. We studied the ageing effect using SNMS to discover the structural transformation. The fresh and aged SNMS curves showed that the oxygen curve is drastically reduced inside the coating for the AA7075 alloy during the ageing process, as seen in Figure 27 (a, b). This finding signifies that there are some changes at an elemental level during the ageing process.

In addition, other curves like Zr and Cr does not undergo any major changes. In the fresh state, the coating formed over AA7075 has a higher oxygen curve compared to that of AA6082. We assume that the sol-gel proportion is a probable reason for this variation. It is also observed from Figure 27 (c and d) that the aluminium content of the AA6082 alloy is slightly reduced after ageing. From this SNMS analysis of fresh and aged samples, we predict that there is a change in the chemical state of the coating. A previous report suggests that the coating undergoes dehydration in the ageing process [9]. Our hypothesis is that once the samples are taken out of the bath, the coating undergoes a continuous transition from sol to gelatinous state. Based on the results of the high vacuum exposure, we found that mostly Zr ions are in sol form, with some Al and Cr ions. In summary, atoms in the coating tend to change their nature from sol to gelatinous states during the ageing process. This sol-gel transformation at room temperature appears to take a surprisingly long time (weeks or months), most probably caused by the slow Zr clusters.

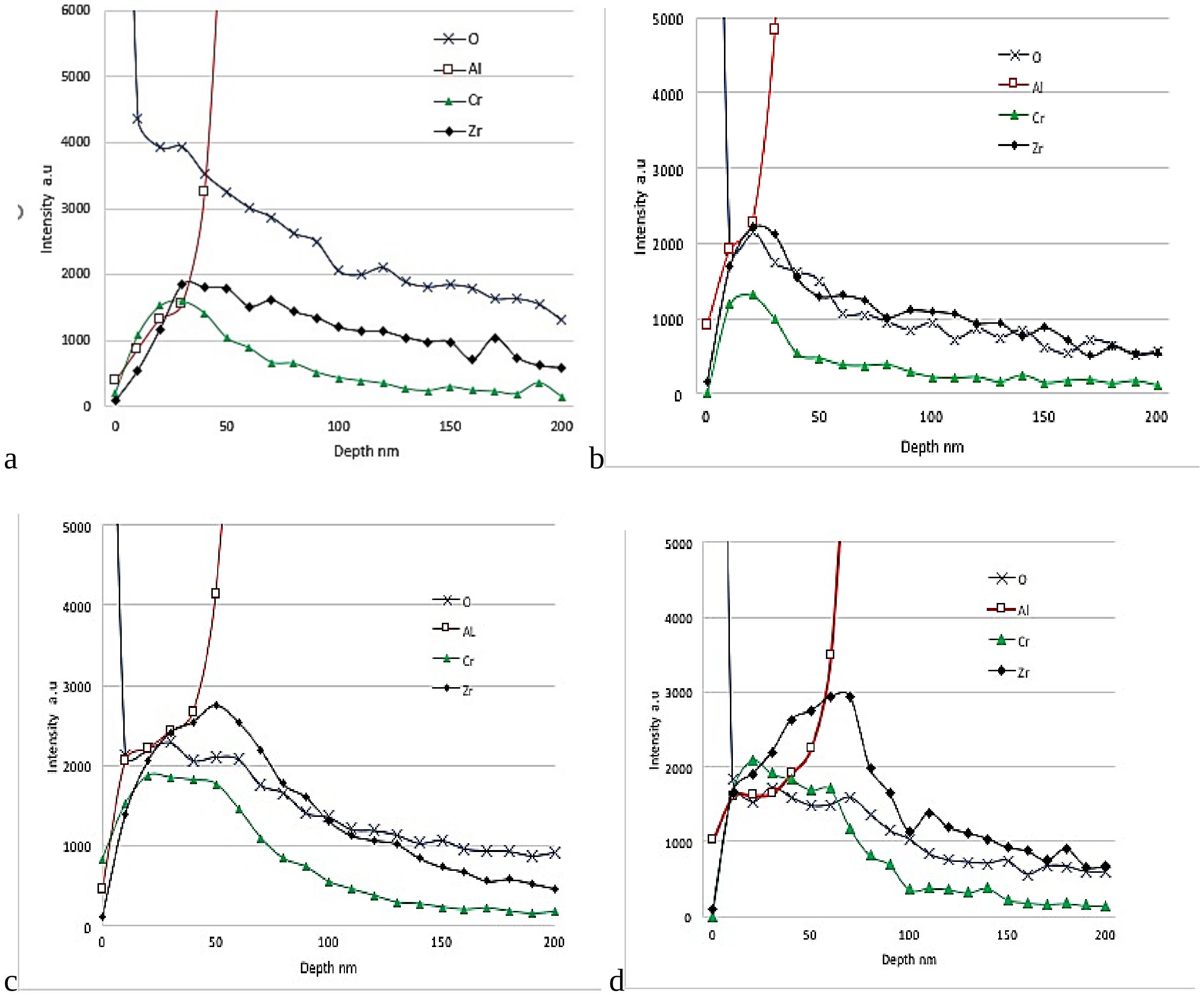

Figure 27. Atomic distribution in fresh (graph a, c) and aged (graph b, d) of coating formed over AA7075 and AA6082

5.8 Coating growth cycle

The growth cycle of conversion coating was investigated by measuring the thickness of coating with the function of immersion time. Comparing other two alloys AA6082 had high coating thickness which tends to study the growth kinetics of Zr4/Cr3 based conversion coating using this alloy. Figure 28 shows five Zr distribution curves elucidating that the coating reaches maximum thickness of 450 nm around 1440 s after which there is a tremendous change in the shape of the curve. The coating growth process obviously ceased. The experimental results summarized in Table 3 represents the variation of coating thickness in function of immersion times.

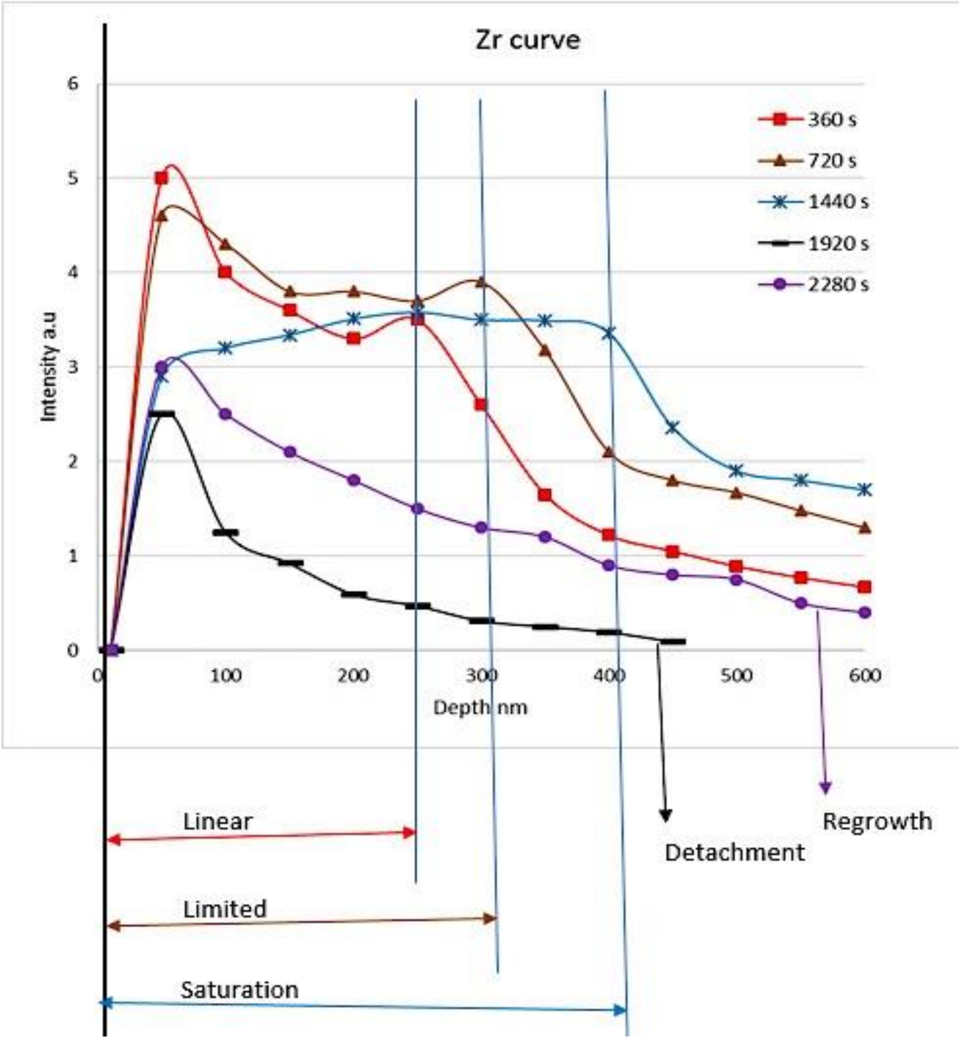

Figure 28. Zr distribution in example coatings formed over AA6082 that removed from coating bath after different immersion time

Table 3.Thickness of coating formed over AA6082 alloy under various immersion time

State	**Time s**	**Coating thickness (nm)**
Activation	0-60	0 – 100
Linear	60-540	~100 -310
Limited	540-900	~310-400
Saturation	900-1440	~450
Detachment	Above 1440	~55

Based on these data, we propose a coating growth model consisting of five different states. The Figure 29 represents the growth cycle of Zr4/Cr3 based conversion coating over AA6082 alloy.

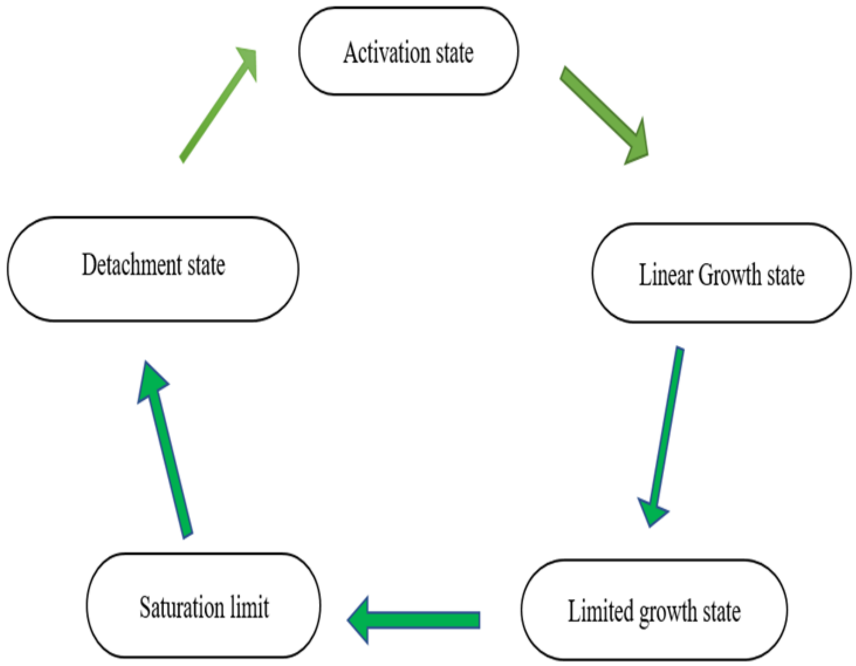

Figure 29. Coating growth cycle

The coating growth consists of five different states that is activation state, linear growth state, limited growth state, saturation and detachment state.

- The activation state is the initial period, when the aluminium starts its dissolution and thus the conversion process begins. The coating reaches a maximum of 100 nm during this state. The state starts quickly below 60 s.

- Linear growth state is the period where the formation of coating is higher. The aluminium dissolution inside the coating bath is abundant and a rapid conversion process occurs over the surface of alloy. Almost, the entire surface of the substrate is covered with a long molecular chain network of Cr, Zr, Al and O ions.
- Limited growth rate is the state where the aluminium dissolution is disturbed by the coating that is previously formed over the substrate. This reduces further formation of the coating because there is not much Al ions that can pass through the molecular network to react with Cr3 and Zr4 ions in the coating bath. We assume that the aluminium somehow dissolve in certain regions like cracks that tends to contribute coating growth. The growth of coating is very slow during this state compared to the previous two states.
- Saturation limit is the point where there are no more ions dissolutes from the substrate. The coating reaches its maximum limit, beyond that there is no more coating growth. This saturation limit is varying according to the size of the sample and its composition. Over all, most of the samples reached this limit approximately at 450 nm. The saturation limit can occur at different time and coating thickness over samples. We conclude that for AA6082 sample with thickness mentioned earlier has saturation limit reaches around 1440 s after which the next state begins
- Detachment state is the point where the coating is dispatched from the substrate and disappears into the coating bath. We predict that after saturation limit the coating cracks in several place and large agglomerates of Cr, Zr and Al ions in coating dispatches from the surface of alloy. However, the chemistry behind this dispatch is unknown. The coating thickness measured beyond this detachment state represents the regrowth of coating.

6 CONCLUSION

6.1 LIST OF THESIS WORK

6.1.1 COATING STRUCTURE

Based on the SNMS and GD-OES measurements, we found that the Zr4/Cr3 based conversion coating exhibits a sol-gel type structure. The conversion coating over AA6082 aluminium alloy is in sol and gelatinous states that were found separable under exposure to the high vacuum. The sol part mostly consists of Zr and small amount of Cr, Al, and O solute in water. Whereas the gel phase constitutes a large molecular network of Cr-Al-O. However the double layer coating structure on AA2024 [10][7] was not confirmed on AA6082.

6.1.2 IMPORTANCE OF Al DISSOLUTION IN CONVERSION PROCESS

The formation mechanism of Zr4/Cr3 based conversion coating is highly dependent on the standard potential of the alloying elements in the substrate. The dissolution of aluminium in to coating bath determines the formation of coating and its growth. This dissolution process is decelerated and halted by the alloying elements like copper in the substrate resulting in a thin layer with a low chromium content.

6.1.3 SUBSTRATE INFLUENCES IN CONVERSION PROCESS

In comparison with other two alloys, AA6082 alloy tends to have high coating thickness. The depth profiling of coating over AA6082 and AA2024 alloys showed that the substrate which is highly alloyed has low coating thickness with less zirconium content. The highly alloyed substrate has low coating thickness compared to low alloyed substrate. In case of AA2024, the dissolution of aluminium ions in bath is decelerated by the neighbouring copper ions resulting in low thickness coating formation with less chromium and zirconium.

6.1.4 AGEING EFFECT

The fresh conversion coating is not stable and there are structural changes in the composition of coating under normal atmospheric condition. The depth profiling of coating formed over AA6082 and AA7075 under both aged and fresh state using SNMS reveals the changes that occur inside the coating. The reduction in oxygen and variation in aluminium intensity under ageing process indicates that the coating undergoes a continuous transformation from sol to gel.

6.1.5 COATING GROWTH

Under sample preparation technique 5, the study about the growth kinetics of Zr4/Cr3 based conversion coating over AA6082 alloy reveals the cycle of the coating growth. The growth kinetics consist of the activation, linear, limited, saturation and detachment states. The results obtained from depth profiling of coated AA6082 samples at various immersion time indicates that after the detached state there is a possibility for regrowth of coating. Once the coating is detached from the substrate, the aluminium ions over the surface dissolves again and regrowth of coating occurs.

State	**Time /s**	**Coating thickness/ nm**
Activation	0-60	0 - 100
Linear	60-540	~100 -310
Limited	540-900	~310-400
Saturation	900-1440	~450
Detachment	Above 1440	~55

7 Current application of this conversion coating

Due to the current stringent rules , Cr6 has been reduced majorly in the automotive industries [2]. Before 2007, the directives set the limit of the hexavalent chromium to a maximum of 2 g per the whole vehicle. So, the automobile industries have completely replaced the Cr6 to Zr4/Cr3 chromate conversion coating. In electrical engineering, the chromate conversion with Cr6 was predominantly used to enhance corrosion resistance of zinc plated fasteners and cases. The reduction in conductivity was the major contribution of the traditional conversion coating. Interestingly, these two requirements have been fulfilled by trivalent chromate conversion coating. Certain industries have started implementing it in the electrical panels. In the European Union, automotive and electrical engineering industries have replaced the classical chromate process by Cr6 free coating techniques.

Updates from aircraft and naval application.

Approval for implementation of SurTec 650 based Zr4/Cr3 conversion coating in navy application. (SURTEC 650, Govt. designation Type II , Class 1A , Form I, Method A)

MIL-DTL-81796 B: Type II- coating: Cr (VI)-free

Approval for class 1A

- 336 h neutral salt spray test
- Paint adhesion
- Coating weight less than 107.5 mg/m^2

Approval for class 3:

- Less than 5000 μOhm per square inch after passivation
- Less than 10000 μOhm per square inch after 168 h of NSS

Thus, this chromate conversion coating can be used for naval application.

Various approval document from several aircraft manufactures.

- Thales (Doc. No. 16 262 746-024)
- Safran (STG 3300373621)
- Ericsson (105 86-MZY 510 15 Uen)
- Nortel (MGS 00200)

8 Publications related to this thesis work

8.1 Scientific publication

1. K. Thirupathi, P. Bárczy, and B. M. Somosvári, “Impact of Corrosive Liquid on Trivalent Chromium over Aluminium Alloys,” Journal of Surface Engineered Materials and Advanced Technology, vol. 7, no. 3, pp. 51–60, 2017.
2. K. Thirupathi, P. Bárczy, and G. Lassu, “Growth Kinetics and Structure of Zr4 / Cr3 Based Conversion Coating over Aluminium,” Functional Nanostructure, vol. 1, no. 3, pp. 114–119, 2017.
3. K. Thirupathi, P. Bárczy, and B. M. Somosvári, “Eliminating Hexavalent Chromium in Conversion Coating for Space Application,” in 5th Interdisciplinary doctoral conference, 2016, pp. 201–215.
4. K. Thirupathi, P. Bárczy, K. Vad, A. Csik, and B. Márton Somosvári, “Effects of Vacuum and Ageing on Zr4/Cr3 based Conversion Coatings on Aluminium Alloys,” Applied Surface Science, vol. 441, pp. 1043–1047, 2018.
5. K. Thirupathi, P. Bárczy, B. M. Somosvári, and T. Bárczy, “Hexavalent chromium free coatings for satellite metallic hardware’s,” in 3rd International conference on research, technology, and education of space, 2017, pp. F-35.

8.2 Oral and Poster Presentations

1. 2016, 5th Interdisciplinary Doctoral Conference May 27 -29, Pecs, Hungary, Oral Presentation on Eliminating Hexavalent Chromium in Conversion Coatings for Space Application.
2. 2017, 3rd International Conference on Research, Technology and Education of Space, February 9-10, Budapest, Hungary, Oral Presentation on Hexavalent Chromium Free Coatings for Satellite Metallic Hardware
3. 2017, 2nd International Conference on Applied Science, June 12-15, Dalian, China, Poster Presentation on Study of Trivalent Chromate Coating on Aluminium Alloys by SNMS.
4. 2017, 3rd International Conference on Surfaces, Coatings and Nanostructured Materials, December 4 -7, Hong Kong, China, Oral Presentation on Effects of Vacuum and Ageing on Zr4/Cr3 based Conversion Coatings on Aluminium Alloys.

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10 APPENDIX I

S. No	Elements Analyses	Conc. Data mg/liter
1.	Al	1.35
2.	Ca	0.88
3.	Cr	502
4.	Cu, Fe, I	Nil
5.	K	974
6.	Mg, Mn, Mo	Nil
7.	Na	265
8.	P	0.014
9.	S	395
10.	Si	2.77
11.	Ti	0.15
12.	V	Nil
13.	Zn	1.35
14.	Zr	1112.8

Table 4 : Elemental analysis of SurTec 650 RTU using ICP-OES

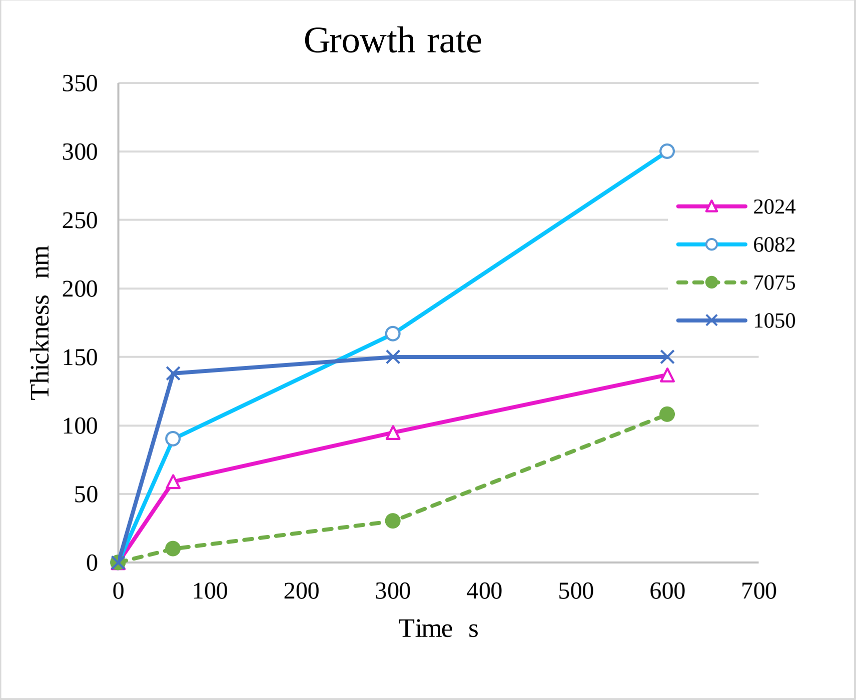
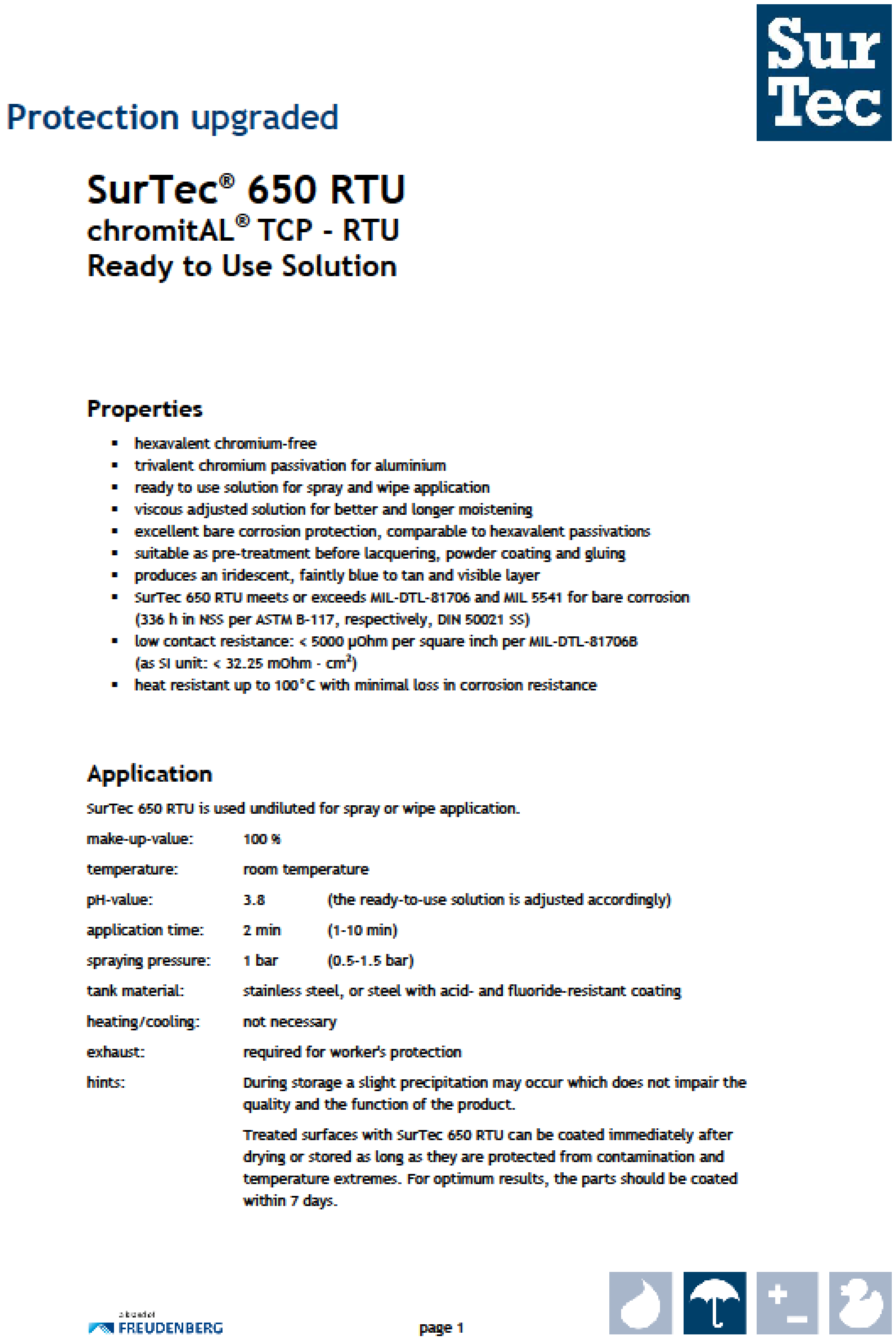


Figure 30: Differences in the coating growth between the high (AA7075) , low (AA 6082) and least (AA 1050) alloyed substrates.

DOI: 10.14750/ME.2018.011



Protection upgraded

SurTec® 650 RTU
chromitAL® TCP - RTU
Ready to Use Solution

Properties

- hexavalent chromium-free
- trivalent chromium passivation for aluminium
- ready to use solution for spray and wipe application
- viscous adjusted solution for better and longer moistening
- excellent bare corrosion protection, comparable to hexavalent passivations
- suitable as pre-treatment before lacquering, powder coating and gluing
- produces an iridescent, faintly blue to tan and visible layer
- SurTec 650 RTU meets or exceeds MIL-DTL-81706 and MIL 5541 for bare corrosion (336 h in NSS per ASTM B-117, respectively, DIN 50021 SS)
- low contact resistance: < 5000 µOhm per square inch per MIL-DTL-81706B (as SI unit: < 32.25 mOhm - cm^2)
- heat resistant up to 100°C with minimal loss in corrosion resistance

Application

SurTec 650 RTU is used undiluted for spray or wipe application.

make-up-value:	100 %	
temperature:	room temperature	
pH-value:	3.8	(the ready-to-use solution is adjusted accordingly)
application time:	2 min	(1-10 min)
spraying pressure:	1 bar	(0.5-1.5 bar)
tank material:	stainless steel, or steel with acid- and fluoride-resistant coating	
heating/cooling:	not necessary	
exhaust:	required for worker's protection	
hints:	During storage a slight precipitation may occur which does not impair the quality and the function of the product. Treated surfaces with SurTec 650 RTU can be coated immediately after drying or stored as long as they are protected from contamination and temperature extremes. For optimum results, the parts should be coated within 7 days.	

Treatment Procedure

pre-treatment: Prior to the passivation with SurTec 650 RTU, the aluminium surface must be cleaned and deoxidized thoroughly. The surface must be water-break free.

Cleaning can be done with:

- solvents or solvent-based cleaners (e.g. by abrasion of the surface with a soaked cloth), if applicable the surface can be treated with Scotch Brite or abrasive paper in order to remove corrosion products from the surface; abrasion should be done under water cooling, the abrasive dust must be removed by a wet cloth
- aqueous, acidic, phosphate-free cleaners (a subsequent rinsing is required)
- a combination of alkaline cleaning and subsequent acidic desmutting (between the two steps and after desmutting, the surface has to be rinsed with water)

treatment with SurTec 650 RTU chromitAL:

Wet the surface with the ready to use solution, e.g. by using a sponge, brush, cloth or spray pistol.

Make sure that the surface is completely wettable with SurTec 650 RTU solution (no contraction/coalescence of the liquid film and no dewetting or formation of separate drops). In case of dewetting the pre-treatment/ cleaning must be repeated.

During the required application period (typically 2-4 min) the surface must be kept permanently wet with SurTec 650 RTU solution. There must not be any drying on the surface. In order to avoid a surface drying use more SurTec 650 RTU solution, if necessary.

Continuously slight mechanical treatment (wiping, brushing) will support the uniform formation of the passive layer.

post-treatment: After passivation in SurTec 650 RTU, the parts have to be rinsed. For best corrosion resistance, a rinsing with deionised water is recommended. For successive lacquering, the last rinse must have a conductivity of less than 30 µS/cm.

The parts can be dried at environmental conditions, in case of forced drying the drying temperature should not exceed 65°C at the part's surface.

Technical Specification

(at 20°C)	Appearance	Density (g/ml)	pH-value *(conc.)*
SurTec 650 RTU	liquid, green, clear-turbid contingency precipitate	1.003 (1.00-1.01)	2.9-4.0

hint: During the first days of storage, the pH-value of the product increases slightly..

Maintenance and Analysis

SurTec 650 RTU is supplied as a ready-to-use solution. Therefore, an analysis is not necessary.

Ingredients

- trivalent chromium salts

Consumption and Stock Keeping

The consumption depends heavily on the drag-out. To determine the exact amounts of drag-out, see SurTec Technical Letter 11.

In order to prevent delays in the production process, per 1,000 l bath the following amount should be kept in stock:

SurTec 650 RTU 1000 kg

Product Safety and Ecology

Classification and designation are noted in the Material Safety Data Sheets (according to the European legislation). The safety instructions and the instructions for environmental protection have to be followed in order to avoid hazards for people and environment. Please pay attention to the explicit details in our Material Safety Data Sheets.

Warranty

We are responsible for our products in the context of the valid legal regulations. The warranty exclusively accesses for the delivered state of a product. Warranties and claims for damages after the subsequent treatment of our products do not exist. For details please consider our general terms and conditions.

Further Information and Contact

If you have any questions concerning the process, please contact your local technical department.

For further information and contact details please visit our homepage:

http://www.SurTec.com

20 February 2017/DK, PV

US006375726B1

(12) **United States Patent**
Matzdorf et al.

(10) **Patent No.: US 6,375,726 B1**
(45) **Date of Patent: Apr. 23, 2002**

(54) **CORROSION RESISTANT COATINGS FOR ALUMINUM AND ALUMINUM ALLOYS**

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(73) Assignee: **The United States of America as represented by the Secretary of the Navy**, Washington, DC (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **09/702,225**

(22) Filed: **Oct. 31, 2000**

(51) **Int. Cl.**^{7} **C23C 22/05**

(52) **U.S. Cl.** **106/14.44**; 106/14.21; 106/14.41; 148/247

(58) **Field of Search** 106/14.44, 14.21, 106/14.41; 148/247

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Primary Examiner—Anthony Green
(74) *Attorney, Agent, or Firm*—Ron Billi

(57) **ABSTRACT**

This invention is for the protection and surface treatment of aluminum, aluminum alloys and coated aluminum substrates against corrosion. The aluminum substrates are treated with an acidic aqueous solution containing small but effective amounts of at least one trivalent chromium salt such as a trivalent chromium sulfate, at least one alkali metal hexafluorazirconate such as potassium hexafluorozirconate in combination with small but effective amounts of at least one water soluble or dispersible thickening agent such as a cellulose compound and at least one water soluble surfactant. The corrosion resistant aluminum substrates of this invention have improved adhesion for overlaying coatings e.g. paints and a lower electrical resistance contact.

14 Claims, No Drawings

CORROSION RESISTANT COATINGS FOR ALUMINUM AND ALUMINUM ALLOYS

ORIGIN OF THE INVENTION

The invention described herein was made by an employee of the United States Government and may be manufactured and used by or for the Government for governmental purposes without the payment of any royalties thereon or therefore.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to the protection and surface treatment and coating of metal substrates and to surface treatment and coating compositions employed as solutions or dispersions and to the method of using these compositions for the treatment of aluminum, aluminum alloys and coated aluminum substrates. The compositions coated on the metal surfaces provide improved corrosion resistance, adhesion of overlaying coatings e.g. paints, and maintains low electrical contact resistance in a corrosive environment. More specifically, this invention relates to a novel corrosion resistant composition and to the process of using the composition on aluminum, aluminum alloys and coated aluminum substrates which comprises an acidic aqueous solution containing effective amounts of at least one water soluble trivalent chromium salt, an alkali metal hexafluorozirconate, at least one water soluble thickener and water soluble surfactants.

2. Description of Prior Art

It is a current practice to improve the corrosion resistance and bonding of subsequent coatings to metal surfaces by initially coating or treating the metal surface with protective films. The coating enhances the corrosion resistance of the unpainted metal surface and prepares the surface for a finish coating such as paint. These conversion coatings are most often applied by the use of hexavalent chromium-containing solutions. While these coatings provide good corrosion resistance, attempts have been made to provide a more acceptable non-chromate derived coating because of the growing concern regarding the occupational, safety, health and environmental effects of hexavalent chromium. Hexavalent chromium is highly toxic and is a known carcinogen. Therefore, the solutions used to deposit these protective films and the films per se are toxic carcinogenic. Chromate films, however, provide outstanding paint adhesion and corrosion resistance and are easy to apply by various methods including immersion, spraying or by the wipe-on technique. Environmental laws and OSH regulations are forcing the military and commercial users to find other non-toxic non-chromate pretreatments. Moreover, the use of chromate conversion coatings is becoming more expensive as the regulations are being enforced and costs become prohibitive with the restrictions being imposed by the EPA. In addition, certain processes like spraying chromate conversion coatings are forbidden because of OSH, thereby forcing the use of less than optimum alternative methods.

More specifically, it is known that aqueous chromate solutions contain chemicals that partially dissolve the surface of the metal and form insoluble films known as chromate conversion coatings. These coatings are corrosion resistant and protect the metal from various elements which cause corrosion. Although the conversion coatings enhance corrosion resistance and improve the paint bonding properties, the coatings have a serious drawback, i.e., the toxic nature of the solutions from which they are made and the presence of hexavalent chromium in the applied films. This is a serious problem from the standpoint of the operators handling the solution e.g. disposing the used chromate solution and the chromate-contaminated rinse water, and the coating systems contaminated with chromates. These problems, however, can be avoided by eliminating the hexavalent chromium from the process. However, this method is expensive and can be a major cost factor in the overall metal treating process. Therefore it is highly desirable to provide processes and protective coatings which are free of hexavalent chromium, but at the same time capable of imparting corrosion resistant and paint bonding properties which are comparable to those imparted by conventional chromate-based conversion coatings. Of particular interest is the use of chromate conversion coatings on aluminum alloys e.g. the coating of large objects such as aircraft. It would be desirable to provide a protective coating for aluminum, its alloys and coated aluminum utilizing relatively non-toxic chemicals that could serve as an alternative to the toxic hexavalent chromium.

SUMMARY OF THE INVENTION

This invention relates to acidic aqueous trivalent chromium compositions i.e. solutions of trivalent chromium salts and to a process of preparing corrosion resistant coatings on aluminum, aluminum alloys and coated aluminum substrates which comprises treating or coating the aluminum substrates at ambient temperatures with effective amounts of the aqueous solution to form a corrosion resistant coating or film on the surface of the substrate. The acidic aqueous solutions of this invention comprise per liter of water, from about 3 to 22 grams of a water soluble basic trivalent chromium salt, and preferably from 3 to 12 grams of chromium salt e.g. 5–7 grams, about 1.5 to 11.5 grams, and preferably 3 to 9 grams e.g. 6–8 grams, of an alkali metal hexafluorozirconate, from about 0 to 10 grams e.g. from 0.5 to 2.0 grams of a water soluble thickener and from about 0 to 10 grams e.g. from 0.5 to 2.0 grams of a water soluble surfactant.

It is therefore an object of this invention to provide a solution comprising a trivalent chromium salt and an alkali metal hexafluorozirconate for preparing corrosion resistant substrates of aluminum, aluminum alloys and coated aluminum.

It is another object of this invention to provide an aqueous solution or dispersion for treating aluminum, aluminum alloys and coated aluminum which contain trivalent chromium salts to improve the corrosion resistant, paint adhesion and provide aluminum substrates with low electrical contact resistance in a corrosive environment.

It is still a further object of this invention to provide an aqueous solution comprising a water soluble trivalent chromium salt in combination with an alkali metal hexafluorozirconate, a water soluble thickener and a water soluble surfactant for preparing corrosion resistant coatings on aluminum and aluminum alloy substrates.

These and other objects will become apparent to those skilled in the art from a further and more detailed description of the invention as follows:

DETAILED DESCRIPTION OF THE INVENTION

More specifically, this invention relates to an acidic aqueous solution of a trivalent chromium salt having a pH ranging from about 2–6 e.g. 4–5 and the use thereof for preparing corrosion resistant coatings or films on aluminum, aluminum alloys and coated aluminum substrates which comprises from about 3.0 to 22 grams per liter of solution and preferably about 3 to 12 grams per liter e.g. 5–7 grams of at least one water =soluble trivalent chromium salt, about 1.5 grams to 11.5 grams and preferably about 3 to 9 grams e.g. 6–8 grams per liter of solution of at least one alkali metal hexafluorozirconate, from about 0.0 to 10 grams per liter of the solution and preferably from about 0.5 to 2.0 grams per liter of at least one water soluble or dispersible thickener e.g. water soluble organic thickener and from about 0.0 to 10 grams per liter and preferably 0.5 to 2.0 grams per liter of the solution of at least one water soluble surfactant or wetting agent selected from the group consisting of nonionic, cationic and anionic surfactants. The trivalent chromium may be added as any water-soluble trivalent chromium compound, preferably as a trivalent chromium salt. Although the resultant coating is rinsed with water, it is desirable to use salts that provide anions that are not as corrosive as the chlorides which include anions selected from the group consisting of nitrates, sulphate, phosphate and acetates.

Specifically, in formulating the aqueous coatings of this invention, the chromium can be added conveniently to the solution in its water soluble form wherein the valence of the chromium is plus 3. The preferred chromium compounds are incorporated in the solution in the form of $Cr_2(SO_4)_3$, $(NH_4)Cr(SO_4)_2$ or $KCr(SO_4)_2$ and mixtures of these compounds. The aluminum surface is either pure aluminum, an aluminum alloy or coated aluminum substrate containing over 60% aluminum. The most preferred trivalent chromium concentration is within the range of about 5 to 7 grams per liter of the aqueous solution. It has been found that particularly good results are obtained economically when the chromium is present in this preferred range. The most preferred metal fluorozirconate addition to the solution ranges from about 6 to 8 grams per liter. The treatment or coating of the aluminum surface can be carried out at various temperatures including the temperature of the solution which ranges from ambient e.g. room temperature up to about 200° F. Room temperature treatment is preferred in that this eliminates the necessity for heating equipment. The coating may be air dried by any of the methods known in the art, for example, oven drying, forced air drying, exposure to infra-red lamps, etc. For purposes of this invention, the terms aluminum and aluminum alloys include pretreated or coated substrates of aluminum and its alloys including a process known as ion vacuum deposition (IVD) where the aluminum alloy substrate is pretreated or coated e.g. with aluminum before the substrate is coated with the trivalent chromium salt solution of this invention.

The following Examples 1–3 illustrate the solutions of this invention and the method of using the solutions in preparing corrosion resistant aluminum and aluminum alloy substrates.

EXAMPLE 1

An acidic aqueous solution for treating aluminum and aluminum alloys to form a corrosion-resistant coating thereon comprises from about 6.0 grams of trivalent chromium sulfate per liter of solution, about 8.0 grams of potassium hexafluorozirconate per liter of solution and about 1.0 gram per liter of solution of a cellulose thickener and about 1.0 gram of a water soluble nonionic surfactant per liter of solution.

EXAMPLE 2

An acidic aqueous solution for treating aluminum and aluminum alloys to form a corrosion-resistant coating thereon which comprises per liter of solution from about 3.0 to 12 grams of trivalent chromium sulfate, about 3 to 9 grams of sodium hexafluorazirconate and from about 0.5 to 2.0 grams of methylcellulose thickener.

EXAMPLE 3

An acidic aqueous solution for treating aluminum and aluminum alloys to form a corrosion-resistant coating thereon which comprises, per liter of solution, from about 5.0 to 7.0 grams of a trivalent potassium-chromium sulfate ($KCr(SO4)_2$) about 6 to 8 grams of potassium hexafluorozirconate and from about 0.5 to 2.0 grams of a methyl cellulose thickener.

Prior to forming the trivalent chromium coating (per Example 1), the aluminum substrates were treated by cleaning the substrates for about 15 minutes at temperatures ranging from about 100° to 140° F. with an alkaline phosphate cleaner, rinsed in tap water and subsequently immersed in a non-chromate deoxidizer for about 15 to 20 minutes under ambient conditions and then rinsed again in ambient tap water. The cleaned substrates were then immersed in the acidic trivalent chromium sulfate solution at ambient conditions for about 30 seconds to 60 minutes and subsequently rinsed in ambient tap water and let stand until dry. In an alternative process, the aluminum substrates were degreased by immersion in a cleaner (Turco 4215) for about 15 minutes at 120° F. then rinsed in warm tap water and again immersed in a cleaner (Turco Smut Go NC) for about 15 minutes under ambient conditions. After a further water rinse, the cleaned substrates were immersed in an acidic aqueous solution of trivalent chromium sulfate containing effective amounts of potassium hexafluorozirconate at ambient temperatures and then rinsed.

Coating the substrates with the trivalent chromium solutions of this invention can be accomplished by spraying, wiping or immersing the substrate. The duration of contact ranges from about 5 to 30 seconds, but longer contact, e.g., up to five minutes, may be required where the trivalent chromium concentration or temperature of the solution is relatively low. The aqueous solution temperature is normally below 100° C., e.g. in the range of 40° to 75° C. The metal temperature ranges from about 40° to 60° C., and often around 50° C., prior to the coating treatment. The coating is rinsed with water, dried and then painted e.g. with an epoxy primer and/or paint.

The following Examples I through V illustrate the trivalent chromium pretreatment solutions of this invention and the use thereof in coating aluminum alloys as shown in Tables C, D, E and F.

EXAMPLE (TCPI) I

A trivalent chromium pretreatment (TCP) acidic aqueous solution was prepared with about 0.6 grams per liter of solution of basic trivalent chromium sulfate and about 0.8 grams per liter of solution of potassium hexafluorozirconate.

EXAMPLE (TCP10) II

A trivalent chromium pretreatment (TCP) acidic aqueous solution was prepared with about 6.0 grams per liter of solution of basic trivalent chromium sulfate and about 8.0 grams per liter of solution of potassium hexafluorozirconate.

EXAMPLE (TCPIM4) III

A trivalent chromium pretreatment (TCP) acidic aqueous solution was prepared with about 0.6 grams per liter of solution of basic trivalent chromium sulfate, about 0.8 grams per liter of solution of potassium hexafluorozirconate and about 0.4 percent by weight of the solution of a cellulose compound (Methocel F4M).

EXAMPLE (TCP 2M4 AND TCP 10M4) IV, AND V

Examples IV and V (TCP2M4 and TCP10M4) are the same as aqueous solutions TCP1 and TCP10, respectively, except that each of these solutions also contained about 0.4 percent by weight of the aqueous solution of hydroxy methyl cellulose (Methocel F4M) as the thickener.

The pH of various trivalent chromium pretreatment (TCP) solutions over time is shown in Table E.

TABLE E

Composition	pH on 10/28 (day mixed)	pH on 11/4	pH on 11/10	pH on 11/22	pH on 12/14
TCP1	3.57	3.93	3.96	4.01	
TCP10	3.48	3.79	3.82	3.81	3.75
TCP1m4	3.55	3.94	3.97	3.97	
TCP2M4	3.41	3.93	3.95	3.93	
TCP10M4	3.23	3.78	3.82	3.79	3.75

The testing of bare corrosion of the trivalent chromium pretreatment is shown in Table F.

TABLE F

Composition	Day 1	Day 2	Day 6	Day 14
TCP1	5	4	4	0
TCP10	10	10	10	9
TCP1M4	7	6	5	3
TCP2M4	9	8	7	6
TCP10M4	10	10	10	9

The coated aluminum alloy (2024-T3) samples were placed in a neutral salt fog (per ASTM-B-117) for about 336 hours at 60° C. The corrosion ratings of the coated samples were based on the ASTM-D1654 test wherein the coated samples were rated from 0 to 10 with 10 representing the best performance.

The necessity of using a thickener in the trivalent chromium pretreatment solutions of this invention is illustrated in the Examples shown in Table C and Table D. In Table C, the aluminum alloy coupons were treated with the solution of Example I (TCP-1) which did not contain the thickener. Table C shows that the average coating weight is about 24.65 mg/ft^2. In comparison, the data in Table D shows that where the thickener (Methocel F4M) was used in the solution (Example III-TCP1M4), the average coating weight was 28.56 mg/ft^2. Thus, in comparing the data of Table C with Table D, it was found that the chromium pretreatment solution (Example III-TCP1M4) containing the thickener (Methocel F4M) resulted in coatings on the aluminum alloy to be about 16% heavier.

TABLE C

Coupon ID	Alloy of Aluminum	Coating Weight (mg/ft2)
6A	6061-T6	23.04
6B	6061-T6	25.95
2A	2024-T3	24.96
2B	2024-T3	25.95

Average CW: 24.65

TABLE D

Coupon ID	Alloy of Aluminum	Coating Weight (mg/ft2)
6A	6061-T6	27.84
6B	6061-T6	28.80
2A	2024-T3	27.84
2B	2024-T3	29.76

Average CW: 28.56

The panels of aluminum no's. 7–1 through 7–108 in Table G show the aluminum coupons (7075–T6) treated with an aqueous trivalent chromium solution (TCP-10/M2) to provide paint adhesion data on various aluminum substrates using Milspec paints. The paint adhesion data was obtained by using modified test (AST D-3359 Method A). The columns 2–5 of Table G identify various paints including SPT as a self-priming topcoat (TT-P-27561), 23377 as a chromated high solids epoxy primer, 85582 as chromated waterborne epoxy primer, and 85582N as a non-chromated waterborne epoxy primer.

Column 6 of Table G shows the wet tape adhesion test performed 1, 4 and 7 days immersed in water followed by scribing and tape pulling. Column 7 of Table G shows the method of applying solutions of the chromium pretreatment including "S" for spraying, "W" for wipe and "I" for immersion of the aluminum coupons. Column 8 of Table G shows the paint adhesion rating for each coupon (ASTMD-33) with 5A being the best and column 9 shows the blistering rate for the paint systems (ASTMD-714).

TABLE G

						Examples 7-1 through 7-53 Columns 2–9		
7075-TB Panel	2 SPT	3 23377	4 85582	5 85582N	6 Test	7 Pretreat	8 Adhesion Rating	9 Blistering
7-1	X				1D WTA	Accelagold-S	4A	none
7-2	X				4D WTA	Accelagold-S	5A	none
7-3	X				7D WTA	Accelagold-S	5A	none
7-4		X			1D WTA	Accelagold-S	5A	none
7-5		X			4D WTA	Accelagold-S	5A	none
7-6		X			7D WTA	Accelagold-S	5A	none

TABLE G-continued

						Examples 7-1 through 7-53 Columns 2–9		
7075-TB Panel	2 SPT	3 23377	4 85582	5 85582N	6 Test	7 Pretreat	8 Adhesion Rating	9 Blistering
7-7			X		1D WTA	Accelagold-S	5A	none
7-8			X		4D WTA	Accelagold-S	5A	none
7-9			X		7D WTA	Accelagold-S	5A	none
7-10				X	1D WTA	Accelagold-S	5A	none
7-11				X	4D WTA	Accelagold-S	5A	none
7-12				X	7D WTA	Accelagold-S	5A	none
7-13	X				1D WTA	Alodine 1200S-W	4A	none
7-14	X				4D WTA	Alodine 1200S-W	4A	~50 #8#10 blisters at random spots and edges
7-15	X				7D WTA	Alodine 1200S-W	4A	~50 #6#8 blisters on one half of coupon and along edges
7-16		X			1D WTA	Alodine 1200S-W	5A	none
7-17		X			4D WTA	Alodine 1200S-W	5A	~15 #8#10 blisters in one corner
7-18		X			7D WTA	Alodine 1200S-W	5A	none
7-19			X		1D WTA	Alodine 1200S-W	5A	none
7-20			X		4D WTA	Alodine 1200S-W	5A	none
7-21			X		7D WTA	Alodine 1200S-W	5A	none
7-22				X	1D WTA	Alodine 1200S-W	5A	none
7-23				X	4D WTA	Alodine 1200S-W	5A	none
7-24				X	7D WTA	Alodine 1200S-W	5A	none
7-25	X				1D WTA	Alodine 1200S-I	4A	none
7-26	X				4D WTA	Alodine 1200S-I	5A	none
7-27	X				7D WTA	Alodine 1200S-I	5A	none
7-28		X			1D WTA	Alodine 1200S-I	5A	none
7-29		X			4D WTA	Alodine 1200S-I	5A	none
7-30		X			7D WTA	Alodine 1200S-I	5A	none
7-31			X		1D WTA	Alodine 1200S-I	5A	none
7-32			X		4D WTA	Alodine 1200S-I	5A	none
7-33			X		7D WTA	Alodine 1200S-I	5A	none
7-34				X	1D WTA	Alodine 1200S-I	5A	none
7-35				X	4D WTA	Alodine 1200S-I	5A	none
7-36				X	7D WTA	Alodine 1200S-I	5A	none
7-37	X				1D WTA	TCP10-W	4A	none
7-38	X				4D WTA	TCP10-W	5A	none
7-39	X				7D WTA	TCP10-W	4A	none
7-40		X			1D WTA	TCP10-W	5A	none
7-41		X			4D WTA	TCP10-W	5A	none
7-42		X			7D WTA	TCP10-W	5A	few random #10 blisters
7-43			X		1D WTA	TCP10-W	5A	none
7-44			X		4D WTA	TCP10-W	5A	none
7-45			X		7D WTA	TCP10-W	5A	none
7-46				X	1D WTA	TCP10-W	5A	none
7-47				X	4D WTA	TCP10-W	5A	none
7-48				X	7D WTA	TCP10-W	5A	none
7-49	X				1D WTA	TCP10-S	4A	none
7-50	X				4D WTA	TCP10-S	5A	none
7-51	X				7D WTA	TCP10-S	5A	none
7-52		X			1D WTA	TCP10-S	5A	none
7-53		X			4D WTA	TCP10-S	5A	none
7-54		X			7D WTA	TCP10-S	5A	none
7-55			X		1D WTA	TCP10-S	5A	none
7-56			X		4D WTA	TCP10-S	5A	none
7-57			X		7D WTA	TCP10-S	5A	none
7-58				X	1D WTA	TCP10-S	5A	none
7-59				X	4D WTA	TCP10-S	5A	none
7-60				X	7D WTA	TCP10-S	5A	none
7-61	X				1D WTA	TCP10-I	4A	none
7-62	X				4D WTA	TCP10-I	5A	none
7-63	X				7D WTA	TCP10-I	4A	none
7-64		X			1D WTA	TCP10-I	5A	none
7-65		X			4D WTA	TCP10-I	5A	~15 #8 blisters along one edge
7-66		X			7D WTA	TCP10-I	5A	none
7-67			X		1D WTA	TCP10-I	5A	none
7-68			X		4D WTA	TCP10-I	5A	none
7-69			X		7D WTA	TCP10-I	5A	none
7-70				X	1D WTA	TCP10-I	5A	none
7-71				X	4D WTA	TCP10-I	5A	none
7-72				X	7D WTA	TCP10-I	5A	none
7-73	X				1D WTA	TCP10M2-W	0A	none
7-74	X				4D WTA	TCP10M2-W	5A	~15 #8 blisters in two small areas
7-75	X				7D WTA	TCP10M2-W	5A	~50 #8#10 blisters in streaks on coupon ends
7-76		X			1D WTA	TCP10M2-W	2A	none
7-77		X			4D WTA	TCP10M2-W	4A	streaks of #8#10 blisters on ~10% of panel
7-78		X			7D WTA	TCP10M2-W	3A	streaks of #8#10 blisters on ~75% of panel

TABLE G-continued

Examples 7-1 through 7-53
Columns 2–9

7075-TB Panel	2 SPT	3 23377	4 85582	5 85582N	6 Test	7 Pretreat	8 Adhesion Rating	9 Blistering
7-79			X		1D WTA	TCP10M2-W	5A	none
7-80			X		4D WTA	TCP10M2-W	5A	none
7-81			X		7D WTA	TCP10M2-W	5A	none
7-82				X	1D WTA	TCP10M2-W	5A	none
7-83				X	4D WTA	TCP10M2-W	5A	none
7-84				X	7D WTA	TCP10M2-W	5A	none
7-85	X				1D WTA	TCP10M2-S	4A	none
7-86	X				4D WTA	TCP10M2-S	4A	none
7-87	X				7D WTA	TCP10M2-S	4A	none
7-88		X			1D WTA	TCP10M2-S	5A	none
7-89		X			4D WTA	TCP10M2-S	5A	row of #10 blisters along one edge (streak)
7-90		X			7D WTA	TCP10M2-S	5A	none
7-91			X		1D WTA	TCP10M2-S	5A	none
7-92			X		4D WTA	TCP10M2-S	5A	none
7-93			X		7D WTA	TCP10M2-S	5A	none
7-94				X	1D WTA	TCP10M2-S	5A	none
7-95				X	4D WTA	TCP10M2-S	5A	none
7-96				X	7D WTA	TCP10M2-S	5A	none
7-97	X				1D WTA	TCP10M2-I	4A	none
7-98	X				4D WTA	TCP10M2-I	5A	none
7-99	X				7D WTA	TCP10M2-I	4A	none
7-100		X			1D WTA	TCP10M2-I	3A	none
7-101		X			4D WTA	TCP10M2-I	3A	line of #10 blisters along center of coupon and edge
7-102		X			7D WTA	TCP10M2-I	3A	none
7-103			X		1D WTA	TCP10M2-I	5A	none
7-104			X		4D WTA	TCP10M2-I	5A	none
7-105			X		7D WTA	TCP10M2-I	5A	none
7-106				X	1D WTA	TCP10M2-I	5A	none
7-107				X	4D WTA	TCP10M2-I	5A	none
7-108				X	7D WTA	TCP10M2-I	5A	none

The data in Table H shows aluminum coupons (7075-T6) treated with the trivalent chromium pretreatment (TCP-10M2) of this invention.

TABLE H

Examples 7-1 through 7-37

7075-TB Panel	1 SPT	2 23377	3 85582	4 85582N	5 Test	6 Pretreat	7 Results
7-1	X				2000 hr nsf	Accelagold-S	10 (s.c.), 10, 10
7-2	X				2000 hr nsf	Accelagold-S	10 (s.c.), 10, 10
7-3	X				2000 hr nsf	Accelagold-S	10 (s.c.), 10, 10
7-4	X				2000 hr nsf	Accelagold-S	10 (s.c.), 10, 10
7-5	X				2000 hr nsf	Accelagold-S	10 (s.c.), 10, 10
7-6	X				500 hr SO_2	Accelagold-S	5, 10, 10
7-7	X				500 hr SO_2	Accelagold-S	5, 10, 10
7-8	X				500 hr SO_2	Accelagold-S	5, 10, 10
7-9	X				500 hr SO_2	Accelagold-S	5, 10, 10
7-10	X				500 hr SO_2	Accelagold-S	5, 10, 10
7-11		X			2000 hr nsf	Accelagold-S	10 (n.e.c.), 10, 10
7-12		X			2000 hr nsf	Accelagold-S	10 (n.e.c.), 10, 10
7-13		X			2000 hr nsf	Accelagold-S	10 (n.e.c.), 10, 10
7-14		X			2000 hr nsf	Accelagold-S	10 (n.e.c.), 10, 10
7-15		X			2000 hr nsf	Accelagold-S	10 (n.e.c.), 10, 10
7-16		X			500 hr SO_2	Accelagold-S	NA
7-17		X			500 hr SO_2	Accelagold-S	NA
7-18		X			500 hr SO_2	Accelagold-S	NA
7-19		X			500 hr SO_2	Accelagold-S	NA
7-20		X			500 hr SO_2	Accelagold-S	NA
7-21			X		2000 hr nsf	Accelagold-S	10 (n.e.c.), 10, 10
7-22			X		2000 hr nsf	Accelagold-S	10 (s.c.), 10, 10
7-23			X		2000 hr nsf	Accelagold-S	10 (s.c.), 10, 10
7-24			X		2000 hr nsf	Accelagold-S	10 (n.e.c.), 10, 10
7-25			X		2000 hr nsf	Accelagold-S	10 (n.e.c.), 10, 10
7-26			X		500 hr SO_2	Accelagold-S	NA
7-27			X		500 hr SO_2	Accelagold-S	NA

TABLE H-continued

Examples 7-1 through 7-37

7075-TB Panel	1 SPT	2 23377	3 85582	4 85582N	5 Test	6 Pretreat	7 Results
7-28			X		500 hr SO_2	Accelagold-S	NA
7-29			X		500 hr SO_2	Accelagold-S	NA
7-30			X		500 hr SO_2	Accelagold-S	NA
7-31				X	2000 hr nsf	Accelagold-S	10 (s.c.), 10, 10
7-32				X	2000 hr nsf	Accelagold-S	10 (s.c.), 10, 10
7-33				X	2000 hr nsf	Accelagold-S	10 (s.c.), 10, 10
7-34				X	2000 hr nsf	Accelagold-S	10 (s.c.), 10, 10
7-35				X	2000 hr nsf	Accelagold-S	10 (s.c.), 10, 10
7-36				X	500 hr SO_2	Accelagold-S	NA
7-37				X	500 hr SO_2	Accelagold-S	NA
7-38				X	500 hr SO_2	Accelagold-S	NA
7-39				X	500 hr SO_2	Accelagold-S	NA
7-40				X	500 hr SO_2	Accelagold-S	NA
7-41	X				2000 hr nsf	TCP10M2-S	10 (50% n.e.c.), 10, 10
7-42	X				2000 hr nsf	TCP10M2-S	10 (50% n.e.c.), 10, 10
7-43	X				2000 hr nsf	TCP10M2-S	10 (50% n.e.c.), 10, 10
7-44	X				2000 hr nsf	TCP10M2-S	10 (50% n.e.c.), 10, 10
7-45	X				2000 hr nsf	TCP10M2-S	10 (50% n.e.c.), 10, 10
7-46	X				500 hr SO_2	TCP10M2-S	4, 10, 10
7-47	X				500 hr SO_2	TCP10M2-S	4, 10, 10
7-48	X				500 hr SO_2	TCP10M2-S	4, 10, 10
7-49	X				500 hr SO_2	TCP10M2-S	4, 10, 10
7-50	X				500 hr SO_2	TCP10M2-S	4, 10, 10
7-51		X			2000 hr nsf	TCP10M2-S	10 (n.e.c.), 10, 10
7-52		X			2000 hr nsf	TCP10M2-S	10 (n.e.c.), 10, 10
7-53		X			2000 hr nsf	TCP10M2-S	10 (n.e.c.), 10, 10
7-54		X			2000 hr nsf	TCP10M2-S	10 (n.e.c.), 10, 10
7-55		X			2000 hr nsf	TCP10M2-S	10 (n.e.c.), 10, 10
7-56		X			500 hr SO_2	TCP10M2-S	NA
7-57		X			500 hr SO_2	TCP10M2-S	NA
7-58		X			500 hr SO_2	TCP10M2-S	NA
7-59		X			500 hr SO_2	TCP10M2-S	NA
7-60		X			500 hr SO_2	TCP10M2-S	NA
7-61			X		2000 hr nsf	TCP10M2-S	10 (n.e.c.), 10, 10
7-62			X		2000 hr nsf	TCP10M2-S	10 (n.e.c.), 10, 10
7-63			X		2000 hr nsf	TCP10M2-S	10 (n.e.c.), 10, 10
7-64			X		2000 hr nsf	TCP10M2-S	10 (s.c.), 10, 10
7-65			X		2000 hr nsf	TCP10M2-S	10 (s.c.), 10, 10
7-66			X		500 hr SO_2	TCP10M2-S	NA
7-67			X		500 hr SO_2	TCP10M2-S	NA
7-68			X		500 hr SO_2	TCP10M2-S	NA
7-69			X		500 hr SO_2	TCP10M2-S	NA
7-70			X		500 hr SO_2	TCP10M2-S	NA
7-71				X	2000 hr nsf	TCP10M2-S	10 (s.c.), 10, 10
7-72				X	2000 hr nsf	TCP10M2-S	10 (s.c.), 10, 10
7-73				X	2000 hr nsf	TCP10M2-S	10 (s.c.), 10, 10
7-74				X	2000 hr nsf	TCP10M2-S	10 (s.c.), 10, 10
7-75				X	2000 hr nsf	TCP10M2-S	10 (s.c.), 10, 10
7-76				X	500 hr SO_2	TCP10M2-S	NA
7-77				X	500 hr SO_2	TCP10M2-S	NA
7-78				X	500 hr SO_2	TCP10M2-S	NA
7-79				X	500 hr SO_2	TCP10M2-S	NA
7-80				X	500 hr SO_2	TCP10M2-S	NA

In the Examples (7-1 to 7-80) of Table H, columns 1–4 identify the paints including SPT as a self-priming top coat, 23377 as a chromated high-solids epoxy primer, 85582 as a chromated waterborne epoxy primer, and 85582N as a non-chromated waterborne epoxy primer. Column 5 shows a 500 and 2000 hour test in a neutral salt fog, with the chromium pretreatments (Column 6 —Accelagold and TCP10M2-S) of this invention. Column 7 shows the results of the corrosion test where the first rating is scribed, the second is unscribed areas, and the third rating is blistering wherein all the ratings range from 1 to 10 with 10 representing the highest or best performance with regard to corrosion. In Table H, the terms N.E.C. indicates no evidence of corrosion and S.C. indicates surface corrosion in the scribe, but no undercutting.

For purposes of this invention, the water soluble surfactants are used in amounts ranging from about 0.0 to about 10 grams per liter and preferably about 0.5 to 2.0 grams per liter of trivalent chromium solution. The surfactants are added to the aqueous composition to provide better wetting properties by lowering the surface tension thereby insuring complete coverage and a more uniform coating on the substrate. The surfactants include at least one water soluble compound selected from the group consisting of the non-ionic, anionic, and cationic surfactants. The water soluble surfactants include the monocarboxyl imidoazoline, alkyl sulfate sodium salts (DUPONOL®, tridecyloxy poly(alkyleneoxy ethanol), ethoxylated or propoxylated alkyl phenol (IGEPAL®), alkyl sulfoamides, alkaryl sulfonates, palmitic alkanol amides (CENTROL®), octylphenyl polyethoxy ethanol (TRITON®), sorbitan monopalmitate (SPAN®), dodecylphenyl polyethylene glycol ether (e.g. TERGITROL®), alkyl pyrrolidone, polyalkoxylated fatty acid esters, alkylbenzene sulfonates and mixtures thereof. Other known water soluble surfactants are disclosed by "Surfactants and Detersive Systems", published by John Wiley & Sons in Kirk-Othmer's Encyclopedia of Chemical Technology, 3^{rd} Ed.

Where large surfaces or substrates do not permit immersion or where vertical surfaces are to be sprayed, thickening agents are used to retain the aqueous composition on the surface for sufficient contact time. The thickeners employed are known water soluble or dispersible thickeners which can be added to the trivalent chromium solution of this invention in amounts ranging from about 0.0 and about 10 grams per liter and preferably from about 0.5 to 2.0 grams per liter of the chromate solution. Specific examples of these additives include the cellulose thickeners e.g. hydroxypropyl cellulose (e.g. Klucel), ethyl cellulose, hydroxyethyl cellulose, hydroxymethyl cellulose, methyl cellulose, and some of the water soluble inorganic thickeners such as colloidal silica, clays such as bentonite, starches, colloidal alumina, gum arabic, tragacanth, agar and any combination thereof.

While this invention has been described by a number of specific examples, it is obvious that there are other variations and modifications which can be made without departing from the spirit and scope of the invention as particularly set forth in the appended claims.

The Invention claimed:

1. A process of preparing a corrosion resistant coating on aluminum, aluminum alloys and coated aluminum substrates which comprises treating said substrates at ambient temperatures with an acidic aqueous solution having a pH ranging from about 2–6 comprising, per liter of solution, from about 3.0 grams to 22 grams of a water soluble trivalent chromium salt, about 1.5 grams to 11.5 grams of an alkali metal hexafluorozirconate, from 0 to 10 grams of at least one water soluble thickener and from 0 to 10 grams of at least one water soluble surfactant selected from the group consisting of non-ionic, anionic and cationic surfactants.

2. The process of claim **1** wherein the trivalent chromium salt is trivalent chromium sulfate.

3. A The process of claim **2** wherein the alkali metal zirconate is potassium hexafluorozirconate.

4. The process of claim **3** wherein the thickener ranges from about 0.5 to 2.0 grams per liter of the aqueous solution and the surfactant ranges from about 0.5 to 2.0 grams per liter of the aqueous solution.

5. The process of claim **2** wherein the trivalent chromium sulfate ranges from about 3.0 to 12 grams per liter of aqueous solution and the alkali metal hexafluorozirconate ranges from about 3.0 to 9 grams per liter of the aqueous solution.

6. The process of claim **2** wherein the alkali metal zirconate is sodium hexafluorozirconate.

7. The process of claim **1** wherein the acidic aqueous solution has a pH ranging from about 3 to 4.

8. An acidic aqueous solution having a pH ranging from about 2–6 for preparing corrosion-resistant coatings on aluminum and aluminum alloys which comprises, per liter of solution, from about 3.0 grams to 22 grams of a water soluble trivalent chromium sulfate, about 1.5 grams to 11.5 grams of an alkali metal hexafluorozirconate, from 0.5 to 2.0 grams of at least one water soluble thickener and from 0.5 to 2.0 grams of at least one water soluble nonionic surfactant.

9. The acidic aqueous solution of claim **8** wherein the trivalent chromium sulfate ranges from about 3.0 to 12 grams per liter of the aqueous solution and the alkalimetal zirconate is potassium hexafluorozirconate ranging from about 3.0 to 9 grams per liter of the solution.

10. An acidic aqueous solution having a pH ranging from about 2–6 for preparing corrosion-resistant coatings on aluminum, aluminum alloys and coated aluminum substrates consisting essentially of, per liter of solution, from about 3.0 grams to 22 grams of a water soluble trivalent chromium salt, about 1.5 grams to 11.5 grams of an alkali metal hexafluorozirconate, from 0 to 10 grams of at least one water soluble thickener and from 0 to 10 grams of at least one water soluble surfactant selected from the group consisting of nonionic, anionic and cationic surfactants.

11. The acidic aqueous solution of claim **10** wherein the alkali metal zirconate is potassium hexafluorozirconate.

12. The acidic aqueous solution of claim **10** wherein the alkali metal zirconate is sodium hexafluorozirconate.

13. The acidic aqueous solution of claim **10** wherein the water soluble thickener is a cellulose compound.

14. The acidic aqueous solution of claim **10** wherein the water soluble surfactant is a nonionic surfactant.

* * * * *