TALAT Lecture 5202

Conversion Coatings

9 pages, 1 figure

Level: Advanced I

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Objectives:

From the understanding of the aluminium surface, the key factors associated with conversion coatings on aluminium can be appreciated:

- general and local behaviour of the aluminium surface,
- range of conversion coatings and interrelationships,
- requirements of conversion coating,
- tailor-making of coatings,
- current and future issues

Prerequisites:

TALAT Lectures 5101, 5102, 5201

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5202.00   General Considerations

The introduction (TALAT Lecture 5101) has provided information on the physical, chemical and electrical properties of the surface of aluminium and its alloys; in addition the local behaviour associated with the inevitable presence of flaws has also been considered. In order to limit the persistence and activity of such defects and to limit interaction of the filmed aluminium surface with environments of various types, coating systems have been developed. In this lecture, so-called conversion coating systems are considered; these generally include inorganic coatings developed on the macroscopic aluminium surface by immersion in appropriate solutions. In reality, a specification or overall procedure is employed which probably includes degreasing, etching (pickling), conversion coating, post-treatment and ageing prior to application of an organic coating, with its required application/curing/drying procedures. In addition to the previously described schedule, various intermediate rinsing and drying stages may be recommended in order to achieve the desired performance under the particular service conditions to be experienced. Whilst recognizing the importance of the overall schedule, this lecture considers mainly the processes occurring during conversion coating development on aluminium and their impact on the performance of the material. Consequently, the general and local behaviour of the aluminium surface is considered in a range of conversion coating systems. Finally, consideration is given to current legislation, limiting use of environmentally unacceptable species, and possible future requirements.

5202.01 Definition of Conversion Coating and Requirements of Conversion Coatings

The aluminium surface, supporting its relatively thin air-formed film with associated flaws or defects, generally has good inherent corrosion resistance. However, for particular functions in selected environments, or for decoration, a requirement may be the presence of an organic coating, i.e. paint or adhesive. In order to enhance organic coating adhesion and durability, the aluminium supporting its air-formed film is treated to 'transform' or 'convert' the original film to provide a tailored or functional conversion coating.

Conversion coating may be carried out by several methods, which can be categorized broadly into two types, immersion and 'electrical'. The former includes direct immersion, spraying, rolling etc, whilst the latter implies use of impressed currents. For clarity in this lecture, only direct immersion-type processes are considered since these are most in demand. Anodizing, where anodic films are generated under constant voltage or constant current density conditions, forming inorganic coatings based on amorphous Al_2O_3, is treated elsewhere (TALAT Lecture 5203).

In considering immersion processes, generating conversion coatings, degreasing is not considered to transform the original surface. However, interestingly, so-called acid pickling or alkaline etching of aluminium does involve immersion of the originally filmed aluminium surface in a chemically reactive environment and hence, may justifiably be considered as conversion coating. Current thinking does not include etching and pickling under the category of conversion coating. In the development of metallic coatings on aluminium, various intermediate processes are involved, i.e. zincating which, perhaps, could be included in the general classification. Further, anodic electrocoating may also generate anodic alumina, sandwiched between the metal and deposited organic coating. Finally, passive films, developed by anodic polarization, could also be included in the classification. However, for simplicity and to follow current philosophy, conversion coatings are generally considered to involve immersion processes whereby the original air-formed alumina film is transformed to develop coatings significantly thicker than 2.5 nm, which have application in many areas, for example automotive, aerospace, packaging etc.

Wernick, Pinner and Sheasby (The Surface Treatment and Finishing of Aluminium and its Alloys, Fifth Edition, Volume 1, ASM International Finishing Publications Ltd, England (1987)) have defined the properties of an ideal conversion coating. A 'wish list' of the coating properties is given below:

1. The coating should be continuous over the aluminium surface.
2. The coating should be impervious to the environment.
3. Ideally, the coating should be inert or have a low environmental reactivity.
4. The presence of the coating should not promote galvanic attack on the substrate.
5. Mechanical properties of the coating are important, and it should resist damage by abrasion, scratching, etc.
6. It should bond readily to the substrate and subsequently applied coatings in the system.
7. Clearly the coating must perform the desired function, i.e. decoration or corrosion resistance.

8. The coating system must comply with current and impending environmental legislation.
9. Ideally, an individual conversion coating treatment should have very wide application.
10. The costs of conversion coating must be consistent with the product, and applicable to high tonnage, low cost materials or low tonnage, high value materials.
11. Maintenance procedures should be in place, i.e. to repair damaged regions.
12. Many other properties may be required under particular circumstances, i.e. non-electrically conducting or electrically conducting depending upon application and concern over sparking.

Having determined a 'wish list' of properties of the ideal coating, it is readily revealed that an individual coating-type will not satisfy all the requirements. Indeed, in some circumstances, the requirements may be conflicting; for example, it may be generally acceptable to employ a conversion coating system that develops an insulating coating. However, in particular locations, electrical conduction may be beneficial to avoid build up of charge and the potentially damaging effect of any consequent spark generation.

Possible conversion coating systems, satisfying some, but not all, of the properties within the 'wish list', are given below:

      a) Coatings developed by hydrothermal treatment
      b) Chromate-containing conversion coatings
      c) Chromium-free conversion coatings

The first category of coating system involves immersion of aluminium in near-neutral water at elevated temperatures, whereby various forms of alumina, for example boehmite and bayerite, can develop according to the specific circumstances. For particular capacitor applications, hydrothermal treatment of relatively pure aluminium foil is carried out in boiling water to develop an outer region of pseudoboehmite and an inner, less-well crystallized region of alumina material, probably containing more water than the outer layer. The total film thickness is of the order of 300 nm. After hydrated film formation, the aluminium is anodized to form the dielectric material for application in capacitors. Since this process is relatively specific to capacitor-type systems, it is not considered further in this lecture.

Chromate-containing conversion coatings have received wide interest and have been employed extensively. After immersion, various films have been considered to develop, including Al_2O_3 and Cr_2O_3; with the additional presence of PO_4^{3-} species in the coating bath, $CrPO_4$ also develops. This type of immersion treatment, operating at temperatures up to 70^oC, develops markedly different films from the variously hydrated aluminas formed in the first category. The chromate-containing system is examined in this lecture.

Given the environmental and toxicity problems associated with the use of chromate-type conversion coating systems, there has been a thrust to use non-chromium processes, i.e. zirconium or titanium-containing systems, or cerium, or, more recently, cerium-molybdenum systems. Important aspects of these systems are considered in this lecture.

Prior to examining individual systems, the basic requirements of a conversion coating

bath, in terms of the understanding of the reactivity of the aluminium surface are now considered (see also introductory TALAT Lecture 5101).

5202.02 Nature of the Aluminium Surface

It is appreciated that aluminium supports an air-formed oxide film of thickness about 2.5 nm. Further, the alumina film reacts in acid and alkali; in the near neutral pH range the chemical solubility of the film is relatively low, with hydration reactions proceeding in water. Thus, comparatively simple methods of converting or transforming the original aluminium surface involve chemical reaction giving rise to dissolution products, which may ultimately precipitate to develop a conversion coating. To the previous simplistic view, the influence of surface roughness and metallurgical nature, i.e. alloying elements, must be added so that a full understanding of the material and its possible chemical and electrochemical behaviour is available. Further, the design of the component may have to be considered since this will influence the geometry of the surface and the final machining will influence roughness on a subtle scale. Additionally, in converting the surface to produce a film of tailored or desired properties, persistent defects in the original material should not be present. Interestingly, novel procedures for their removal have been considered; for example, a treatment developed in Norway involves cathodic polarization of the component to remove second phase material. Whilst this does not constitute conversion coating, it is an interesting, possible initial treatment prior to conversion coating in the selected bath.

5202.03 Principles of Conversion Coating

For the systems under consideration, and particularly the chromate-containing baths, a general requirement is to stimulate interfacial reactions which lead to local pH changes and to eventual precipitation of reaction products to form the so-called conversion coating.

In a general sense, considering a metal, M, in an acid phosphate solution, corrosion of the metal, supported by the cathodic process of hydrogen evolution, leads to an increase in interfacial pH. Such alkalinity leads to the presence of HPO_4^{2-} or PO_4^{3-} in the interfacial region; such species lead to the formation of $M_2(HPO_4)_n$ or $M_3(PO_4)_n$ salts of limited solubility. Thus, the precipitated conversion coating may be a metal phosphate of the metal being treated or a further metal (M_f), whose ions have been added to the conversion coating bath. Other species may be added to the bath to accelerate coating formation by assisting oxidation of metal ions generated from dissolution of the substrate, i.e. in the case of ferrous substrates.

Examining further processes of the previous kind, an essential component of any

conversion coating bath will be species which film the surface generally, or locally 'plug' anodic or cathodic sites of activity. This basic knowledge gives rise to the concept of tailor-making of coatings, based upon the understanding of their mechanisms of development.

Specifically, for aluminium, it is recognized that in water at ambient temperatures, other than for hydration, aluminium undergoes relatively little reaction. If chromate species are added to the system, chromates are reactive to the alumina film, thus encouraging chemical dissolution. If the solution is made acid, by addition of H^+ ions, the initial chemical reaction can be enhanced. Thus, by immersion of aluminium in a solution containing chromate ions, transformation of the original air-formed film to a relatively open porous-type alumina film is possible. The rates of transformation in such solutions are relatively slow; under alkaline conditions, broadly similar processes proceed. This confirms previous suggestions that immersion of aluminium in many situations leads to transformation of original filmed surfaces to produce a 'new' film which is characteristic of the environment which aluminium has experienced.

5202.04   Further Consideration of Processes Occurring in Conversion Coating Baths

Many baths contain fluoride species which are particularly reactive or aggressive to alumina and aluminium. Indeed it has been considered that fluoride species remove the protective alumina film from the aluminium surface during initial immersion in the conversion coating bath! Thereafter, aluminium dissolution (anodic process) proceeds with Cr^{6+} reduction (cathodic process) to solid hydrated $Cr_2O_3.nH_2O$ (conversion coating) and initial hydrogen evolution.

In reality, fluoride species are reactive to the air-formed alumina and they enhance the rate of chemical reaction. However, as the film decreases in thickness, the driving force for its reformation increases; this leads to a dynamic equilibrium between chemical dissolution in the acid, fluoride-containing solution and reformation of the essentially alumina film material. The anodic process is that of Al_2O_3 formation; with the parallel cathodic process of $Cr_2O_3.nH_2O$ formation; however, importantly, the sites of $Cr_2O_3.nH_2O$ formation require definition. This arises because alumina films have a relatively high band gap and are not electrically conducting unless extremely thin, i.e. sufficiently thin for electron tunnelling.

The site of the cathodic process, dictating where deposition occurs, depends on metal purity. Generally, aluminium is associated with impurity segregates where ready electron conduction is possible. Thus, the processes involved in conversion coating growth are envisaged as follows. Initial chemical reactions of the solution species with the alumina film, thus thinning the film. As a consequence of the high field established across the film, ionic transport proceeds to reform the film (anodic process). At impurity sites, deposition of $Cr_2O_3.nH_2O$, together with any hydrogen evolution (cathodic process), proceeds. The coating, developed at cathodic sites, spreads over the surface, masking the

residual alumina film and hindering the anodic process. When the anodic process is stifled sufficiently, the coating reaches a limiting thickness of about 400 nm.

For highly pure aluminium, with relatively few impurity segregates, sites of ready electron conduction are in poor supply. For this situation, the chemical reaction of fluoride species with the alumina film proceeds to give an alumina film of reduced thickness, which enables electron tunnelling. Thus, coating formation proceeds as considered previously, although the detailed mechanism is subtley different from that of 'less-pure' aluminium.

Given the previous information, the basic models for chromate-containing films, developed in the presence of fluoride species, can be generated (**Figure 5202.04.01**). With changes of bath formulation, the detailed morphology and composition of the film can be amended although structurally the films are composed largely of amorphous, hydrated $Cr_2O_3.nH_2O$ with an underlying, thin Al_2O_3 layer which has been penetrated by fluoride species. In the presence of phosphate species, generating the very important and very widely-used chromate-phosphate conversion coating system, the $Cr_2O_3.nH_2O$ material is replaced largely by solid chromium phosphate of unknown water content.

Further developments of the above processes include no-rinse processes which are applied to continuous strip. The conversion coating is applied to the pretreated aluminium strip, with no rinsing operations, thereby limiting environmental pollution. The coating formulations are altered markedly from the normal immersion-type processes, with the addition of organic material and silica. Precise mechanisms of formation are currently awaited as is detailed understanding of coating morphology, composition and structure.

Model of Fluoride-Containing Chromate Conversion Coating Formation   5202.04.01
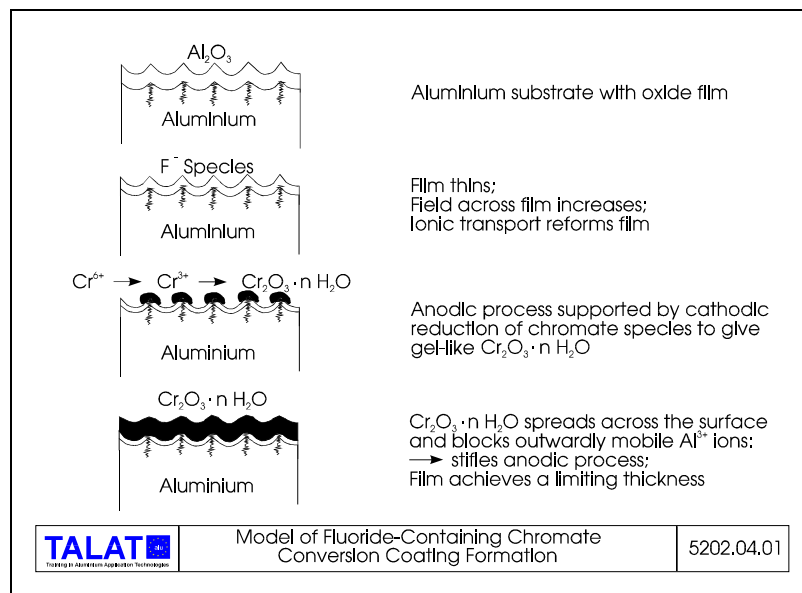
5202.05   Chromium-Free Conversion Coatings

In order to avoid contact of chromium compounds with foodstuffs, as well as previously highlighted environmental aspects, alternative processes have been developed, giving rise to zirconium or titanium-containing conversion coating bath formulations. The resultant

corrosion resistance of the coatings is not considered to match that of chromate coatings, limiting their widespread applicationHowever, in the container industry, they limit staining of aluminium and provide suitable adhesion of lacquers and protective interior coatings.

The conversion coating bath contains fluoride species as well as zirconium species, i.e. ZrF_6^{2-} ions. Clearly, the coating does not develop in a similar manner to Cr_2O_3 or $CrPO_4$ coating since ZrO_2 type material can only be produced by interfacial pH change.It has been considered that zirconium species are bonded to the hydrated aluminium film covering the aluminium surface. From in-depth elemental profiles through the resultant film, the film has been considered to be a multi-layer, with Al_2O_3 adjacent to the aluminium surface, a Zr/O/F containing outer layer and ZrO_2 sandwiched between the previous layers.

Undoubtedly, this area represents one of expanding activity, with resultant optimized bath compositions and formulations for non-chromium containing coatings. Other coatings in this broad area include silicates, cerium species, cerium-molybdenum species etc.

5202.06   Further Developments

Based on the understanding of the mechanism of aluminium reaction with particular environments, understanding of the particular requirements for conversion coating development enable baths to be optimized and real replacements for chromate to be considered across many application areas. Areas of possible future interest may include dry technology, i.e. increasing use of vacuum technology and, of course, the possibility of fabrication for minimal surface treatment.

Additionally, and of major importance, detailed understanding of adhesion of organic films to the conversion coating is required. Such knowledge will then provide a real thrust to tailor-makings systems for adhesion promotion and durability under service conditions. The inter-relationships between corrosion (and hydration) and adhesion require precise clarification.

5202.07   Literature

Wernick, Pinner and Sheasby: The Surface Treatment and Finishing of Aluminium and its Alloys, Fifth Edition, Volume 1, ASM International Finishing Publications Ltd, England (1987)

5202.08 List of Figures

Figure No.	Figure Title (Overhead)
5202.04.01	Model of Fluoride-Containing Chromate Conversion Coating Formation

5202.09   APPENDIX

Some Typical Conversion Coating Baths and Conditions

Various baths are highlighted in Wernick et al (referenced previously); selected baths are given here.

a) Beechnuts coatings

(i.)   5-200 mm sheet coatings produced at temperatures above 85°C by immersion of aluminium in distilled water plus hydrazine at pH 7-11 for 5-15 s.

(ii.)   Pylumin Process; aluminium immersed in sodium carbonate (7%), sodium chromate (2.3%), basic chromium carbonate (0.5%) plus sodium hydroxide (0.5%) solution at 70°C. Resistance coating used as a paint base.

a) Chromate-containing conversion coatings

(i.)   Chromate-phosphate; optimum solution range contains 20-100 g/l PO_4^{3-}, 2-6 g/l F^- and 6-20 g/l CrO_3. Optimum F^-/CrO_3 ratio is 0.27; if the phosphate content is too low the F^-/CrO_3 concentrations are critical. If the F^-/CrO_3 ratio is low, no coatings are formed; if too high the coatings are non-adherent.

Coatings obtained by spraying are thinner than those applied by immersion. The colour of the coating depends on formation conditions, with F^- concentration probably being the critical factor. Boric acid additions to the bath are also used to control the rate of formation and properties, i.e. contact resistance.

(ii.)   Chromate-fluoride conversion coatings: One bath composition is given as 3.4-4.0 g/l CrO_3, 3.0-3.5 g/l $Na_2 Cr_2O_7$ and 0.8 g/l NaF; treatment 3 minutes at pH 1.5 and 30°C. Accelerators may be added to the bath - ferricyanide. For optimum corrosion resistance, the following cycle has been recommended:

(a) clean in non-etching alkaline cleaner
(b) rinse for at least 1 minute
(c) deoxidize using chromate-sulphate deoxidizer
(d) as (b)
(e) apply MIL-C-81706, Class 1A chromate film (US Military specification for thickness and resultant corrosion resistance)
(f) as (b)
(g) air dry at 60°C

(iii)   No rinse chromate processes: coating is water based and consists of partially reduced chromic acid containing filmed silica; organic reducing agents employed; Cr^{6+}/Cr^{3+} ratio is in range 0.5-0.75 to 1; silica or silicate added to form an homogeneous colloidal solution.

(iv)   Chromate-free conversion coatings: One example gives a bath composition of 0.4 g/l K_2ZrF_6, 5.0 g/l $HzBO_3$, 10.0 g/l HNO_3 an 0.4 ml/l HNO_3 (4N); the solution pH is in the range 3-5 and, at temperatures of 50-65°C, clear coatings develop.