TALAT Lecture 5101

Surface Characteristics of Aluminium and Aluminium Alloys

13 pages, 10 figures

Basic Level

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Objectives:

- To provide a realistic view of the aluminium surface in order to understand the need for “effective“ surface treatment

Prerequisites:

- Metallurgy of aluminium

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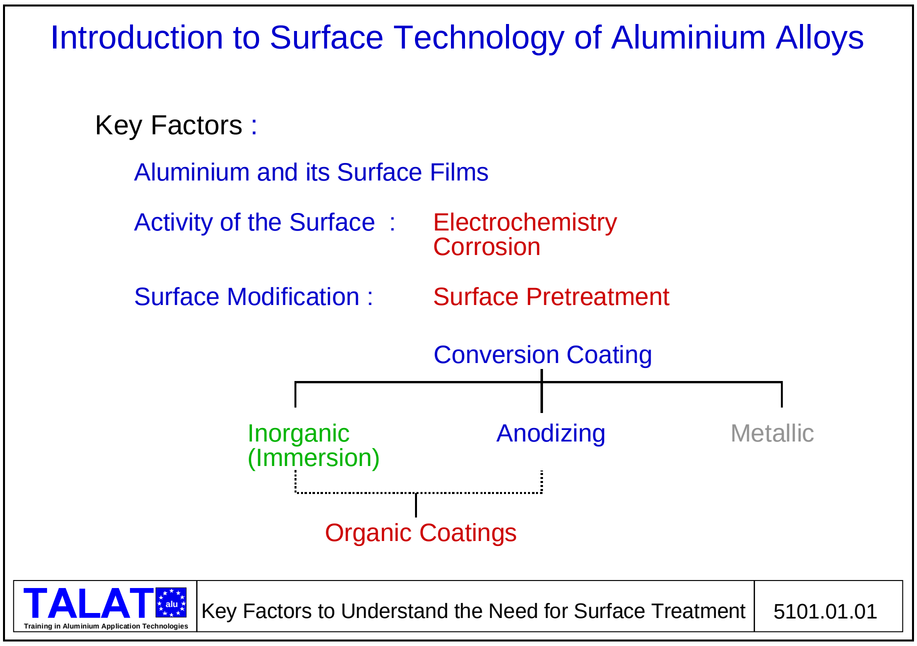
5101 Surface Characteristics of Aluminium and Aluminium Alloys

Table of Contents

5101.01 General Considerations

The use of aluminum was the subject of activity nearly 100 years ago, with limited production of aluminium powder in 1825 by Oersted. However, commercial production had to wait for more than 50 years when large scale production of aluminium was possible from alumina and molten cryolite. The necessity of electrolytic processes for the production of aluminium, utilising molten melts, signals immediately the high reactivity of the metal. Further, given the appropriate circumstances, the metal will readily return to a chemical compound, or corrosion product, similar to that from which it was originally extracted. Consequently, effective use of aluminium must be sensitive to its potential reactivity under various environmental circumstances. As a result of this reactivity, surface treatment and protection schemes have been developed, which contribute effectively to the product achieving its design life under the anticipated service conditions, aided by planned or specified maintenance schedules (**Figure 5101.01.01**).



Introduction to Surface Technology of Aluminium Alloys

Key Factors :

Aluminium and its Surface Films

Activity of the Surface : Electrochemistry
Corrosion

Surface Modification : Surface Pretreatment

Conversion Coating

Inorganic (Immersion)
Anodizing
Metallic

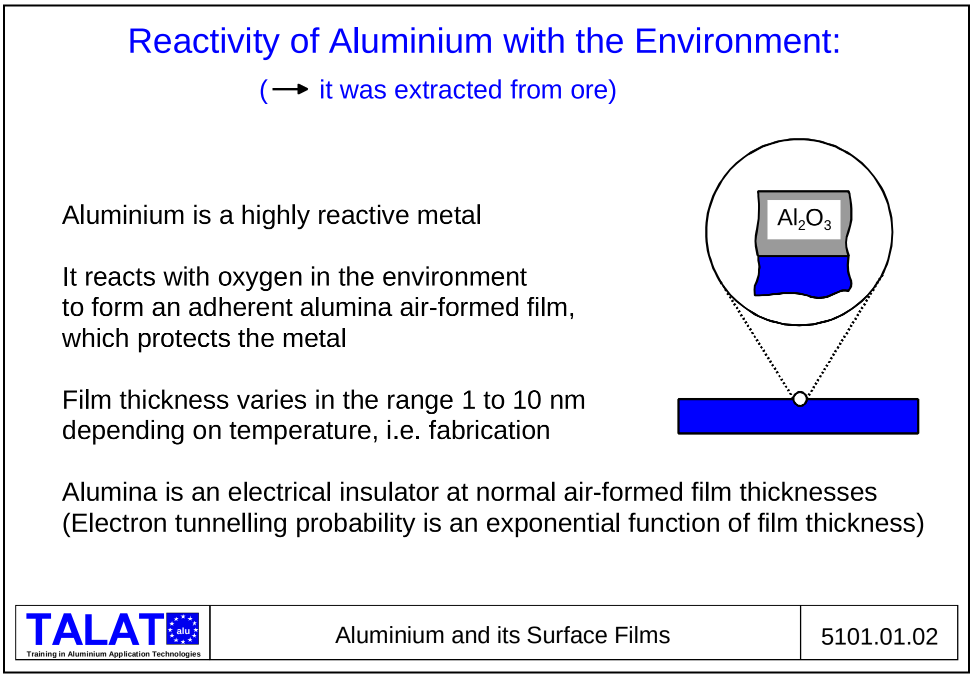
Organic Coatings

TALAT Training in Aluminium Application Technologies | Key Factors to Understand the Need for Surface Treatment | 5101.01.01

It is well known that aluminium has a comparatively low density and sufficient mechanical strength, particularly when alloyed, to provide a range of alloys of high strength to weight ratio. Efforts continue to develop new alloys (bulk modification), altered surface regions (surface modification) and aluminium matrix composites (advanced materials) with high strength to weight ratio and increased stiffness such that the section thickness of the material in a particular application can be reduced further than presently possible. Thus, whilst many established surface treatment and protection schedules are possible, these must be sensitive to the exacting demands placed on advanced materials based on aluminium.

Given the high strength to weight ratio of aluminium alloys, which is of particular value in aerospace, other important properties include high thermal and electrical conductance and high reflectivity. In addition to aerospace, many applications involving the latter properties are obvious and include electric power distribution. Furthermore, aluminium has widespread use in chemical and food processing and beverage industries; clearly in such cases any surface treatment must not lead to degradation of the overall protection scheme and the unwanted presence of aluminium ions in the process stream or product. For example, the ductility of aluminium is beneficial in beverage can production; however the material performance in beverages of widely differing pH values must be consistent with the demanded shelf-life.

Reference was made previously to the expected high reactivity of aluminium; this is indeed true but, fortunately, exposure of aluminium in many circumstances leads to the rapid production of an air-formed film of alumina (**Figure 5101.01.02**). At ambient temperatures, the film developed is amorphous but, for formation conditions at and above 500^o C, both amorphous and crystalline aluminas are present. Considering the amorphous film developed on aluminium at room temperature, this readily achieves a limiting thickness of about 2.5 nm, thereby stifling further oxidation of the substrate.



Reactivity of Aluminium with the Environment:

(→ it was extracted from ore)

Aluminium is a highly reactive metal

It reacts with oxygen in the environment
to form an adherent alumina air-formed film,
which protects the metal

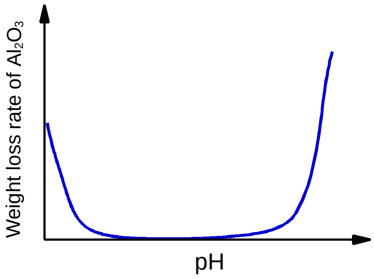
Film thickness varies in the range 1 to 10 nm
depending on temperature, i.e. fabrication

Alumina is an electrical insulator at normal air-formed film thicknesses
(Electron tunnelling probability is an exponential function of film thickness)

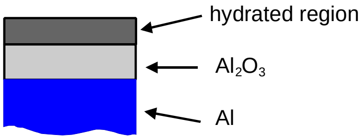
TALAT Training in Aluminium Application Technologies	Aluminium and its Surface Films	5101.01.02

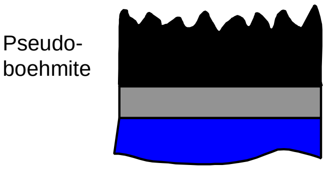
Depending on the particular circumstances, the established film will react further with the environment; thus, hydration of the outer surface of the alumina film can proceed to develop multi-layered films (**Figure 5101.01.03**). However, regardless of surface hydration, the relative loss of aluminium to reaction product is small. The presence of these protective films on aluminium can be readily demonstrated by immersion of aluminium in an aqueous mercurous chloride solution. Generally, aluminium will remain in the solution without reaction; however, if the material is scratched, allowing solution access to the bare metal, amalgamation of aluminium with mercury proceeds rapidly. Amalgamation continues, undermining the air-formed film, which eventually is released from the substrate and floats to the surface of the solution; consequently, the substrate, having ′lost′ its protective film, reacts rapidly with mercury with large quantities of aluminium lost to the solution as metal ions. In other words, rapid corrosion of aluminium proceeds in the absence of the protective alumina film.

- The alumina film reacts with acids and alkalis →



- The film hydrates even in minimum solubility range
- Wide range of Al_2O_3 depending on temperature and environment
- Films have various water contents or discrete structures:



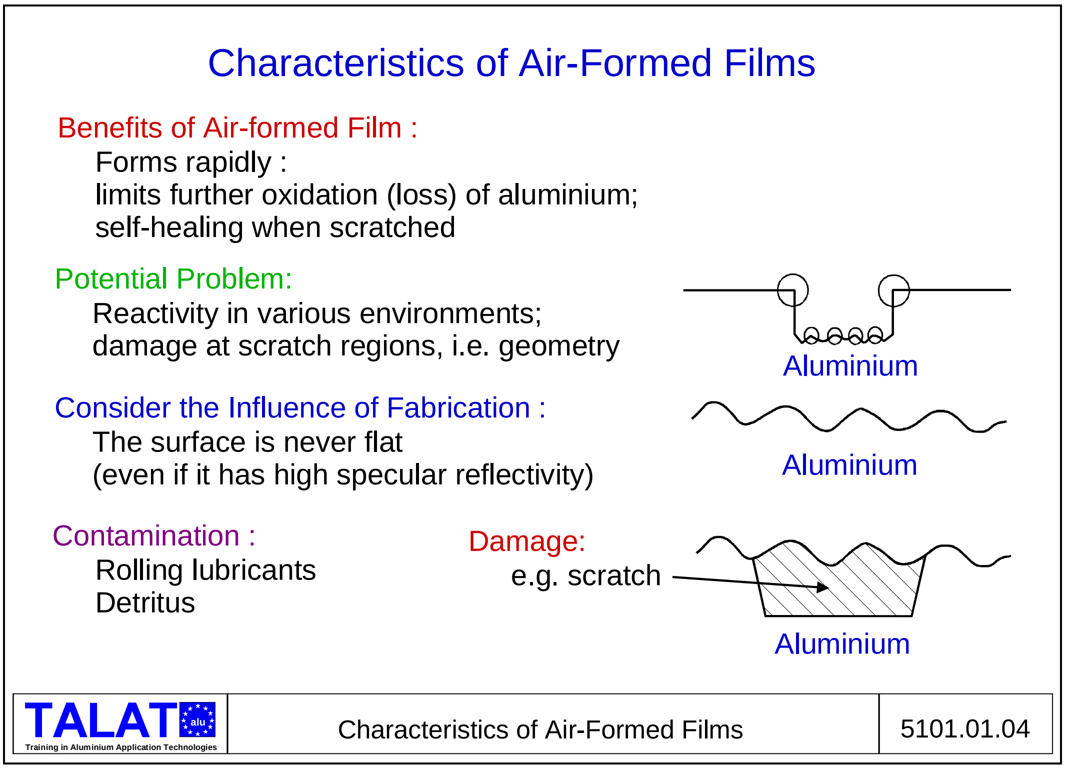


Moist environment ⇔ Bayerite ⇔ Immersion in boiling water

Residual films may still render "protection" to substrate, but will continue to "react" in their environment: water staining, atmospheric pollutants !

TALAT Training in Aluminium Application Technologies | Stability of Aluminium Oxide Films | 5101.01.03

The high affinity of aluminium for oxygen, resulting in development of alumina films, also ensures that similar films will develop in damaged or scratched regions of the substrate. Thus, at face value, an ideal situation arises where the metal is protected by a very thin, self-repairing aluminium film. However, in real-life, the ideal situation of perfection over the macroscopic aluminium surfaces is rarely, if ever, achieved. Thus, defects of various kinds, generally called flaws, are present in the air-formed film on the aluminium surface. In reality, whilst the total area occupied by such flaws is low, processes proceeding at them largely determine the effective behaviour of aluminium.Consequently, surface treatments must recognise the role of flaws in dictating to a large extent the behaviour of aluminium; furthermore, the individual or combination of surface treatments employed in aluminium finishing must bridge over such features, limiting physically their activities and/or must provide a chemical/electrochemical means for inhibiting processes that proceed at flaws which would otherwise impair the successful application of aluminium in many environmental circumstances (**Figure 5101.01.04** and **Figure 5101.01.05**).



Characteristics of Air-Formed Films

Benefits of Air-formed Film :

Forms rapidly :
limits further oxidation (loss) of aluminium;
self-healing when scratched

Potential Problem:

Reactivity in various environments;
damage at scratch regions, i.e. geometry

Consider the Influence of Fabrication :

The surface is never flat
(even if it has high specular reflectivity)

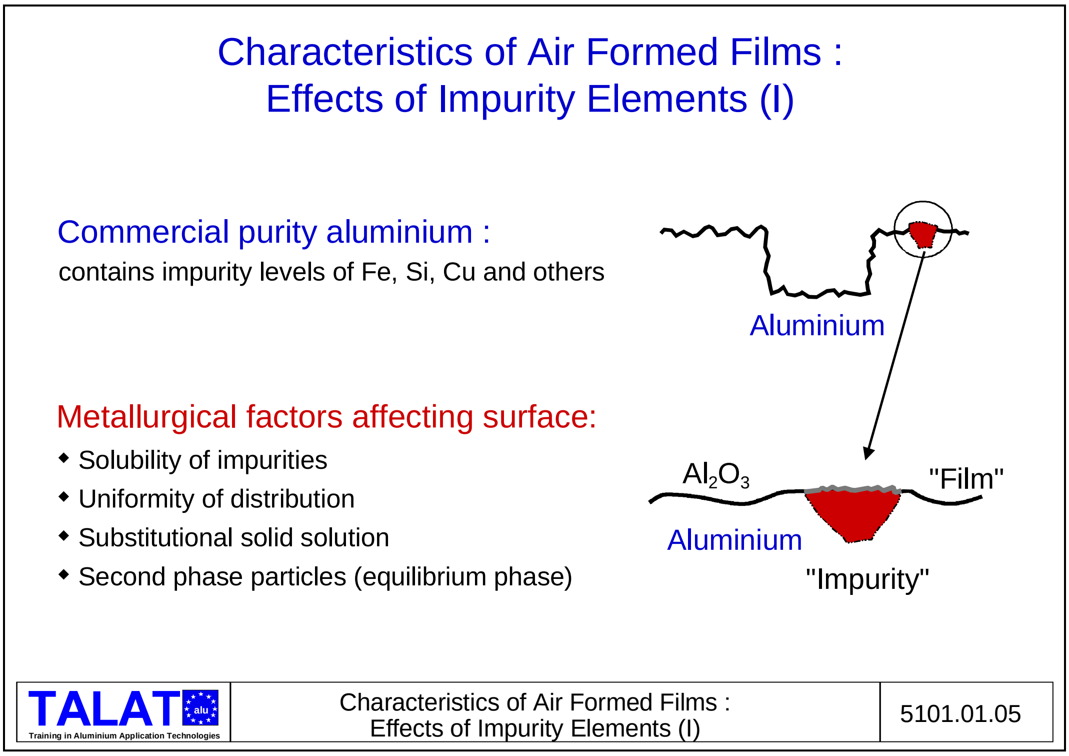
Contamination :

Rolling lubricants
Detritus

Damage:

e.g. scratch

TALAT Training in Aluminium Application Technologies | Characteristics of Air-Formed Films | 5101.01.04



Characteristics of Air Formed Films : Effects of Impurity Elements (I)

Commercial purity aluminium :

contains impurity levels of Fe, Si, Cu and others

Metallurgical factors affecting surface:

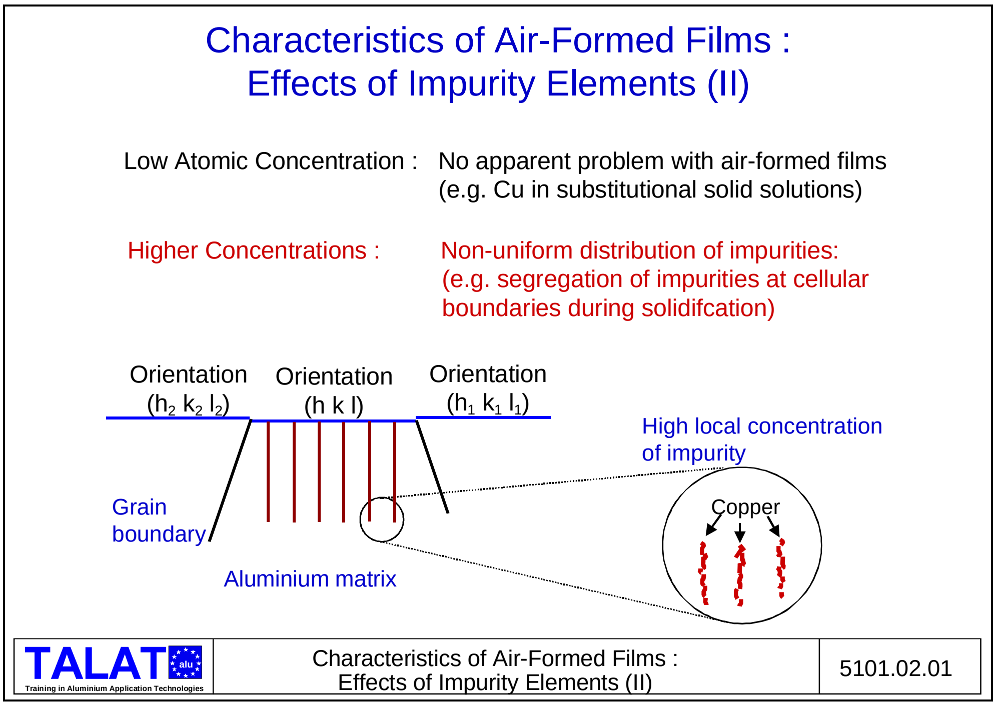
- Solubility of impurities
- Uniformity of distribution
- Substitutional solid solution
- Second phase particles (equilibrium phase)

TALAT Training in Aluminium Application Technologies | Characteristics of Air Formed Films : Effects of Impurity Elements (I) | 5101.01.05

5101.02 The Surface Nature of Aluminium

- Towards a realistic description of the aluminium surface
- Deliberate alloying
- Corrosion processes

On the microscopic level, aluminium has a close packed, face centred cubic arrangement of atoms comprising the unit cell. In a given grain, the unit cells are arranged in a systematic manner to provide the macroscopic material. Additionally, for the bulk material, many different grains and their grain boundaries intersect the material surface. Such grains develop during casting and can be influenced markedly by cooling rate; the distribution of grains is also affected by rolling and subsequent heat treatment to provide the fabricated material. Thus, the material, in its simplest form, comprises grains of aluminium of various orientations separated by their grain boundaries; clearly above the grains, the air-formed film is present, providing a barrier between the outside environment and the aluminium substrate (**Figure 5101.02.01**). However, it should also be realized that the macroscopic surface will be relatively rough with undulations in the surface resulting from the particular fabrication process employed. Thus, so far, it is evident that a microscopically rough surface is present, with macroscopic effects due to different grain orientations intersecting the surface; the grains are also separated by grain boundaries which intersect the surface.


Characteristics of Air-Formed Films :
Effects of Impurity Elements (II)

Low Atomic Concentration : No apparent problem with air-formed films
(e.g. Cu in substitutional solid solutions)

Higher Concentrations : Non-uniform distribution of impurities:
(e.g. segregation of impurities at cellular boundaries during solidifcation)

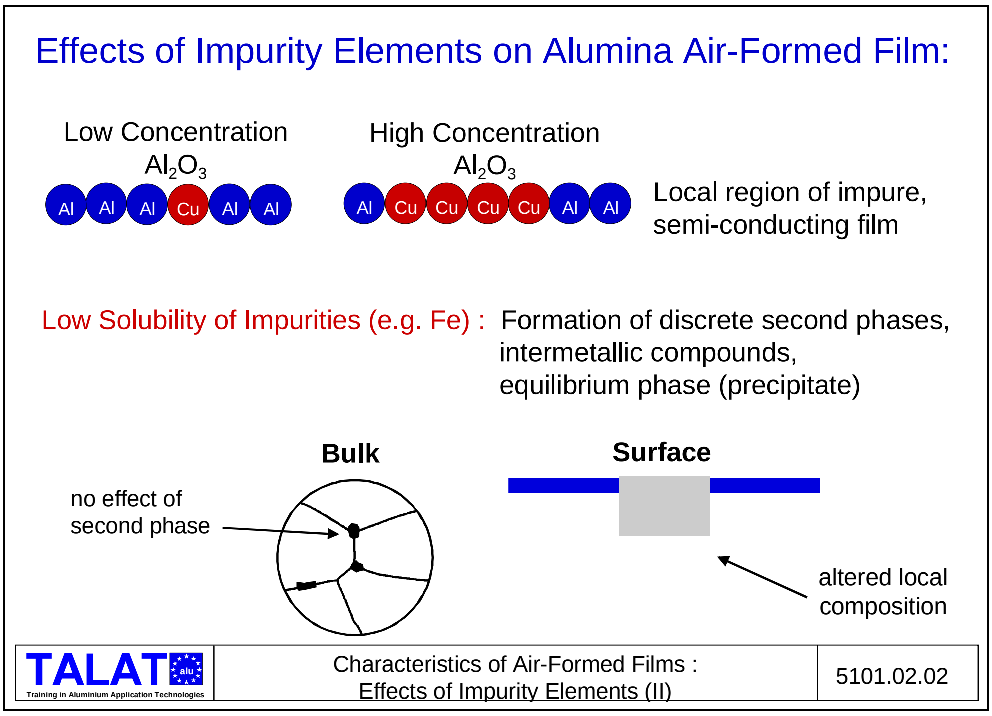
Characteristics of Air-Formed Films :
Effects of Impurity Elements (II)

5101.02.01

Various lubricating fluids are employed in fabrication processes resulting in organic contaminations at the surface. Additionally, impurities may be rolled into the surface providing further regions of locally altered chemistry.

Deliberate Alloying

Whilst there is a requirement for relatively pure aluminium, high tonnage use generally involves aluminium alloys with their improved mechanical properties. Several effects can arise from alloying which must be considered in surface treatment and material durability under service conditions. Firstly, alloying additions may be present in substitutional solid solution in the aluminium matrix; however, once the primary solid solubility is exceeded, second phase or intermetallic constituents will develop (**Figure 5101.02.02**). However, for the age-hardening alloys, comparatively fine intermediate phases, responsible for significant strengthening, also precipitate; controlled precipitation, or age-hardening, provides relatively high strength alloys with appropriate temperature stability for specified applications. A final category of alloying effect is associated with the common impurity elements in aluminium; aluminium is frequently associated with copper, silicon and iron. Iron has a very low solid solubility in aluminium and thus, in commercial purity materials, is present as distinct second phase material of relatively coarse nature.


Effects of Impurity Elements on Alumina Air-Formed Film:

Low Concentration Al_2O_3

High Concentration Al_2O_3

Local region of impure, semi-conducting film

Low Solubility of Impurities (e.g. Fe) : Formation of discrete second phases, intermetallic compounds, equilibrium phase (precipitate)

Bulk

no effect of second phase

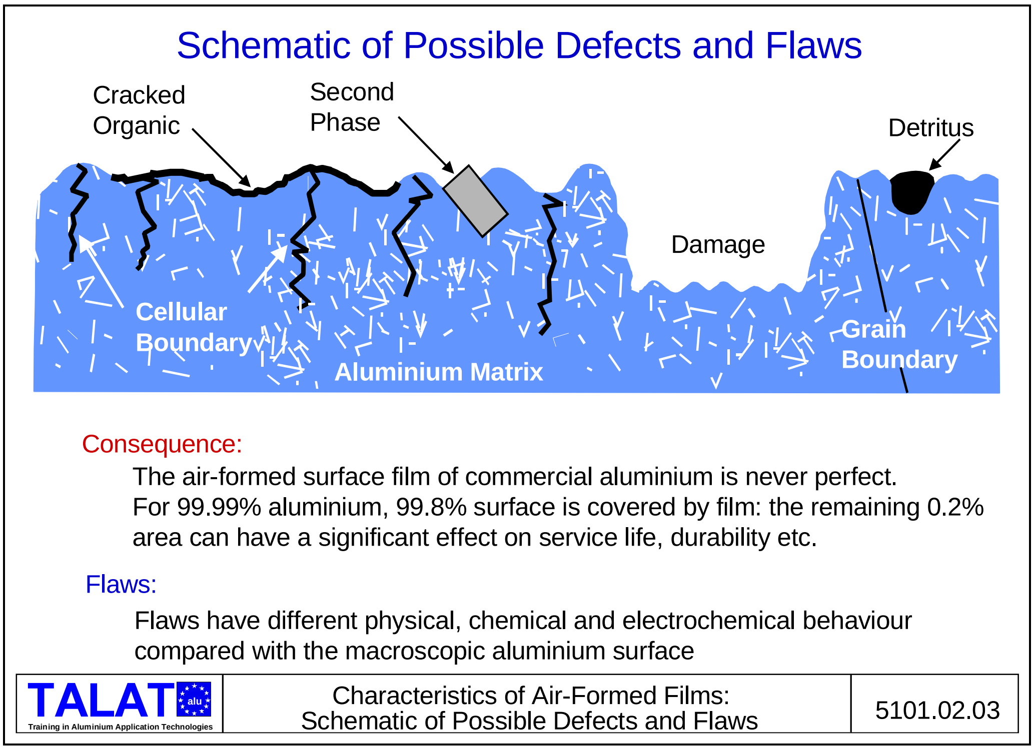
Surface

altered local composition

TALAT Training in Aluminium Application Technologies | Characteristics of Air-Formed Films : Effects of Impurity Elements (II) | 5101.02.02

In reality, the surface nature of an aluminium alloy, selected for appropriate mechanical properties and durability under service conditions, is far more complex than the relatively simple pure aluminium. Various features need to be considered further, which are listed below (see also **Figure 5101.02.03**):

1. Grain size, orientation and distribution.
2. Alloying additions and location, e.g. solid solutions, fine precipitates in age-hardening alloys, coarse equilibrium phases or finer eutectics, intermetallic particles.
3. Impurity segregation through casting and fabrication.
4. Surface roughness through fabrication, i.e. rolling or machining.
5. Surface stresses as a result of final fabrication processes which may encourage disruption or retention of second phase in the near-surface regions of the alloy.
6. Contamination with oils or other hydrocarbons.
7. Incorporation of alloying elements into the air-formed film.


Schematic of Possible Defects and Flaws

Consequence:

The air-formed surface film of commercial aluminium is never perfect.
For 99.99% aluminium, 99.8% surface is covered by film: the remaining 0.2% area can have a significant effect on service life, durability etc.

Flaws:

Flaws have different physical, chemical and electrochemical behaviour compared with the macroscopic aluminium surface

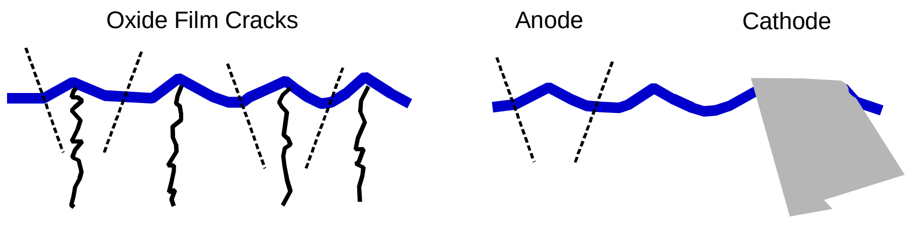
TALAT Training in Aluminium Application Technologies
Characteristics of Air-Formed Films: Schematic of Possible Defects and Flaws
5101.02.03

For a pure material, in single crystal form, the distribution of high energy or potentially active sites on the surface is relatively clear. Thus, in corrosion or metal dissolution, loss of metal ions occurs preferentially from kink sites at the surface or ledge sites as opposed to the lower energy terrace sites. However, for aluminium alloys, supporting their air-formed films, any additional features arising influence particularly the activity of local regions at the surface.

Corrosion Processes

Corrosion of aluminium, whereby the aluminium metal effectively returns to the inorganic compound form or, more precisely, to aluminium ions in an aqueous phase at the surface of the material, will proceed in appropriate environments. Thus, under situations where the chemical stability of the air-formed film is altered, in low or high pH environments which are reactive to the alumina film, the metal will corrode albeit in a general or uniform manner at a relatively slow rate. In such cases, evolution of hydrogen is the supporting cathodic reaction. For alloys, where the alloying elements may be present as second phase, an increase in the rate of the cathodic process is evident which results in an increase in the rate of the anodic process of loss of aluminium from the matrix (**Figure 5101.02.04**). Furthermore, for alloys, local heterogeneities in the material morphology and composition may be highlighted giving rise to particular forms of corrosion, e.g. intergranular corrosion and exfoliation corrosion, where dissolution follows preferred paths at, or adjacent to, the grain boundaries. In situations where so-called aggressive anions are present, i.e.chloride, or in the presence of activating cations, localized corrosion of the passive metal proceeds, initiating at sites where the alumina film is breached and where healing is hindered. Clearly this is a situation to be avoided since while the extent of material loss may be small, the presence of pits may give rise to loss of product or destroy the structural integrity of the material.

Solution (environment) can ingress oxide film through cracks



Pure Aluminium

Whether corrosion attack occurs or not, depends on the type of enviroment

"Aggressive" species hinder repassivation and can cause corrosion at crack sites

Commercial Aluminium (Alloys)

"Nobler" equilibrium phases act as cathode and may cause corrosion attack at crack site

TALAT Training in Aluminium Application Technologies | Sites for Corrosion Attack | 5101.02.04

In the light of the known behaviour of aluminium and its alloys, awareness in its application has developed. Furthermore, surface treatments have been specified to ensure that the selected alloy achieves its design life in specified conditions. Such surface treatment may involve extensive processing to give a complete protection system; on the other hand, little pretreatment may be necessary in well-defined circumstances where general corrosion or weathering is accommodated by a substantial section thickness. However, in all cases, awareness of the material, its design life and the particular environmental circumstances are essential.

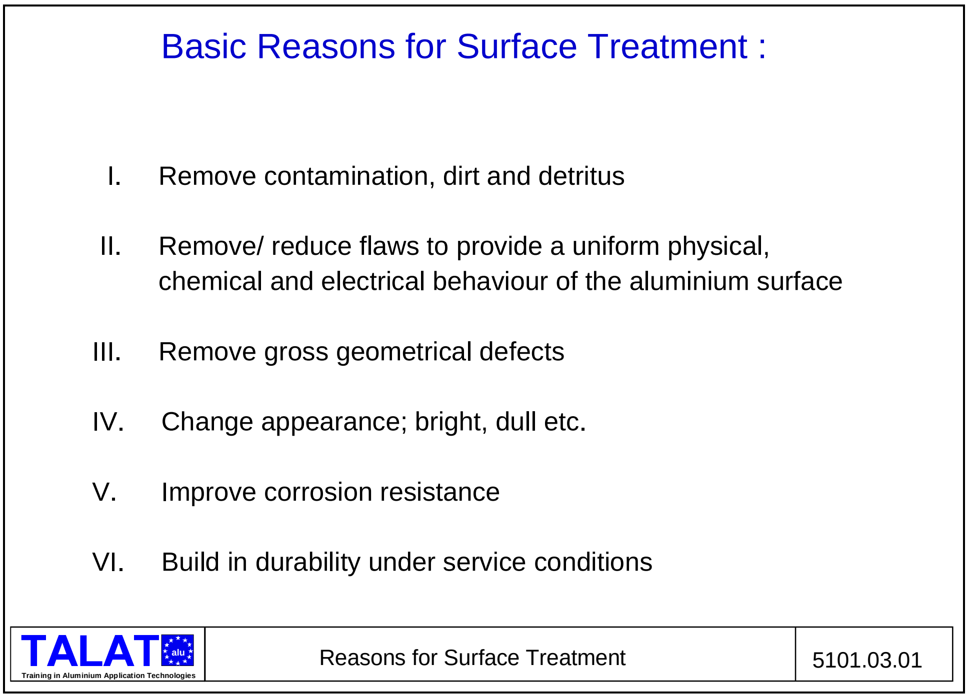
5101.03 Surface Treatment and Protection

(**Figure 5101.03.01**)

- Improvement and protection of the surface
- Applications and future trends

Improvement and Protection of the Surface

It was indicated previously that the aluminium alloy surface is relatively complex and is difficult to characterize precisely. Thus, for example, hydrocarbons present on the surface may shield the substrate giving rise to non-uniform behaviour; aesthetic reasons may also dictate removal of such contamination. Consequently, an initial reason for surface treatment is to remove such contamination and detritus. Degreasing in organic solvents or vapours has been an initial approach, but a subsequent etching treatment in alkali usually follows. Appropriate rinsing schedules must also be adopted to remove residual solution or solvent and to limit cross contamination. It should also be appreciated that electrochemical processes, such as alkaline etching, leave a residual film on the aluminium surface. A so-called desmut in nitric acid follows, which removes contaminants, but the alumina film developed in the alkali, perhaps reinforced through immersion in the acid, largely remains. In addition, such film formation over the macroscopic surface leaves a more uniform surface, with the nitric acid immersion serving to remove some residual metal impurity segregates. Such segregates may result from dissolution of second phase material, with appropriate cations relocated by deposition on the aluminium surface. Consequently, a surface with reduced local activity ensues, with a reduced driving force for corrosion in particular environments.



Basic Reasons for Surface Treatment :

I. Remove contamination, dirt and detritus

II. Remove/ reduce flaws to provide a uniform physical, chemical and electrical behaviour of the aluminium surface

III. Remove gross geometrical defects

IV. Change appearance; bright, dull etc.

V. Improve corrosion resistance

VI. Build in durability under service conditions

Reasons for Surface Treatment

5101.03.01

Other surface treatments include chromate-sulphuric acid pickling; here features similar to that of alkaline etching develop. It should also be recognised that chromate, a recognized inhibitor of aluminium corrosion is present. However, the role of chromate in acid solution is to increase the reactivity of aluminium by dissolution of the alumina-film. A resultant open-textured film develops over the aluminium surface, with reduced local activity; this film is also of importance in applications such as adhesive bonding in aerospace.

Films of significantly increased thickness can be developed on aluminium by anodizing in suitable electrolytes. Indeed with knowledge of the factors controlling film growth, compositionally- and morphologically-defined alumina films can be produced for architectural applications, adhesive bonding, magnetic recording devices etc. A major application of anodizing to produce porous anodic films has been for architectural applications; the porous material must be filled by so-called sealing to develop films of thickness of about 25 µm, which provide appropriate resistance to atmospheric corrosion and erosion. Furthermore, given a porous anodic film, it is relatively easy to impregnate such films with organic and inorganic pigments to produce decorative articles. Porous films, generally of reduced thickness, allow retention of organic layers produced by conventional or other means, for example, by electrophoresis. A well known successful application of aluminium in aerospace involves anodizing in chromic acid followed by primer coating and top coating. Clearly the organic coating assists in limiting environmental ingress to the aluminium substrate; further, inhibitive pigments within the primer coat reduce corrosion or loss of adhesion through interfacial degradation and also provide protection at damaged regions.

In addition to development of protective coatings on aluminium by anodizing or other means, surface treatments may also be employed to develop metallic coatings, i.e. electroplating of aluminium. Here it must be recognised initially that the original air-formed film is a poor electronic conductor. Thus, treatment processes have been tailored to allow widespread coverage of the plated metal rather than local plating at active sites associated with flaws.

Applications and Future Trends

The mechanical properties of aluminium are exploited in many applications including off-shore, architecture, transport, aerospace and electronics. Usage in foodstuffs, beverages and packaging is also very prominent. In all cases, awareness of the requirements of the product allow tailoring of the material for economic use. Interestingly, off-shoots of such tailoring include the development of free-standing alumina membranes with applications across many aspects of filtration; knowledge of the particular morphology of attack during pitting corrosion has led to processes such as electrograining to produce roughened aluminium surfaces in a controlled manner. Aluminium as a power source, i.e. aluminium/air batteries, is a further example where corrosion is exploited. However, in other applications, corrosion is controlled by application of appropriate protection measures. There has been a long history of such remedial treatments, providing confidence in the performance of aluminium.

Considering the future, environmental issues will have significant impact. Thus, many processes or procedures associated with the application of aluminium use chromic acid or chromates; additionally chromate pigments are widely employed as inhibitors in paints. Environmental issues are forcing change here, with tailored treatments of the aluminium surface being developed, i.e. zirconate or titanate surface treatment with organic coatings of modified binder formulations and new inhibitive (non-chromium-containing) pigments.

Surface modification of aluminium alloys is also exploited, with processes such as ion implantation and laser treatment employed. Given the widespread and diverse applications of aluminium, its extensive use will continue, with new developments always anticipated.

5101.04 Literature/References

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5101.05 List of Figures