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Effect of Anodising on the Fatigue Properties of Aluminium Alloys

Bruce R. Crawford

Air Vehicles Division
Defence Science and Technology Organisation

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ABSTRACT

Anodising has been used to modify the surfaces of aluminium and its alloys for several decades. It is used because its significantly increases the corrosion and wear resistance. However, it can also significantly reduce the fatigue endurance of these alloys. This reduction in fatigue endurance is ascribed to the acceleration of crack initiation due to the brittleness and consequent crazing of anodised layers and the presence of defects in these layers. There is also evidence that anodising also accelerates crack propagation.

This report provides an overview of the detrimental effect of anodising on the fatigue of aluminium alloys. It also describes the effects of process variables such as anodising time and anodising solution on the nature of the anodised film. Details of the fracture of anodised films under load are also discussed. Finally, some comments are made regarding the implications of this literature survey for current and future Australian Defence Force Aircraft.

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Effect of Anodising on the Fatigue Properties of Aluminium Alloys

Executive Summary

Anodising has been used to modify the surfaces of aluminium and its alloys for several decades. It is used because of the significant increases in corrosion and wear resistance it can produce. Many components in aircraft of European manufacture are anodised to reduce corrosion and wear. However, anodising is less popular with American manufacturers. The main reason for this is the reduction in the fatigue endurance caused by anodising. Chromic acid anodising, however, produces minimal or no reduction in fatigue endurance. This reduction in fatigue endurance is ascribed to the acceleration of crack initiation due to the brittleness and consequent crazing of anodised layers and the presence of defects in these layers. However, there is some evidence that anodising also accelerates crack propagation.

This report provides an overview of the detrimental effect of anodising on the fatigue of aluminium alloys. It also describes the effects of process variables such as anodising time and anodising solution on the nature of the anodised film. Details of the fracture of anodised films under load are also discussed.

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Author

Dr. Bruce R. Crawford
Air Vehicles Division

Dr. Bruce Crawford, Senior Research Scientist, graduated from Monash University in 1991 with a Bachelor of Engineering in Materials Engineering with first class honours. He subsequently completed a Doctor of Philosophy at the University of Queensland in the field of fatigue of metal matrix composite materials. Bruce then lectured on materials science and engineering for four years at Deakin University in the School of Engineering and Technology before joining DSTO in 1999. Since joining DSTO Bruce has worked on the development of deterministic and probabilistic models of corrosion-fatigue and structural integrity management for aerospace aluminium alloys. In the past six years, he has managed the certification of Retrogression and Re-ageing, a technology with the potential to significantly reduce the incidence of exfoliation corrosion and stress corrosion cracking in the 7075 T6 components of the RAAF C-130 Hercules.

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1. Introduction

Anodising has been used to modify the surfaces of aluminium and its alloys for several decades. It is used because of the significant increases in corrosion and wear resistance it can produce. Many components in aircraft of European manufacture are anodised to reduce corrosion and wear. However, anodising was historically less popular with American manufacturers who have used chromic conversion coatings instead. The main reason for this historic refusal to use anodising is the reduction in the fatigue endurance it causes. However, the carcinogenic nature of the hexavalent chromium in conversion coatings means they are now being phased out and anodising is seen as a viable replacement.

The reduction in fatigue endurance is seen for anodised layers produced using sulphuric acid, oxalic acid and phosphoric acid. Chromic acid anodising, however, has been reported as producing minimal or no reduction in fatigue endurance. The reduction in fatigue endurance due to anodising is ascribed to the acceleration of crack initiation due to the brittleness and consequent crazing of anodised layers and the presence of defects in these layers. However, there is some evidence that anodising also accelerates crack propagation.

This report provides an overview of the detrimental effect of anodising on the fatigue of aluminium alloys. It also describes the effects of process variables such as anodising time and anodising solution on the nature of the anodised film. Details of the fracture of anodised films under load are also discussed. Finally, some comments are made regarding the implications of this literature survey for DSTO's research into corroded aircraft aluminium alloys.

2. The Nature of Anodising Process Specifications

It should be noted that in the last decade or so that generic anodising specifications, such as the US standard MIL-A-8625F [1], have become performance standards rather than prescriptive standards. As such as long as an anodised surface is able to pass a series of prescribed tests it is considered to have been successfully anodised. For example, MIL-A-8625F requires testing of the anodised coating thickness, its weight, corrosion resistance, light fastness, abrasion resistance and paint adhesion. It also prescribes acceptable values for these tests. However, it does not prescribe a set of processing conditions to achieve these requirements. This is left to the anodiser.

In response to these generic performance specifications, original equipment manufacturers (OEMs) have developed proprietary anodising treatments to meet the required properties. However, the exact processing conditions used by each OEM are likely to vary. Airbus, Boeing, Lockheed Martin and BAE SYSTEMS each have process specifications of this type. Unfortunately, the proprietary nature of these OEM process specifications means they cannot be discussed in this technical note.

3. The Anodising Process

Anodising is an electrochemical process in which the natural oxide layer on the surface of aluminium alloys is artificially thickened. This causes an increase in both corrosion and wear resistance. The chemical half reaction governing the anodising process is:

$$2Al + 3H_2O \rightarrow Al_2O_3 + 6H^+ + 6e^-$$

It should be noted that this reaction only describes the anodic reaction in the anodising bath. The cathodic reaction will vary depending on the particular anodising process used. There are several variants of the anodising process each of which is adapted to a particular application of anodising. The major anodising processes currently in use are:

- Chromic Acid Anodising,
- Sulphuric Acid Anodising,
- Oxalic Acid Anodising, and
- Phosphoric Acid Anodising.

Of these, chromic acid anodising is the process most commonly used on aluminium aircraft components. This is principally because it produces the least damage to the fatigue properties of aluminium alloys while still providing a worthwhile increase in corrosion resistance. In addition, the electrolyte used in this process will not cause corrosion if traces of it remain on the component after anodising is complete [2]. However, chromic acid anodising releases hexavalent chromium (Cr^{6+}), which is a powerful carcinogen, into the environment. Therefore, alternate methods, such as boric acid-sulphuric acid anodising, are currently being developed to replace chromic acid anodising [2].

Anodising is a process consisting of some or all of the following steps:

- **Mechanical preparation:** Buffing, polishing, grit blasting etc..
- **Chemical preparation:** Which includes nitric acid pickling, degreasing in organic solvents, pickling with caustic soda, electrolytic degreasing and desmutting[1]
- **Chemical polishing** or electrolytic brightening
- **Anodic oxidation**: sulphuric acid, chromic acid or oxalic acid (or other electrolytes)
- **Dyeing:** Not used for aircraft applications
- **Sealing:** Hot water immersion (sometimes with additives in solution) or steam exposure.

The above sequence represents a generic anodising process. Not all of the stages listed will be performed in a given process. In addition, a rinsing stage is typically inserted between each production stage and after the last stage. Dyeing and sealing are generally not necessary on aircraft components as colouring of the surface is not required and, in any case, chromic acid anodising produces a very thin anodised layer without the porous region. In addition, sealing

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[1] Desmutting, which is also called deoxidisation, is the process of removing 'smut' which is the residue of pickling with caustic soda (NaOH). This smut forms due to the high temperatures and chemical reactions at the surface of the material combining with residues on the surface of the material during the pickling operation. If not removed the smut can lead to patches of unanodised material on the otherwise anodised material.

has a detrimental effect on fatigue endurance. Further details of the microstructure of anodised films can be found in Section 4 of this report.

Given that anodising is an electrochemical process it is carried out in a treatment bath containing an acidic solution, the component to be anodised is made the anode and either the bath or a steel plate are used as the cathode. The solution used depends on the anodising process. The most common solutions are chromic acid, sulphuric acid and oxalic acid. The concentration of the solution and its temperature are important variables in the anodising process and will be discussed briefly below.

Unlike other electrochemical surface modification techniques, the component to be treated is not the cathode of the electrochemical cell. That is, no material is deposited onto the component's surface by electrolytic reduction. Instead, the component to be treated forms the anode of the electrochemical cell and is, therefore, being oxidised. Unlike many other materials, however, this does not cause material loss. Instead, it thickens the aluminium oxide[2] layer on the metal's surface. The thickness of the aluminium oxide layer is proportional to the duration and current of the anodising process. This is because the amount of material oxidised depends on the number of electrons removed from the aluminium during oxidation. However, there is an upper limit to how thick the anodised layer will become. The electrical resistance of the anodised layer increases as it thickens. Eventually, the resistance rises to a level which prevents further oxidation. This level depends on the anodising process used. The resistance of the oxide film is higher in chromic acid anodising and, as such, thinner films are formed [3]. This is useful as chromic acid anodising is much less sensitive to variations in anodising current than other anodising processes. This allows chromic acid anodised layers of well controlled thickness to be produced easily. This is one of the major impediments to replacing chromic acid anodising with less noxious processes such as sulphuric acid anodising.

4. Microstructure of the Anodised Layer

The anodised layer is an artificially thickened layer of aluminium oxide (Al_2O_3) on the outer surface of aluminium and its alloys. Depending on the anodising process used this film can also contain appreciable amounts (up to 14%) of sulphate, chromate and oxalate, amongst others [2]. Artificial anodised layers typically have more complicated microstructures than naturally occurring or thermally thickened layers. As shown in Figure 1, the anodised layer is divided into two regions. The first is the base layer which adheres to the surface of the aluminium component. This layer is continuous and provides the corrosion resistance. The layer above this is the columnar region which consists of a large number of hexagonal pores of approximately 0.01 to 0.05 μm in diameter [2]. This region is primarily thought to be responsible for the reduction in fatigue endurance produced by anodising. In addition to this defects in the coating can occur due to intermetallic particles on the surface of the aluminium alloy. Given that these intermetallics are not aluminium, they do not anodise and, as such,

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[2] Aluminium oxide is also known as aluminium oxide and has the chemical formula (in unhydrated form) of Al_2O_3.

they produce a defect above them. In general, however, the chemical preparation steps of the anodising process typically remove all exposed intermetallic particles to produce a continuous anodised layer.
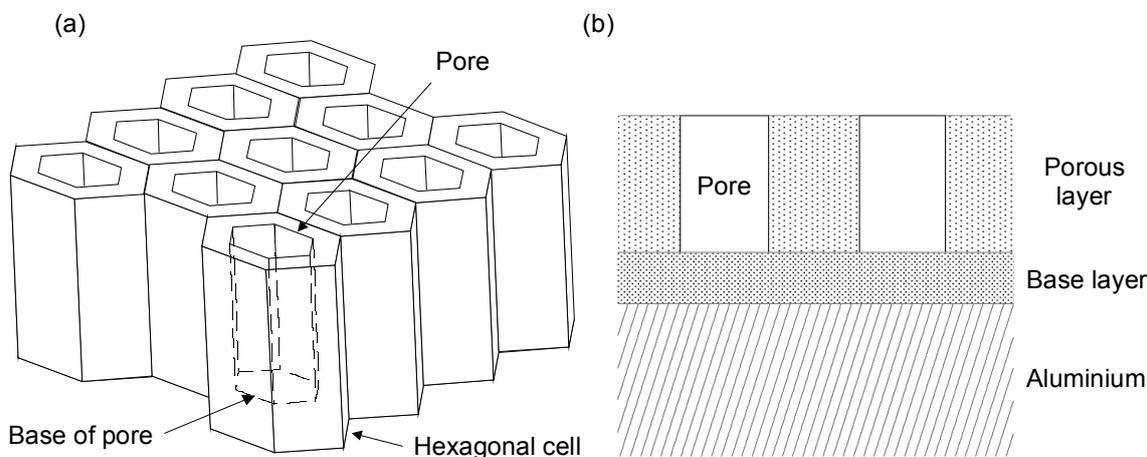

Figure 1: Schematic diagrams of the microstructure of an unsealed anodised layer. (a) Isometric view of an anodised layer showing the hexagonal cells with their central pores. (b) Cross-sectional view showing the aluminium alloy substrate, the continuous Al_2O_3 layer and the porous amorphous Al_2O_3 layer. Note that the size of the pores relative to the hexagonal cells is exaggerated for clarity.

Anodised layers are classified into three types depending on the function and the process used to form them [3]. These types, and the process used to make them, are:

1. Type I: Corrosion resistant layers – typically chromic acid anodising
2. Type II: Relatively thick decorative layers – typically sulphuric acid anodising
3. Type III: Abrasion resistant layers – typically combined sulphuric and oxalic acid anodising.

Type I anodised layers are the thinnest and often lack a porous layer. In this case, they only have the continuous film layer which provides a barrier between the substrate alloy and the surrounding environment. Type II layers are thicker than Type I and consist of the continuous base layer of Al_2O_3 with a porous layer of amorphous Al_2O_3 overlaying it. Type II layers are typically used for decorative purposes and generally have the porous layer filled with dyes or interference colouring agents to colour the film. These agents and dyes are added during the sealing process which closes the pores in the anodised film. Type III layers are the thickest and are used for applications requiring a surface with a high resistance to wear. In the case of Type III sulphuric acid anodising they are produced by using a lower solution temperature during the anodising process.

Following anodic oxidation, anodic films are porous as the hexagonal pores described above open onto the outer surface of the film. This characteristic is quite useful as it allows anodised films to be coloured by placing dyes or interference colouring agents into the pores. It is also possible to place lubricants or other such agents in these pores. If, however, the anodised film is intended for corrosion resistance then the open pores are undesirable as they will function as corrosion cells. For this reason, anodised layers are commonly sealed after anodic oxidation. This is typically achieved by immersing the anodised component into boiling water

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or playing steam over it. In some cases additives such as sodium dichromate are added to the sealing solution to further increase corrosion resistance.

Sealing closes the pores by hydrating the aluminium oxide surrounding them. This causes a volumetric expansion of this aluminium oxide which shuts the pores. In some cases the colouring agents described above are added to the sealing solution so that they are incorporated into the anodised film during the sealing process.

4.1 Effect of process variables on anodised coating microstructure

4.1.1 Solution composition

Anodising processes are commonly described in terms of the solution used to create the anodised layer. For example, most aircraft components are performed using a solution of chromic acid in a process called 'chromic acid anodising'. Other common solutions used in anodising are sulphuric acid, oxalic acid and phosphoric acid. The anodising solution dictates, to a large extent, the remaining variables of the anodising process. These include the bath temperature, the anodising voltage, current density and process duration.

The microstructure and properties of the anodised layer can be altered by modifying the composition of the anodising solution. In the case of sulphuric acid anodising, a dilution of the anodising solution combined with a decrease in anodising bath temperature from 25 °C to 20 °C results in an anodised layer that is significantly harder than that produced by conventional sulphuric acid anodising. This is the so-called 'hard anodising' process.

4.1.2 Chemical Preparation

Prior to anodising the component to be treated must be thoroughly cleaned and degreased. In addition to the removal of grease, scale from rolling or extrusion processes needs to be removed. Failure to do this will produce an oxide film that contains a large number of defects and has poor adhesion. Such a film will not provide adequate wear or corrosion resistance.

4.1.3 Process Time

Control of process time is used to determine the thickness of the oxide film produced. In general, the longer that anodising continues the thicker is the resulting oxide film. This can also change the microstructure of the film as thicker anodised layers tend to have a porous region on their outside (see Figure 1). If anodising is continued for too long at high temperatures it produces an anodic film that is powdery or perforated. This leads to poor corrosion protection properties.

4.1.4 Process Temperature

The process temperature used depends on the solution used in the anodising bath. Table 1 shows the temperature typically used for several common anodising processes. Some processes, such as the oxalic, allow a wide range of temperatures to be used while others, such as chromic acid anodising, only produce acceptable results within a narrow temperature

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range. Sulphuric acid anodising is a special case in that it works over a wide range of temperatures but produces very different coating types depending on the temperature used. At 10 to 16 °C it produces a hard colourless film, at 18 to 20 °C it produces an ordinary film and at 20 to 22 °C it produces a thick absorbent anodised film [2].

4.1.5 Process Current Density and Potential Difference

The current density and potential difference used in an anodising process are primarily dependant on the solution used in the bath. Table 1 shows typical current densities and potential differences for several of the more commonly used anodising processes.

4.1.6 Sealing process

After anodising the anodised layer is commonly sealed if it is thick enough to have a porous layer. This is achieved by inserting the sample into boiling water or by exposing it to steam. This hydrates the aluminium oxide in the outer porous section of the anodised layer which closes the pores preventing the entry and egress of material from the pores. This sealing occurs because hydrated aluminium oxide has a higher specific volume than unhydrated aluminium oxide. The sealing of the porous section is particularly important given that the hexagonal voids in the porous section of the anodised layer will form corrosion cells if exposed to a hostile environment [4]. Sealing therefore maximises the corrosion resistance of anodised films.

Table 1: Typical values of current density, potential difference and temperature used in common anodising processes. All data in this table are derived from [2].

Process[3]	Current Density (A/ft^2)	Potential Difference (V)	Temp (°C)
DC[4] Oxalic Acid	5-15	60	18 - 60
DC Sulphuric Acid (normal)	5-25	12-20	10 - 22
Hard anodising (sulphuric acid)	20-30	25-30	0 ± 2
Chromic Acid	5-10	Stepped between 20 and 50	5 - 10

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[3] Note that there is a very large number of proprietary anodising processes whose parameters vary from those in this table. The values in this table are typical values only and should not be construed as the outer limits of values used in practice.

[4] DC = Direct Current

5. Cracking of Anodised Layers Under Load

As stated previously the anodised layer consists of aluminium oxide which may be hydrated by sealing. Aluminium oxide is a ceramic and is, therefore, brittle. As a result, anodised layers tend to crack under load. Given that anodised layers are typically produced to protect the underlying surface, this fracture is undesirable.

The fracture of anodised layers has been observed under tensile [5] and bend loading [2]. It has also been observed in the vicinity of growing fatigue crack tips and has been suggested as a mechanism that accelerates crack growth [6]. The main factors that control the fracture of anodised layers are the applied strain and the thickness of the anodised layer. In general, the density of cracks in an anodised layer increases with the applied strain and the layer's thickness [5]. Given that the thickness of anodised layers is controlled largely by the anodising process this gives anodised layers produced by different anodising processes different susceptibilities to fracture.

't Hart and Nederveen [5] examined the effect of sulphuric acid, chromic acid and phosphoric acid anodised layers on the fatigue of specimens of 2024-T3 and 7075-T6. Table 3 shows the fracture strains of sulphuric and chromic acid anodised specimens of these alloys in sealed and unsealed state. As can be seen, sulphuric acid anodised layers had a lower fracture strain than chromic acid anodised layers. Phosphoric acid anodised layers did not fracture at applied stresses below the yield stress of the alloys to which they were applied. Sealing of chromic acid anodised layers further reduced the fatigue resistance of the alloys to which the layer was applied.

The density of cracks, which was defined as the number of cracks per unit length parallel to the loading direction, increased with the applied strain (see Figure 2). This increase, however, reached a plateau which varied with the substrate alloy, the anodising process and the sealing process on the anodised surface. The author of this technical note hypothesises that this plateau occurs because of a minimum effective length similar to that found with reinforcement fibres in composites. It should be noted that fracture of the oxide films was investigated using three point bending which is likely to give different results than to those from a tensile test.

Stickley found that sulphuric acid anodised layers on Alclad 2024-T3 and 7075-T6 alloys crazed[5] under tensile loads below the materials' yield stresses [7]. The applied stress at which these layers fractured decreased with increasing layer thickness. An anodised layer of 7.6 μm crazed at 193 MPa while a 25 μm layer crazed at 131 MPa. Fatigue loading caused the crazing of the anodised layer at a maximum stress of 86 MPa. This crazing did not occur on the first loading cycle but they did occur shortly thereafter. Fatigue cracks were observed to initiate from the cracks initiated in the anodised layer.

In addition to generalised crazing, anodised layers can also fracture near microstructural features of the substrate alloy. Habib [8] examined the fracture of nitric acid anodised films on

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[5] A 'crazed' surface is one that is covered with cracks at approximately regular spacing. In the current case these cracks are approximately parallel and are perpendicular to the applied loading.

a 2024 alloy. The anodised film was found to crack in the vicinity of inclusions and precipitate clusters during fatigue loading. These fracture which leads to the initiation of microcracks in the aluminium substrate, which in turn grow to macroscopic sizes. Cree and Weidmann observed that the anodised film layer fractured in the vicinity of fatigue crack tips [6].
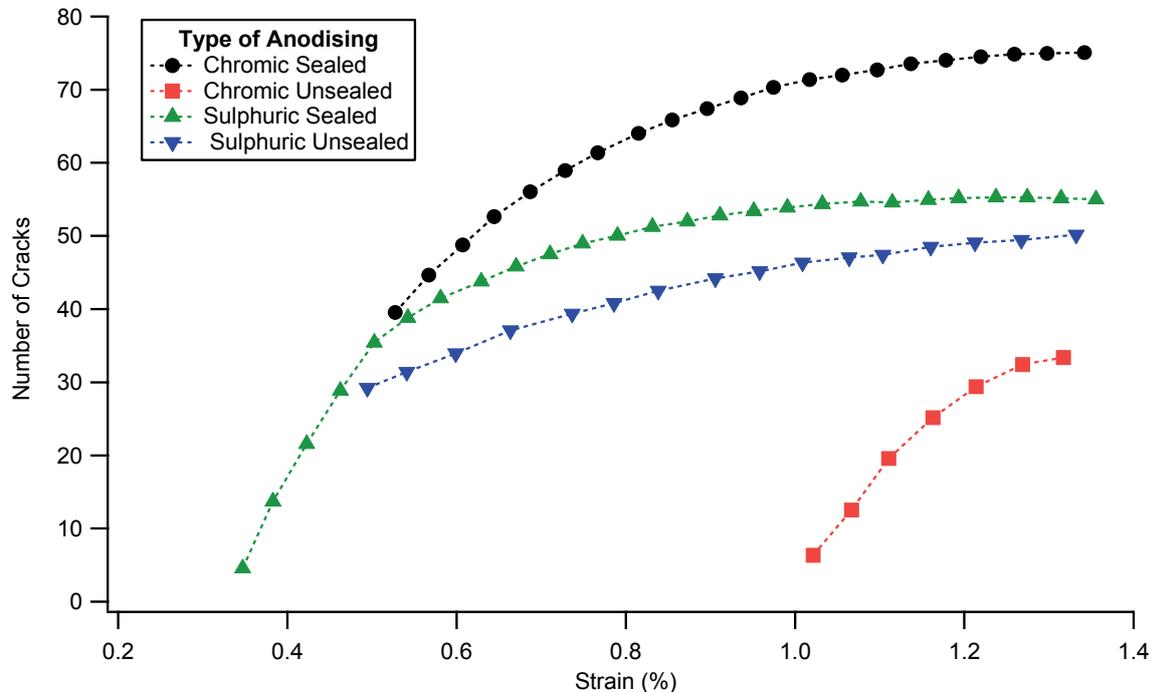

Figure 2: Density of microcracks in an anodised layer on 2024-T3 alloy versus maximum applied strain. Notes: (i) that the sealed chromic acid anodised layer shows a similar behaviour to the sealed sulphuric acid anodised layer below a strain of 0.5%. (ii) the symbols are for identification only. They do not represent data points.

Jacobs et al [9] observed the fracture of the chromic acid anodised layer on an Alclad 2024-T3 aluminium alloy. This cracking takes on the appearance of a crazing as it occurs widely over the surface of the aluminium alloy. Specimens of the alloy were examined while being loaded in tension in a scanning electron microscope. The oxide layer was observed to fracture at an applied stress of 290 MPa. This was significantly less than the alloy's yield stress of 361 MPa (in the rolling direction).

6. Effect of Anodising on Fatigue Endurance

It is well known that anodising reduces the fatigue resistance of aluminium alloys. This is most commonly demonstrated in terms of reduced fatigue endurance. However, the magnitude of this reduction in fatigue life varies with the anodising process used and the microstructure of the substrate aluminium alloy [5].

The main reason for this reduction in fatigue life is the acceleration of crack initiation due to surface defects and cracks in the anodising layer. However, there is some evidence that anodising also accelerates crack growth [6,10]. Figure 3, from Cree and Weidmann [10] shows the general effect of anodising on the fatigue endurance of high-k_t specimens of a 2024-T4 aluminium alloy tested in tension at R = 0.1. The effect is most pronounced at long lives and decreases as the magnitude of the applied stress cycle increases.
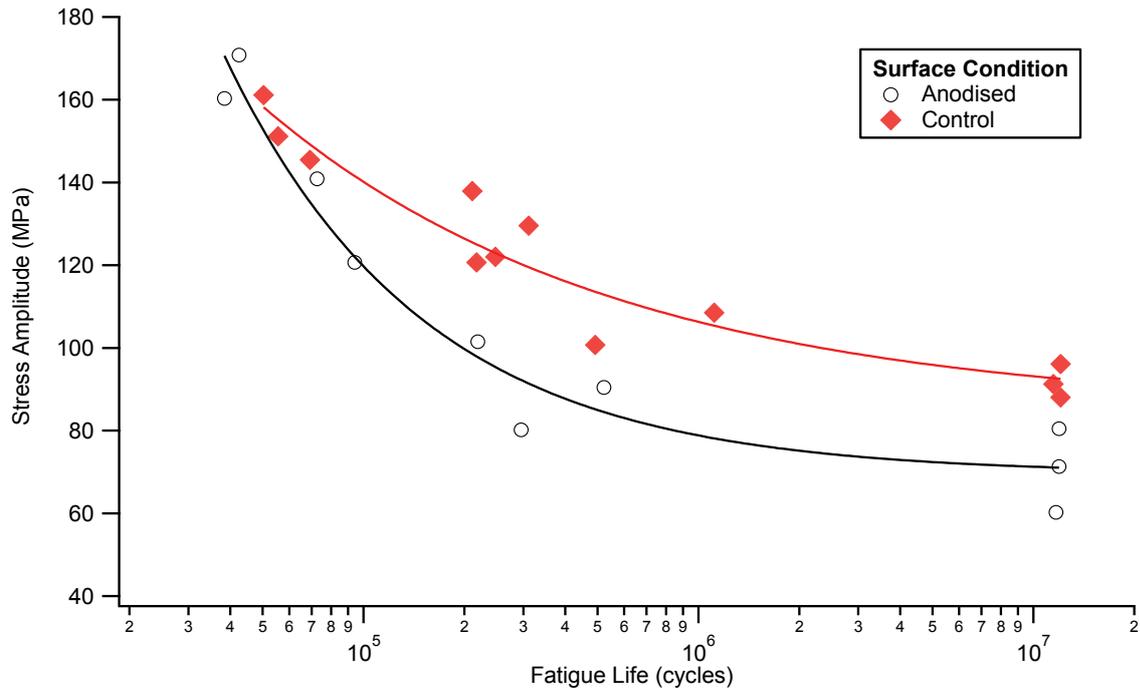

Figure 3: Effect of Anodising on the fatigue endurance of a boric-sulphuric acid anodised 2024-T4 aluminium alloy [10]. The control surface has not been anodised; it is in an as-machined state.

6.1 Anodising process

Each of the common anodising processes produces anodised layers with significantly different microstructures. The major difference is the thickness of the anodised layer produced. As a consequence, the effect of anodising on fatigue properties varies with the anodising process used. In general, the thicker the anodised layer the greater the decline in fatigue endurance produced by anodising. This is thought to be due to the decreased strength of brittle materials with increased size. A thicker anodised layer is more likely to contain a defect of critical size and is, therefore, likely to have a lower fracture strength. The thickness ranges obtained with typical anodising processes are shown in Table 2.

Table 2: Thicknesses of anodised layers produced by common anodising processes from Reference [5]

Anodising process	Film thickness (μm)	Anodising process	Film thickness (μm)
Sulphuric Acid	5 – 20	Phosphoric Acid	0.2 – 0.5
Chromic Acid	2 – 5	Oxalic Acid	10 - 60

As described above 't Hart and Nederveen [5] investigated the fracture of anodised layers on aluminium alloys 2024-T3 and 7075-T6. They found that the effect of anodising on fatigue endurance depended on the particular anodising treatment used. In addition, they examined the behaviour of the anodised layers under load and found that layers produced by different processes had different susceptibilities to fracture. Furthermore, the susceptibilities to fracture of a particular anodised layer related directly to how detrimental that process was to the fatigue resistance of the alloy. Components anodised using either sulphuric acid or chromic acid had the lowest fracture strain in the anodised layer and the lowest fatigue endurance. In contrast, the unsealed chromic acid anodised layer actually caused a small increase in fatigue strength at fatigue endurances exceeding $6x10^5$ cycles. This is attributed to the high fracture strain of unsealed chromic acid anodised layers (see Table 3).

Post treatment of the anodised surface has also been observed to affect fatigue endurance. 't Hart and Nederveen examined separately the effects of sealing and priming of anodised surfaces. Sealing an anodised surface using boiling water further decreased the fatigue resistance of the alloys investigated. This appears to be due to a reduction in the fracture strain of the anodised layer as a result of sealing. Table 3 shows the detrimental effects of sealing on the fracture strain of chromic and sulphuric acid anodised layers. In the case of chromic acid anodising of a 2024-T3 alloy, the fracture strain is reduced to half its unsealed value. In general, the reductions in fracture strain of the chromic acid anodised layer were much larger than those experienced by the sulphuric acid anodised layer. It should be noted, however, that the fracture strains of the chromic acid anodised layers are still higher than those of the sulphuric acid anodised layers.

Table 3: Effect of sealing on the fracture strain of anodised layers

Alloy and temper	Anodising process	Fracture Strain		% Reduction
		Unsealed	Sealed	
2024-T3	Chromic acid	1.10	0.51	54
	Sulphuric acid	0.60	0.51	15
7075-T6	Chromic acid	0.92	0.70	24
	Sulphuric acid	0.41	0.37	10

Stickley also examined the effect of sealing on the fatigue endurance of an anodised alloy. The sealing process used was to immerse the same in boiling water for between 10 and 30 minutes. Sealing was found to significantly reduce the fatigue endurance of sulphuric acid anodised

components. The addition of dichromate to the sealing bath produced a slight improvement in fatigue endurance relative to sealing using boiling water alone. The opposite effect was observed on combined sulphuric acid-oxalic acid anodised coatings where sealing produced a small increase in fatigue endurance. This increase, however, was insufficient to raise the fatigue endurance of these coatings to anywhere near those of sulphuric acid anodised coatings.

The apparent contradiction between the results of Stickley and those of 't Hart and Nederveen may be a result of differences in the thicknesses of the anodised layers being examined. Unfortunately, 't Hart and Nederveen did not state the thickness of the anodised layers they investigated so this can only be conjectured.

6.2 Anodised layer thickness

Anodised layer thickness can be varied by controlling the duration or current of the anodising process. Stickley [7] examined the effect of anodised layer thickness for several anodising processes on 7075-T6 rod. Figure 4 shows the trends that were observed in terms of the fatigue strength of the material at an endurance of 10^8 cycles. Coatings below 12 μm and 5 μm for sulphuric acid and chromic acid anodised layers, respectively, actually produce slightly increase the fatigue endurance of the 7075. Above these thicknesses, however, anodising significantly decreases fatigue endurance. This decline is most obvious in the chromic acid anodised material where an oxide layer of approximately 10 μm thickness decreases the fatigue endurance by 20%. In contrast, the sulphuric acid anodised layer must be 40 μm thick to produce a similar decrease in fatigue strength. Stickley also found that sulphuric acid-oxalic acid anodising halved the fatigue strength and showed no dependence on oxide layer thickness. No reason for this lack of effect was given. Kallenborn and Emmons [3] obtained similar results for chromic and sulphuric acid anodised coatings on 2024, 6061 and 7075 aluminium alloys.

Rateick et al. [11] investigated the effect of anodising film thickness on the fatigue endurance of an AA6061 aluminium alloy. The film thicknesses examined were 30 and 56 μm. Fatigue tests were conducted in both rotating bending and axial loading. Comparison with unanodised AA6061 data from the Military Specifications Handbook showed a significant reduction in fatigue endurance. This decline in fatigue resistance was larger for the thicker anodised coating. However, the difference between the 30 and 60 μm coatings was not statistically significant.
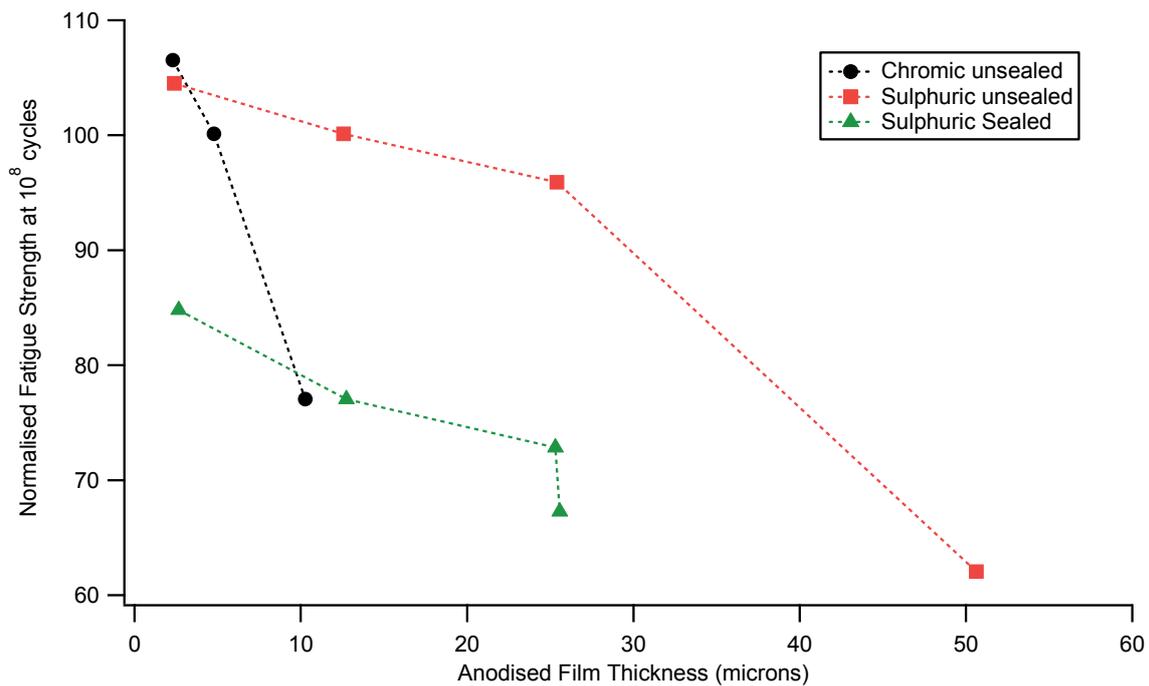
Figure 4: Effect of anodised film thickness on the fatigue endurance of a 7075-T6 aluminium alloy as a function of fatigue endurance of the un-anodised alloy [7]

6.3 Alloy composition

The effect of anodising varies with the alloy being anodised. This principally appears to be due to intermetallics and precipitate clusters in the surface microstructure of the anodised alloy producing defects in the resulting anodised film [12]. This occurs because these intermetallics do not react to form an anodised layer. Instead, they either are inert during anodising or are corroded. In either case there are holes in the anodised layer over these intermetallic defects. Given that intermetallics are favoured sites for crack initiation, this leads substantially decreases fatigue endurance.

Bolam et al. [12] compared the effects of anodising on the fatigue endurance of 2014-T651 and 8090-T351 alloys. Anodising, which was performed using chromic acid, decreased the fatigue endurance of both alloys. In the unanodised state, the 2014 had a markedly superior fatigue endurance to the 8090 alloy. Table 4 compares the effects of anodising on the fatigue strength of both alloys at a fatigue life of 10^7 cycles. As can be seen, anodising reduced the fatigue strength of the 2014 alloy by over 50%. This compares with the 8090 whose fatigue strength has only decreased by 10%. Examination of the anodised film on the 2014 alloy revealed large defects located over intermetallics or precipitate clusters in the substrate alloy. By contrast, any such defects were significantly smaller in the 8090 alloy. Studies of the adhesion strength of these anodised films showed that the anodised film on the 8090 adhered far more strongly than that on the 2014.

Table 4: Fatigue Strength at a fatigue life of 10^7 cycles.

Alloy	Surface treatment		Reduction in fatigue strength
	Bare	Anodised	
2014	202 MPa	87 MPa	56.9%
8090	135 MPa	121 MPa	10.4%

The effect of anodising is much less significant on cast alloys [7] than on wrought alloys. This is due to the presence of large pre-existing defects in castings such as intermetallics and pores. These are much larger than any of the microstructural features of the anodised layer and will therefore dominate the initiation of fatigue cracks.

6.4 Cladding

Many of the aluminium alloys used in aircraft are clad. This is typically done to produce increased corrosion resistance as opposed to increasing wear resistance, the other common use of anodising. Unfortunately, cladding reduces the fatigue endurance of aluminium alloys. This is due to the lower alloy content and, therefore, lower strength of a clad layer compared to its substrate. This complicates any examination of the effects of anodising on fatigue because the effects of anodising and cladding are not necessarily cumulative.

Wanhill [13] investigated the effects of cladding and anodising on the fatigue endurance of 2024-T3 and 7475-T761 alloys under a MiniTwist load spectrum. Three different specimen geometries were examined. These were a dogbone specimen, a plate specimen with a central hole and a lap joint specimen. Cladding was found to decrease the fatigue endurance of both 7475 and 2024 alloys. Endurance in the case was measured as the number of MiniTwist cycles that were survived by the specimen before failing. Anodising of the clad layer lead to a further decrease in fatigue endurance.

The effect of cladding also depends on specimen geometry. In general, the higher a specimen's k_t value the smaller was the detrimental effect of cladding. A similar effect was observed with anodising except that anodising actually increased the fatigue endurance of the lap-jointed specimens studied by Wanhill [13]. Wanhill attributed this increase to a reduction in fretting damage due to the higher hardness of the anodised layer.

6.5 Removal of anodised layers

Many aluminium components are anodised prior to the completion of machining. As a consequence, the anodised layer does not completely cover these components. Those sections of the component that were machined after anodising are no longer covered by the anodised coating. Hartman found that removing the anodised layer from an Alclad 2024-T3 alloy improved fatigue endurance while the opposite process, which would occur in components anodised after machining, significantly decreased fatigue endurance.

The effect of the removal of anodised layers was also examined by 't Hart and Nederveen [5] who found that the removal of a sulphuric acid anodised layer from a 2024-T3 alloy produced a large increase in fatigue strength at all fatigue lives between 10^4 and 10^8 cycles compared to the anodised material. Removal of the anodised layer was effected using a solution of chromic acid and phosphoric acid into which the specimens were immersed for 25 minutes. Wanhill found that the fatigue endurance of 2024-T3 and 7475-T761 increased when the anodised and clad layer was removed by chemical milling.

It should be noted that the increase in fatigue endurance occurred regardless of the method used to remove the anodised layer. This shows that the improvement is due to the removal of the layer and not, for example, due to compressive residual stresses induced by the removal process.

7. Effect of Anodising on Fatigue Crack Growth

Most of the research that has been conducted on the effect of anodising on fatigue has concentrated on fatigue endurance. Very little work has examined the effect of anodising on crack propagation.

Cree and Weidmann [6,10] investigated the effect of anodising on fatigue crack growth in a clad and unclad versions of a 2024-T4 alloy that were anodised using a boric acid-sulphuric acid process. They found that anodising significantly increased the rate of fatigue crack rate in the Paris Law region. At a ΔK of 10 MPa$\sqrt{m}$ the growth rate in the anodised material was 8×10^{-4} m/cycle compared to 4×10^{-4} m/cycle in the control material. Investigation of the growing fatigue crack indicated two possible mechanisms for this acceleration. Firstly, the oxide film in the vicinity of the crack tip had fractured. These cracks provide a favourable path for crack growth by concentrating the strain at the bases of these coating cracks. Secondly, aluminium oxide is significantly stiffer than aluminium. A thin film on the surface will therefore alter the stress state of the crack tip from one of pure plane stress to one approaching plane strain. This would reduce the level of plasticity induced closure at the edges of the crack, which will increase its growth rate [14]. Evidence for this second mechanism was provided in the form of a comparison of the growth fronts of a fatigue crack in anodised and unanodised specimens. The crack in the anodised specimen was significantly less bowed than that in the anodised specimen which suggests reduced closure at the edges of the specimen.

8. Conclusions

Examination of the literature makes it clear that anodising detrimentally affects the fatigue properties of aluminium alloys. The magnitude of this effect depends on the nature of the anodising process used and any pre- and post-anodising treatments applied. However, the chromic acid anodising process releases hexavalent chromium, a powerful carcinogen, into

the environment. As a result, the use of hexavalent chromium is becomingly increasingly restricted by regulations. As a result, less environmentally sensitive methods are currently being developed. Anodising is one of these methods. From the literature review in this technical note the following conclusions can be made:

1. The detrimental effect of anodising is related to the thickness of the anodised layer and increases with the thickness of this layer.

2. The combination of cladding and anodising is more detrimental to the fatigue endurance of an aluminium alloy then either of these processes alone.

3. Sealing of anodised surfaces produces further decreases in fatigue endurance. This appears to be due to a reduction in the fracture strain of the anodised layer.

4. Chromic acid anodising, which is the anodising process most commonly used on aircraft components, is the least detrimental to fatigue endurance of the anodising processes currently in use.

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4. AUTHOR(S) Bruce R. Crawford	5. CORPORATE AUTHOR DSTO Defence Science and Technology Organisation 506 Lorimer St Fishermans Bend Victoria 3207 Australia		

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19. ABSTRACT

Anodising has been used to modify the surfaces of aluminium and its alloys for several decades. It is used because its significantly increases the corrosion and wear resistance. However, it can also significantly reduce the fatigue endurance of these alloys. This reduction in fatigue endurance is ascribed to the acceleration of crack initiation due to the brittleness and consequent crazing of anodised layers and the presence of defects in these layers. There is also evidence that anodising also accelerates crack propagation.

This report provides an overview of the detrimental effect of anodising on the fatigue of aluminium alloys. It also describes the effects of process variables such as anodising time and anodising solution on the nature of the anodised film. Details of the fracture of anodised films under load are also discussed. Finally, some comments are made regarding the implications of this literature survey for current and future Australian Defence Force Aircraft.