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Protective Treatment of Aluminum and its Alloys

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1.2 There are however a number of conditions, commonly encountered, under which aluminium gets extensively corroded. The corrosion takes place either through the pores in the oxide film or in the areas from which the oxide film has been removed due to abrasion under normal environmental conditions. Also under certain circumstances, the protective film does not form at all leading to high rate of corrosion.

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Protective Treatment of Aluminum and its Alloys

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I. INTRODUCTION

Aluminium is a very reactive metal with a high affinity for oxygen. Nevertheless, the metal behaves as resistant to corrosion under most environmental conditions due to inert and protective character of the aluminium oxide film which forms naturally on the metal surface. Thus in most environments, the rate of corrosion of aluminium decreases rapidly with time. These properties exhibited by aluminium are also present in the alloys of aluminium; though the protection given will depend upon the type of alloy and its condition.

1.2 There are however a number of conditions, commonly encountered, under which aluminium gets extensively corroded. The corrosion takes place either through the pores in the oxide film or in the areas from which the oxide film has been removed due to abrasion under normal environmental conditions. Also under certain circumstances, the protective film does not form at all leading to high rate of corrosion.

The type of corrosion observed on aluminium alloys are as follows:

- a) *General Dissolution*: This occurs in strongly acidic or strongly alkaline solutions though there are specific exceptions. Certain inorganic salts (for example, aluminum ferric and zinc chlorides) hydrolyse in solution to give acidic or alkaline reaction and thus cause general dissolution. Lower alcohols and phenols in anhydrous condition do not allow protective layer to form and cause corrosion. Wet freons slightly attack aluminium. Also at temperatures above 90°C, the metal is uniformly attacked by aqueous systems.
- b) *Pitting*: This is most commonly encountered form of aluminum corrosion. In certain, near neutral aqueous solutions, a pit once initiated will continue to propagate owing to the solution within the pit becoming acidic and the alumina not able to form a protective film close to the metal. Solutions containing the chlorides are very harmful in this respect particularly when they are associated with local galvanic cells, which can be formed for example by deposition of copper from solution or by particles such as iron unintentionally embedded in the metal surface. As little as 0.02 parts per million of

copper in hard water could initiate pitting, although more is required for soft water. Aluminium is corroded by sea water. In alkaline media, pitting may occur at mechanical defects in the oxide. The aluminium alloys weather outdoors to grey colour which deepens to black in industrial atmospheres.

- c) *Intercrystalline Corrosion*: This is also electrothermal in nature, the galvanic cell being formed because of some heterogeneity in the alloy structure which may arise from certain alloying elements present.
- d) *Stress Corrosion*: This form of corrosion is of limited occurrence with only aluminum alloys, in particular the higher strength materials such as the Al-Zn-Mg-Cu type and some of the Al-Mg wrought and cast alloys with higher magnesium content. The occurrence of stress corrosion increases in these alloys after specific low temperature heat treatments such as stove enamelling.
- e) *Bimetallic Corrosion*: Aluminium is anodic to many metals and when it is joined to them with a suitable electrolyte, the potential difference causes a current to flow and considerable corrosion can result. In some cases surface moisture on structures exposed to an aggressive atmosphere can give rise to galvanic corrosion. In practice, copper, brasses and bronzes in marine conditions cause most trouble. The danger from copper and its alloys is enhanced by the slight solubility of copper in many solutions and its subsequent redepositions on the aluminium to set up local active cells. Contact with steel is comparatively less harmful. Stainless steels may increase attack on aluminum notably in sea water or marine atmospheres but the high electrical resistance of the two surface oxide films minimize bimetallic effects in less aggressive environments. With salts or heavy metals notably copper, silver and gold, the heavy metal deposits on to the aluminum subsequently causes serious bimetallic corrosion.

1.3 Corrosion resistance of aluminum alloys could be improved by cladding these alloys with pure aluminum. In addition to the above, a number of chemical and electrochemical processes are available namely anodizing and chromate treatment, which improve corrosion resistance.

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1.4 In addition to the problem of corrosion, aluminum fails poorly under conditions of wear and abrasion due to its low hardness. It is, therefore not extensively used under these conditions. However hardness could be dramatically improved by "Hard Anodizing" and certain other electroplating processes.

1.5 These processes are widely used in aircraft industries for improvement in corrosion and wear resistance properties of aluminium and its alloys. The following paragraphs highlight the properties of protective films formed by various protective treatment processes and give the uses and limitations of these processes. Though the help has been taken from various references mentioned in para7, the conclusions have been drawn based upon the actual experience of the author in the industry.

II. ANODISING

a) General

2.1.1 Anodising of aluminum and aluminium alloys is carried out by chromic and sulphuric acid processes as per Def 151 type II and I or IS 7088-73. These processes produce relatively thick, continuous and adherent oxide film as compared to the naturally formed oxide film, thereby providing increased corrosion protection. It also promotes adhesion of organic protective coatings.

2.1.2 The film produced by anodising largely consists of alumina (Al_2O_3) and a small amount of water. This type of anodic coating is porous as it leaves the bath and is easily stained; but sealing in hot/gently boiling water partially converts the alumina to aluminum monohydrate known as "Bohemite", which renders the coatings impermeable and non absorptive without any visible change. Thus maximum corrosion protection is provided by sealing the pores of the surface. If the coating is to be coloured for appearance purposes; dyeing precedes sealing because the anhydrous form of coating links more readily with dyes than the monohydrate form. This makes the dyestuff to be effectively held in the film. Such film after sealing cannot be stained by finger marking or leached out.

2.1.3 The type of anodizing is selected depending upon the functional requirements and composition of the alloys to be anodized. In general in aircraft industry, chromic acid anodizing is preferred on all aluminium alloys except for some casting alloys, or parts which have to remain in contact with H_2O_2 after anodizing and also where dyeing of film is required for decorative /identification purposes. The above exceptions must be anodized in sulphuric acid bath. A detailed account of the selection of specific coating is given in para 2.3 below.

b) Properties

2.2.1 Thickness of films: The chromic acid process provides a film of 1 to 6μ depending upon alloy, while the sulphuric acid process builds up anodic

film from 7 to 13μ . However it may be noted that the dimension of the component increases during anodizing. The thickness of the surface is 50% below the original surface and 50% above it.

2.2.2 Corrosion and Abrasion Resistance: Both types of anodic films are harder than the base metal. In general, the anodic film produced by chromic acid process is softer than the film produced by sulphuric acid process. However as the coatings are thin, the improvement in abrasion resistance is marginal.

2.2.3 Heat Resistance : Both types of anodic films are resistant up to melting point of base metal. A slight crazing occurs at high temperatures due to difference in rates of expansion of the coating and underlying metal, but this does not appreciably affect the protective properties of the film.

2.2.4 Electrical Insulation: Both types of anodic films provide electrical insulation. The electrical breakdown voltage of anodic film produced by chromic acid process is a minimum of 50V while that produced by sulphuric acid process is a minimum of 200V. Increase in temperature up to $400^\circ C$ has little effect on this breakdown voltage.

2.2.5 Fatigue : The anodizing referred in this section has little effect on fatigue properties except at holes where a reduction may be caused. Out of the two, the chromic acid process results in lesser reduction in fatigue strength.

2.2.6 Dyeing of anodic films : Film thickness of chromic acid anodic films is of the order of 1 to 6μ and thus, dye stuff penetration is small, yielding surface of poor color fastness. The clear colors are obtained on sulphuric acid films. The relatively thick films 7 to 13μ permit sufficient dye absorption to ensure good fastness properties. This process is always recommended for color anodizing and gives most permanent range of colors.

c) Application

2.3.1 The chromic acid process is the preferred process for all generally used wrought aluminum and its alloys (bars, forgings, sheets and tubes) and for castings of suitable compositions with the following exceptions:

- Casting alloys containing more than 5% copper or more than 7.5% of total nominal alloying elements.
- Parts which have to remain in contact with hydrogen peroxide after anodizing.
- Where dyeing of film is required.

These alloys are to be anodized by sulphuric acid process. For castings chromic

acid process is preferred because of innocuous nature of electrolyte which could get entrapped in pores of castings. However sulphuric acid process covers wider range of castings. In borderline cases a modified chromic acid process is preferred for castings as per DEF 151, which differs with the standard process only in

temperature and voltage conditions.

2.3.2 For anodising, surface of castings is to be free of blow holes, porosity etc to the extent possible. Gravity die casting or pressure die casting gives good results. Sand castings are least suitable for anodizing. Improved results on castings can be obtained by soaking castings in boiling water after cleaning and before anodizing. This treatment attempts to fill surface voids with water so that voids do not entrap anodizing solution.

2.3.3 Generally anodising of assemblies is to be avoided. In case it is absolutely necessary, the riveted and welded assemblies may be anodized by chromic acid process as the entrapped electrolyte is innocuous in nature.

2.3.4 If interference is required for assemblies accompanied by force fitting, films produced from chromic acid process are too thin, too soft and too brittle to overcome abrasion resistance. The coatings may crack or spall due to force fitting.

2.3.5 Anodising is not carried out after hard anodizing or plating as the hard anodized surface/plated surface would dissolve by anodic treatment.

2.3.6 Parts produced by chromic acid process are sealed in water at 55-60°C if final coat of paint is required and at 100 °C if no further treatment is required. Sealing at 100 °C renders the anodic coating impermeable and non-absorptive.

2.3.7 Films formed by sulphuric acid process are sealed in boiling solution of 5% potassium dichromate. Alternatively, it can be sealed in boiling water or dyed red, green, yellow or black followed by sealing in boiling water. The dichromate sealing, which imparts a yellow colour is used when specially high resistance to corrosion is desired and appearance is less important. The dichromate solution tends to render the effect of residual sulphuric acid less harmful and is therefore less harmful and is therefore helpful. Alloys other than casting alloys which are given sulphuric acid anodizing may be dyed and then sealed in boiling water.

Anodizing is not suitable for composite parts embodying other materials (e.g. steel). It is also not suitable for very thin sheets. In case of blind and threaded holes, film may not form at all in certain areas. Under these conditions chromate treatment is applied. Chromate treatment is also used for the repair of locally damaged anodic films.

III. CHROMATE TREATMENT

3.1 General : chromate treatment of aluminium and its alloys is an immersion process and is generally carried out by using salt Alocrom 1200/Aledyne 1200. The treatment produces a conversion coat on aluminium and its alloys. The film imparts some resistance to corrosion and offers good paint adhesion.

As such it could be widely used on surfaces which are to be painted subsequently. The conductivity for radio frequencies is extremely high resulting in its use for electrical shields and wave guides.

3.2 Properties : The corrosion resistance offered by film usually varies inversely with iron and copper content. The resistance to abrasion and corrosion is much inferior to that provided by anodizing. Temperatures above 150°C on chromate surfaces not protected by organic finishes reduces the corrosion resistance of chromate film. This treatment does not normally impair electrical conductivity and cause negligible dimensional changes.

3.3 Application : Aircraft panels and skin are generally chromate treated before painting. In aircraft accessories field, except on internal where adequate corrosion protection is provided by oil/grease or where it is used in localized application for electrical bonding/repair of damaged films, the process is followed by the application of paint scheme. The treatment is not used for surfaces where rubbing occurs. This treatment is not suitable for, where there are chances for process solution to remain entrapped.

IV. HARD ANODISING

a) General

4.1.1 Hard anodizing of aluminium and its alloys is carried out as per DEF 151 type III or IS7088-73. The hard anodic coatings are intended to provide wear and abrasion resistance surfaces with improved corrosion resistance. These coatings are used in such applications as valves, sliding parts, hinge mechanisms, cams, lightly loaded gears, wivel joints, pistons, rockets nozzles, insulation plates, blast shield etc. it is not recommended where rubbing speeds are high or bearings are highly loaded.

4.1.2 This process is also used as a salvage scheme for the building up of undersized/worn out machined surfaces. Hard anodic coatings have good insulation resistance and are used on aluminium formers of solenoid coils. These coatings form an excellent base for most types of paint schemes, adhesives and dry lubricants.

b) Properties

4.2.1 Corrosion resistance : The corrosion resistance of hard anodic films is better than the normal chromic and sulphuric acid anodized coatings due to its greater thickness.

4.2.2 Hardness : The hardness of hard anodized film is of the order of 500VPN. The top surface of the hard anodized coating is softer than the down surface in the core of the coating towards the base metal. Such coatings may be processed oversize and then lapped or honed down to the final desired dimension. General recommended lapping allowance is 0.012 mm.

4.2.3 Electrical insulation : The hard anodic film provides excellent insulation. The breakdown voltage of 0.05mm thick coating is of the order of 1000V.

4.2.4 Surface Finish: The treated surface finish is inferior to the original machined finish and becomes rougher as the film thickness increases. In case surface finish is important, it is necessary to process such coatings oversized and then lapped, honed and polished down to final desired dimensions or else, the finish of part prior to hard anodizing shall be of very high quality.

4.2.5 Fatigue: Fatigue strength may be reduced to 50% by hard anodizing which restricts its use in regions of high dynamic stress. The reduction in fatigue strength can be alleviated by sealing in sodium dichromate at the expense of some softening and loss of abrasion resistance. Hard anodised coatings shall not be sealed if the main function is abrasion or wear.

4.2.6 Growth: Hard anodizing results in dimensional increase of the component. The dimensional increase is approximately equal to one half of total thickness of the coating. Suitable allowance is to be given on the surface to allow the growth of dimensions.

c) Application

4.3.1 Effect of alloying elements: Hard anodizing is generally carried out on alloys having less than 3 % copper and less than 7% silicon. However it is possible to hard anodize alloys having copper content up to 5% though the surface finish would be rougher and abrasion resistance poorer.

4.3.2 Castings : In general hard anodizing of castings is to be avoided. Castings can be anodized provided their composition is within the limits defined above. Porous castings may not be hard anodized as they are likely to entrap electrolyte. Improved results can often be obtained by soaking castings in boiling water after cleaning and before anodizing.

4.3.3 Thickness of coatings : for applications using a hard surface, thickness of 0.025 to 0.075 mm is satisfactory. For purpose of salvage build up etc, hard anodic coating may vary in thickness from 0.013 mm to more than 0.1 mm. However deposits tend to be flaky if the thickness of anodic film is greater than 0.1 mm. all anodic coatings affect thread dimensions for external and internal threads; the major and minor diameters increase by two times the amount of growth. The pitch diameter for threads having an included angle of 60° increases four times the amount of growth.

4.3.4 Fabrication : Successful use of hard anodic coating depends on proper product design. Because of the manner of formation, anodic coatings will develop voids at sharp corner and edges. Chamfering is not used unless sharp edges are radiused. The minimum permissible radius is 0.25 mm but a minimum of 0.75 mm is recommended whenever

possible. The coating is allowed to enter holes to a depth of up to 2.5 mm. If force fitting is required for assembly, this may be accompanied by grinding, lapping or otherwise removing the surplus coating. Coatings are brittle and may crack and spall due to force fitting.

4.3.5 Painting : Only external surfaces of the equipment are painted. Prior to painting, wiping, buffing and other mechanical operations on anodized or sealed surface are minimized. This damages the relatively good outside layer of the anodic coating and make paint coat susceptible to subsequent paint adhesion failure.

V. OTHER PLATING PROCESSES

Aluminium and its alloys hard chromium plated or given a electroless nickel treatment for providing greater wear and abrasion resistances. However the difference in electrical potential between these metals and aluminum makes it essential to consider the service environment from the point of view of possible electrolyte corrosion either at the edges of deposit or in the regions of any damage or porosity.

VI. CONCLUSION

6.1 Pitting and galvanic corrosion are the most commonly encountered form of corrosion in aluminium and its alloys. The corrosion resistance could be improved by artificially creating thick adherent aluminum oxide film on the surfaces by electrochemical process known as anodizing. It could be further improved if the pores in these films are sealed by hot water or hot dichromate solution.

6.2 A dip process is also available to improve the corrosion resistance, though to a lesser extent as compared to anodized films. In this process a passive chromate film is formed on the surface.

6.3 Aluminum and its alloys have poor hardness and are not suitable for wear and abrasion resistance conditions in untreated form. These properties are improved by hard anodizing and other plating processes which provides a hard and wear resisting surface that could withstand most of the wear and abrasive conditions

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