Surface Treatment of Aluminium by Anodizing: A Short Review

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Abstract – *Anodic oxide coatings are most commonly used in the protection of aluminium alloys . Oxide films can also be formed on metals like titanium, zinc, magnesium and niobium. Aluminium alloy parts are anodized to greatly increase the thickness of the natural oxide layer for corrosion resistance. This aluminium oxide film, that seals the aluminium from further oxidation when it is exposed to air. The anodizing process increases the thickness of the oxidized surface. The process of anodizing is accomplished by immersing the aluminium into an sulphuric acid electrolyte bath by passing an electric current through the medium. In an anodizing cell, the aluminium work piece is made the anode by connecting it to the positive terminal of a dc power supply and the cathode is connected to the negative terminal of the dc source. Sealing is needed to seal the pores in oxide layer to prevent the alloy from further environment corrosion. Oxide layer on the anodized aluminium has a, porous structure that allows for secondary processes such as dyeing, printing and sealing.*

Key Words: **Aluminium, Anodizing, Corrosion, Oxide layer, Sealing, Dyeing.**

1. INTRODUCTION

Since 1920s anodizing exist as an electrochemical technique for corrosion control of various aluminium alloys. Due to its High durability and aesthetic values ,the process of anodizing offers various opportunities for architects, builders and artists. Protection of Duralumin seaplane parts from corrosion by anodizing in 1925 was the first industrial scale use. This method is the most eco-friendly process. By anodizing process, thin oxide film can be deposited on metals such as aluminium, niobium, tantalum, titanium, tungsten, zirconium etc. These metals form barrier oxide layer of uniform thickness under specific conditions. Based upon metal properties ,the thickness of the oxide layer vary greatly. Aluminium has become one of the most widely used metal today in the production of millions of consumer and industrial products, with the help of anodizing process which makes aluminium highly corrosion resistant.

The Surface of the metal/alloys is converted to a durable, corrosive resistant metal oxide layer during anodizing. It is the electrolytic oxidation process where a thin and oxide layer formed when aluminium alloys are immersed in acid bath. The Anodic oxide films produced are generally more stronger, brittle and more adherent than most of the coatings formed by paint or plating. The Oxide layer formed becomes the integral part of the underlying metal surface and which cannot be peel or chip. Anodizing is different from electroplating as it forms an aluminium oxide layer which becomes integrated part to the underlying metal. This process permanently alters the outer surface of the metal. Hard and abrasion resistant oxide layer increases the corrosion resistance capacity.

The surface on which oxide coating is to be done is made as anode in an electrochemical circuit and therefore it is called as anodizing. Metal oxides are formed by passing electric current through an acid electrolyte bath. Dimensional stability, corrosion resistance and workability such as grinding, polishing etc. vary from alloy to alloy. The process of Anodizing can control the coating quality by various process control measures included in the process. Consistent oxide layer can be formed by adjusting the conditions such as electrolyte concentration, acidity, solution temperature, and current. High voltage and low temperature can produce harder and thicker coatings in dilute solutions.

The coatings obtained from Paints, primers and glues cannot adhere tightly to a bare metal but the

coating obtained from anodizing provides better adhesion and also increases corrosion and wear resistance. Anodic coating becomes integral part of the metal with highly ordered porous structure which allows secondary processes such as dyeing printing and sealing.

1.1 Aluminum Anodizng

Aluminium can form barrier as well as porous oxides when it is anodized ,thereby making it ideal metal for this process . The porous oxide layer is formed on aluminium by electrochemical oxidation when it is dipped in electrolytic bath of dil sulphuric acid. The process Anodization of aluminium is a methhod which has been used for several decades. Pure aluminium exhibits passivity by forming a layer of amorphous oxide of 1.5 to 3.5 nm thick. This provides effective protection from corrosion and as a result aluminium exhibit more corrosion resistance than expected. Thicker oxide layers of thickness 4-14 nm are formed by aluminium alloys but have more susceptibility towards corrosion. The porous oxide layer is formed on aluminium which allows subsequent secondary workability such as dyeing (colouring) and improves properties such as lubrication and adhesion.

Thick barrier aluminium oxide layer with thickness1.5-2.5nm is always formed on aluminium base metal next to the metal surface. Barrier oxide layer act as an good electrical insulator and stabilize the surface against further reactions with the environment. Porous aluminium oxides are generally grown in dilute sulphuric acid of concentration 12% by weight. Inorganic and organic acids can be used for growing oxide films on the metal surface (E.g. Sulphuric acid, Phosphoric acid, chromic acid, oxalic acid). In the process of Anodization using sulphuric acid bath, about 55% of the oxidized aluminium is in the film and the rest is retained by the acidic solution.

Well defined thin aluminium oxide layers are formed by researchers by developing anodization techniques under more controlled operating conditions. It is possible to alter the pores formed in the process by adjusting the conditions. The voltage can be adjusted during anodizing process to control the pore diameter. These aluminium oxide sheets have closely packed parallel pores penetrating through the material. Pore diameter can be altered between 15-270 nm. The various parameters such as electrolyte concentration, acidity, solution temperature, and current must be cont rolled in good manner to obtain durable coatings.. Dilute acid solution at low temperature with higher voltage tend to produce harder and thicker films. Thic kness of the film can range from 0.48um for bright decorative work up to 145 μm for architectural applications.

The Acidic electrolyte should be selected in such a way that oxide layer formed should be insoluble in the bath and hence an adherent oxide layer grows on the metal surface. The nature of forming barrier or porous oxide is determined mainly by the composition of the bath electrolyte . Neutral solution helps the formation of barrier oxide, as the oxide is hardly soluble in neutral solution. Ammonium borate is the most commonly used neutral solutions for aluminium anodizing. Acidic electrolyte helps the formation of porous oxide layer on the surface. Oxide layer gets deposited as well as dissolves in acidic electrolyte. Anodic coatings are usually formed in chromic acid, sulphuric acid, phosphoric acid or oxalic acid solutions. Sulphuric acid anodizing is preferred for decorative applications. Most widely used bath for anodizing contains 12% by weight concentration of sulphuric acid. Important types of aluminium anodizing are chromic (type I), sulphuric (type II) and hard (type III) coatings.

Oldest process is the chromic acid anodizing. Thinner (0.6 μm to 20 μm) soft and ductile self-healing films can be formed in chromic acid. 60% of the oxide penetrates into the surface and 40% grows over the surface. Subsequently the process dyeing is difficult in this case and it can be applied as a primer coat for paint. Most widely used anodizing method is sulphuric acid anodizing. Thickness of the oxide coating vary from 1.5 μm to 24 μm (0.00006" to 0.002") can be produced by this method 70% of the oxide coating penetrates into the substrate and 30%

grows on the substrate surface. Sulphuric acid anodizing is good for dyeing due to its permeability. Coating formed by this method act as excellent base for primers, paints etc. Oxide coating formed by sulphuric acid anodizing is highly durable and also exhibit very high corrosion resistance against environment.

The coating obtained from anodizing is more hard compared to pure aluminium. Wear resistance can be improved by suitable sealing process and also by increasing the thickness of oxide layer.

2. Experimental Procedure

The process of Anodizing is done by immersing the aluminium metal into an electrolyte bath and by passing electric current through the acidic electrolyte. The aluminium article to be anodized is made the anode by connecting it to the positive terminal of a dc power supply. The cathode is connected to the negative terminal of the source. The cathode is usually an inert conductor of electricity which is unreactive in the acidic anodizing bath. Commonly used inert electrodes are a plate or rod of *carbon*, lead, nickel, stainless steel etc. When the circuit is closed, aluminium part at the anode release electrons and form aluminium ions at the surface. These metal ions at the surface react with water to form an oxide layer on the metal. At the cathode electrons are received by hydrogen ions, which get reduced to form hydrogen gas. Oxygen ions are released from the electrolyte to combine with aluminium ions, to form aluminium oxide at the surface. It can be done in controlled manner for best results.

The overall reaction given below :

$$2Al + 3H_2O \Longrightarrow Al_2O_3 + 3H_2$$

The part to be anodized is first cleaned to remove surface dirt by dipping in cleaning agent like NaOH.

It has to be then dipped in acidic solution to remove non-uniform aluminium oxide surface. Then again it is rinsed to avoid futher contamination. Etching in sodium hydroxide solution is done in order to remove the natural shine of aluminium and to provide a soft, matte, textured appearance. This part is then suspended in anodizing tank which contains dilute acid solution. Desired finish and colour depends on the concentration and type of acid and also on the temperature of the solution. The amount of current used for anodizing depends on the amount of surface to be treated. Thicker coatings are formed on the surface very near to the cathode. Time of treatment depends on the nature and quality of coating of oxide layer.

Acidic solution used in aluminium anodizing may slowly dissolve the aluminium oxide and hence produce pores in the anodized coating. The highly ordered porous structure of aluminium oxide coating allow subsequent secondary processes such as dyeing, printing, sealing and retain lubricants, but may lead to corrosion. The acid action is balanced with the oxidation rate to form a coating with nanopores, 20-130 nm in diameter. These pores allow the electrolytic solution and current to reach the aluminium part and hence continue oxidation to form coatings with greater thickness beyond that formed by auto passivation.

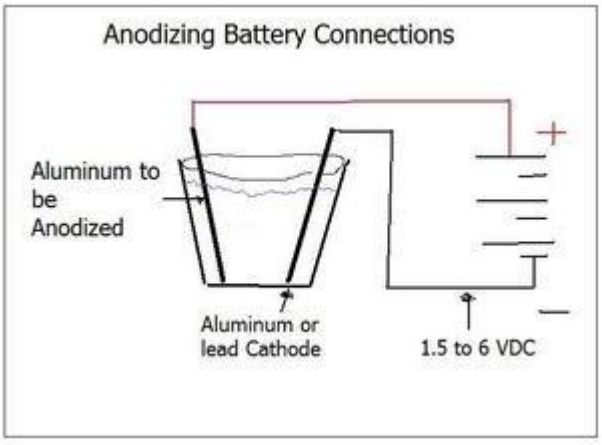

Fig 1: Anodizing set up

Digital printer can be used to print photo quality images and graphics in vivid colour into the unsealed porous aluminium oxide layer. Printers can be used to achieve line art quality graphics on the anodized aluminium part. Images in colour can be directly painted on the anodized aluminium substrate by using airbrush, sponge or paint brush with hand. Printed

anodizing part has to be sealed to prevent or reduce dye bleed out. Without sealing the pores, the usefulness of this method would be quite limited. Anodized surface without sealing undergoes corrosion gradually. Sealing of the pores can be done by different methods. The Alumina coating produced by anodizing is typically 3µm to 30µm thick, and consists of a non-porous barrier layer next to the metal surface with a porous outer layer that can be sealed later.

3. DYEING

The most common sulphuric acid anodizing process produces a porous surface which can filled with dyes with various colours. Black dyes and gold produced by inorganic means are more light fast.

Dyes distributes throughtout the pores in the coating. Alternative;y to this approach ,the color may be produced becomes integral to the film. This can be done during the anodizing process using organic acids such as malic acid which is mixed with sulphuric acid electrolyte and a pulsed current power supply.

Aqueous and solvents based dye mixtures may also be applied since the coloured dyes will resist each other and leave spotted effects.

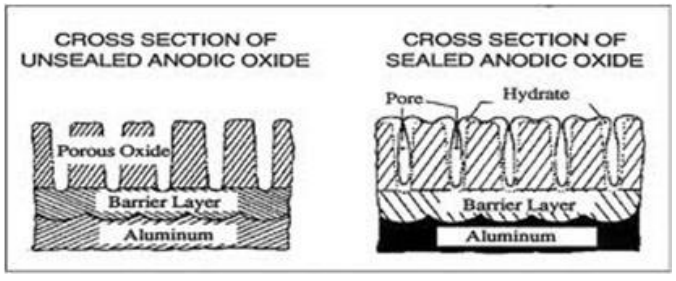

Fig 2: Cross section of anodic oxide

4. SEALING

The process of anodizing on aluminium produces pores in the coating of oxide layer. These pores can absorb dyes and retain lubricants , but are also is an method to prevent corrosion. Long immersions in boiling hot water or steam is the basic method to seal and it reduces abrasion resistance by 20%.

The oxide is converted into its hydrated form and the resulting swelling reduces the porosity of the surface .

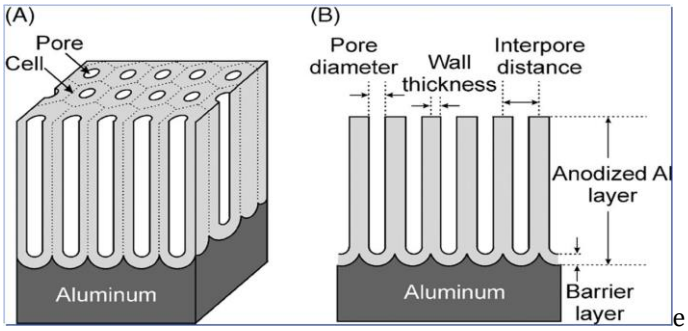

Fig 3: Porous layer of alumina

5. Applications

Anodizing finishing process has made aluminum the most widely used material in the periodic table. Because of its aesthetic values, eco friendly nature , external appearance etc it is widely accepted material. Anodizing is widely used in various fields like in making computer hardware ,manufacturing of scientific instuments , home appliances and building materials.

- Home appliances such as television, refrigerators, dryers, microwaves, coffee brewers etc.
- Motor vechicle components in automobile industry is nowadays anodized.
- Furniture: Tables , beds ,files and storage cabinets.
- Aerospace Industry
- Food Industry

6. Advantages of anodizing

- Anodized coatings are easy to maintain as it can be cleaned with soap and water solution to restore its original look.
- Colors and glossy metallic appearance add aesthetic values to anodizing process
- Low processing reduces its cost
- Because of its good external appearance and good metal finishing process, it is widely used.
- Anodic coatings do not decompose because of its chemical stability.

7. Conclusion

When aluminum is exposed to air it naturally develops a thin layer of aluminum oxide film that seals the aluminium from further oxidation in open atmosphere. The electrolytic anodizing process increases the thickness of the oxide layer which is thicker when compared to natural oxide layer. The resistance due to abrasion of aluminum increases by anodizing as the hardness of the anodized aluminium oxide coating is high. The increased thickness of the oxide layer enhances the corrosion resistance of the aluminium and also making the cleaning process an easier one. Consistent oxide layer can be formed by controlling the conditions such as electrolyte concentration , acidity , solution temperature and current.

Harder and thicker films are produced in dilute solutions at lower temperatures when a high voltage is used. This result in the formation of film with thickness (0.5 um to 150um), which find decorative as well as architectural applications.

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