A Review of Anodizing of Aluminium

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1. Introduction

Anodizing of aluminium is an electrolytic process for producing thicker oxide film which improves its physical and chemical properties.[1-4] The anodizing industry is firmly established in all the industrial countries and many of the emerging nations have also adopted anodizing as a finishing process of aluminium after forming or machining operations.

The oxide films formed on aluminium by anodizing in appropriate electrolytes show excellent resistance to corrosion, electrical conduction or abrasion, and their porous nature allows to absorb dyestuffs, lubricating oils and various materials, thereby rendering a wide range of colours, low friction coefficient, and various optical, magnetic and catalytic properties.[2] So, the anodizing process has been widely applied for protective, electrically insulative and decorative coatings, bearings, pistons for petrol engine, and heat or light reflective coatings. Another application of the anodizing process is for an undercoat for organic coatings or electrodeposits. The combination of an organic finish or electrodeposits with an anodic oxide coating on aluminium provides good adhesion of the deposits to the substrate and hence ensures their maximum life.

Structural characteristics and growth kinetics of anodic oxide films on aluminium are determined by the forming conditions under which they are formed.[5-9] There are six major variables affecting the formation of anodic oxide films[6] : electrolyte type, electrolyte concentration, electrolyte temperature, applied voltage, current density, and anodizing time. Since these variables are interdependent and affect both formation and dissolution of the oxide film, growth mechanism of the anodic oxide film is of a rather complex nature.

The field of anodizing of aluminium is actually replete with many review books[1-4] and articles.[10-12] However, many of them are now outdated and recently very valuable and new experimental results on anodizing of aluminium have been reported. So, it is necessary to survey new experimental data and results for better understanding of growth mechanism of anodic oxide films during anodizing of aluminium. This article approaches to a fundamental aspect of anodizing of aluminium based upon new experimental data and results rather than practical viewpoint.

In this review, the authors have attempted to present some interesting points on the structural characteristics and growth kinetics of anodic

oxide film on aluminium in aqueous solutions. The structural characteristics are discussed in view of the type of the oxide film, and the growth kinetics are described in terms of the formation and dissolution of anodic oxide film based upon relevant electrochemical reactions occurring at the aluminium/oxide film and oxide film/electrolyte interfaces.

2. Structural characteristics of anodic oxide film on aluminium

There are two distinct types of anodic oxide film on aluminium, depending on the rate at which the oxide is dissolved during the anodic oxidation of aluminium in electrolyte. Where the electrolyte has little solvent action, thin non-porous barrier-type films, which are used for dielectric film in electrolytic capacitors, are formed. Where there is appreciable solvent action, thick porous-type films are developed.[1-4] The porous-type anodic oxide films are composed of inner thin barrier layer and outer thick porous layer with a large number of parallel pores extending through the oxide almost to the metal/oxide interface. The barrier-type anodic oxide films are limited in thickness to several hundred nanometers because of dielectric breakdown, while the porous-type anodic oxide films can grow up to hundreds of micron.[4]

2.1 Barrier-type anodic oxide film

The unit barrier thickness, which is defined as the thickness per volt of film formation potential, is dependent on the type and concentration of electrolyte and electrolyte temperature. In general, the unit barrier thickness is constant, irrespective of film formation potential.[6] This

means that the total thickness of barrier layer is proportional to the formation voltage. However, the maximum thickness of true barrier-type films is of the order of $1 \mu m$, the film thickness being limited by dielectric breakdown.[13] The barrier-type films contain some anions incorporated from the forming solution, but generally less than porous-type films. The non-porous barrier-type films on aluminium are usually grown in neutral solutions of borates, citrates, tartrates and phosphates etc.[3]

2.2 Porous-type anodic oxide film

There are two models for the growth of porous-type anodic oxide films on aluminium. One is geometric pore model proposed by Keller et al.[5] which hypothesize that electrolytic oxidation of aluminium proceeds simultaneously with the dissolution of the oxide film at selected points, resulting in a hexagonal cellular structure. Fig. 1 shows the hexagonal cell of the oxide film containing pores extending from the oxide/electrolyte interface to the bottom of pores at which dissolution of the oxide occurs during anodizing.

The other is colloidal gel model by Murphy and Michelson[14] in which the anodic film was considered to be a duplex structure of the innermost barrier layer and outer porous layer(Fig. 2). The inner barrier layer is believed to be anhydrous aluminium oxide containing some anions of the electrolyte. The electrolyte and hydroxide ions probably play an important role in breaking up the inner barrier layer to discrete particles which finally become the porous layer. The conversion process of the oxide film from relatively anhydrous barrier layer to an agglomeration of hydrated particles of aluminium
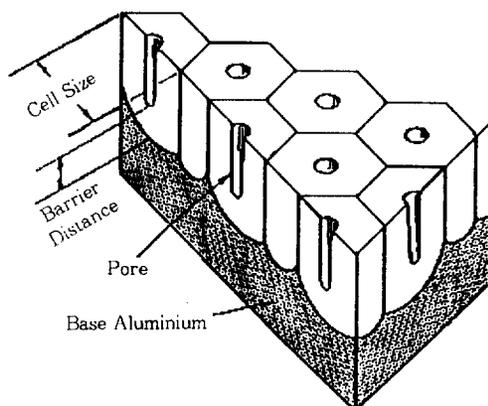
Fig. 1. Hexagonal cellular structure of porous-type anodic oxide film on aluminium suggested by Keller et al.[5]

oxide, is field-sensitive.

In the geometric pore model, the composition of the porous layer is identical to that of the barrier layer because the porous layer results from dissolution of the oxide film at the pore base. However, the colloidal gel model regards the porous layer as a converted barrier layer

consisting of many crystallites which are highly hydrated and contain anions of electrolyte.

Porous-type aluminium anodic oxide film is usually formed when aluminium is anodized in sulfuric, oxalic and phosphoric acid solutions. An important factor describing the structural features of the porous-type film is the porosity of the film which is defined as the total volume of pores divided by the total volume of the oxide film. The porosity can be also expressed as the total area of pores per unit surface area of the anodized specimen, since the average pore radius scarcely changes with the depth of pores, h, which is nearly equal to the total film thickness. The total film porosity does not depend on the voltage, but increases with increasing temperature.[15] The pore size is a function of the type and concentration of electrolyte, the temperature and the film formation voltage.

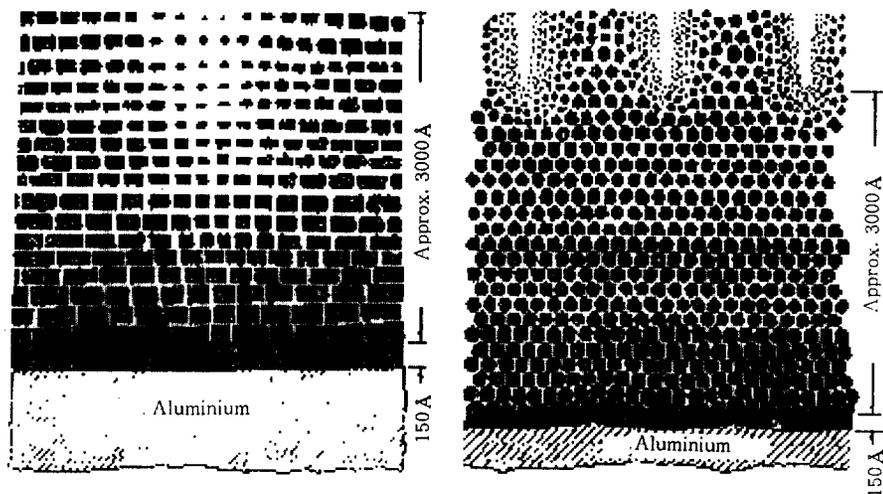Several means are available in investigating the structure of anodic oxide films on

Fig. 2. Colloidal gel model for the structure of porous-type anodic oxide film on aluminium proposed by Murphy and Michelson.[14] Black areas are anhydrous oxide, while white areas represent conducting hydrated and hydrous oxide. In the left hand illustration, the region with smaller and fewer black particles represents the bottom of a pore. The right hand illustration shows the bottoms of three pores.

aluminium. Direct observation by using electron microscope,[15-20] gravimetric determinations of the oxide weight,[17] adsorption techniques,[21,22] refraction properties,[23] and a.c. impedance measurements[10,24-26] are some of the methods which have been employed for this purpose. More detailed information on the structure of the oxide film could be gained by comparing the results obtained with different methods.

Wood et al.[18] made a direct examination of barrier layer and pore and cell structure for porous-type anodic oxide films formed on pure aluminium in phosphoric acid electrolytes at high formation voltage. They reported that the barrier layer thickness is proportional to the voltage, the ratio being about $10/V$ in phosphoric acid electrolytes. As the outer surface of the oxide film is approached, the size and irregularity of the pores increase. Paolini et al.[17] reported that pores are in the shape of truncated cones with very slightly slanted walls and the wall slant does not vary considerably with the film thickness.

The diameter of the oxide cells is about twice the thickness of the barrier layer and proportional to film formation voltage.[15] Direct measurements from photomicrographs of film section replicas,[15] after anodizing in the range of 80 to 120V for 1 h in 0.4M phosphoric acid at 25 °C, yield a barrier layer of $1.04\ nm\ V^{-1}$ and a cell diameter of $2.77\ nm\ V^{-1}$. If the voltage rises progressively during anodizing, inverse funneling is observed because the pores and cells produced next to the barrier layer are larger than those formed earlier.

2.3 Sealing of porous-type anodic oxide films

Porous-type anodic oxide films are usually treated hydrothermally in hot water, water vapour, or in aqueous organic and inorganic salts to improve their resistance against corrosion, which is known as "sealing".[21,27,28] The sealing treatment leads to the closure of pores by a swelling of the oxide film that must occur when the oxide film uptakes water.

The swelling of the oxide film was suggested to take place by the formation of oxide hydrate, or through the reaction of pore wall microcrystalline oxide with water, followed by an ion exchange process between adsorbed electrolyte anions and water molecules/hydroxide ions.[27] The maximum amount of water uptake into the oxide film was reported to be directly related to the porosity of the initially produced oxide films.[27]

The sealing of porous-type anodic oxide film on aluminium is of great importance for commercial anodizing process. So, many researchers[21,27,28] have expended considerable effort on the study of the mechanism by which the oxide absorbs and binds water. One of the more widely accepted concepts is that Al_2O_3 becomes hydrated to form boehmite($AlOOH$) which plugs the pores to a certain extent because of its greater specific volume. Another theory suggested by Murphy et al.[27] regards sealing as a surface effect rather than a pore plugging effect. They postulated that replacement of surface sulfate ions by hydroxide ions which changes the surface from active one, that is receptive to dyes, stains and corrosive agents, to more inert one. This type of ion exchange must certainly occur to some extent, but it is not clear how it would affect coating properties. During sealing, alumina crystallites agglomerate to some extent, forming hydroxylated surfaces and trapping mo-

lecular water in the crystallite voids.

3. Growth kinetics of anodic oxide films on aluminium

There are three regions between aluminium and electrolyte over which potential is applied : these are the aluminium/oxide film interface at which aluminium oxidation occurs, the oxide film itself through which cation and/or anion transport proceeds, and the oxide film/electrolyte interface at which anion injection into the oxide film and/or cation ejection into the solution takes place.

(i) The aluminium/oxide film interface

The transfer of an aluminium atom from the metal phase into the oxide to form an ion should occur by a simultaneous charge transfer, in the same way as in all electrochemical metal dissolution in the electrolytes. Two electrochemical reactions are possible at the aluminium/oxide film interface[29-31] during the anodic oxidation of aluminium according to point defect model[32]

$$Al_{Al}(m) + V_{Al}^{3-}(ox) = Al_{Al}(ox) + 3e \qquad (1)$$

$$Al_{Al}(m) = Al_{Al}(ox) + V_O^{2+}(ox) + 3e \qquad (2)$$
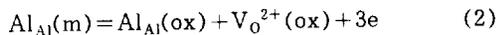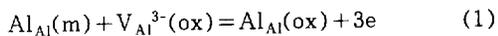
where $Al_{Al}(m)$ is the normal aluminium atom in the regular site of aluminium metal, $V_{Al}^{3-}(ox)$ is the negatively charged aluminium vacancy in the oxide film, $Al_{Al}(ox)$ is the normal aluminium ion in the regular site of the oxide film, e is the electron and $V_O^{2+}(ox)$ represents the positively charged oxygen vacancy in the oxide film. The aluminium ions formed at the aluminium/oxide film interface will preferentially enter their vacant sites within the oxide film via reaction (1),

resulting in the annihilation of aluminium vacancy and then they will adsorb on the oxide film via reaction (2), thus causing the generation of oxygen vacancy.[33,34]

It was reported that only the aluminium/oxide film interface is the region where stresses are generated during the growth of anodic oxide films on metals,[31] and the annihilation of aluminium vacancy and generation of oxygen vacancy at the aluminium/oxide film interface result in compressive and tensile stresses, respectively.
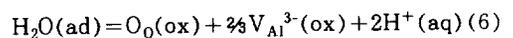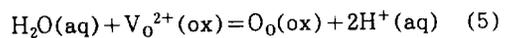
(ii) The oxide film/electrolyte interface

The ion transfer across the oxide film/electrolyte interface is considered as the same type of activation-controlled charge transfer kinetics. The electrochemical double layer here is of the usual type for aqueous systems. One could expect protons to cross over the oxide film/electrolyte interface causing protonation (hydration) of the oxide film

$$H_3O^+(aq) = H^+(ox) + H_2O(aq) \qquad (3)$$
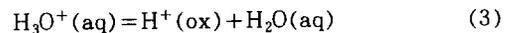
where $H_3O^+(aq)$ is the hydrated hydrogen ion in aqueous solution, $H^+(ox)$ is the hydrogen ion in the oxide film and $H_2O(aq)$ represents the water in aqueous solution.

When anodic potential is applied to the aluminium specimen, the following electrochemical reactions could occur at the oxide film/electrolyte interface[33,34]

$$Al_{Al}(ox) = Al^{3+}(aq) + V_{Al}^{3-}(ox) \qquad (4)$$

$$H_2O(aq) + V_O^{2+}(ox) = O_O(ox) + 2H^+(aq) \qquad (5)$$

$$H_2O(ad) = O_O(ox) + \tfrac{2}{3}V_{Al}^{3-}(ox) + 2H^+(aq) \qquad (6)$$

where Al^{3+}(aq) is the aluminium ion in aqueous solution, O_O(ox) is the normal oxygen ion in the regular site of the oxide film and H_2O(ad) represents the adsorbed water on the oxide film surface. Reaction (4) represents a field-assisted dissolution of the oxide film which involves direct ejection of aluminium vacancy from the oxide film into the electrolyte, thereby generating aluminium vacancies within the oxide film.[29,31,35]

(iii) Transport of ions through the oxide film

The relationship between the electric field strength E in the oxide film and the nonohmic ionic current density j is generally described as

$$j = A \exp(BE) \qquad (7)$$

where A and B are constants, depending on the temperature. The high field ion conduction model was first suggested by Cabrera and Mott[36] and later developed by Kirchheim[37] and others.[38-40]

During anodizing of aluminium, the current through the oxide film itself is transported by either cations or anions, or by a combination of both ions. If cations move more dominantly than anions through the film, fresh oxide will be laid down at the oxide film/electrolyte interface. But, if the movement of anions is predominant, the new oxide will be formed at the metal/oxide film interface. Radiotracer studies have been made to find out whether succeeding oxide layers are formed inside or outside the tagged layer.[41-45] The transport number of aluminium ion in aluminium oxide film was reported to increase with increasing applied anodic current density.[43] Bernard[42] suggested that although both aluminium ions and anions move through

the oxide film during anodizing of aluminium in aqueous solutions.

There are some evidences that certain of the migrating anions are OH^- ions, the remainder being either O^{2-} ions or acid oxyanions.[46,47] It is reasonable to consider that OH^- ions should enter the barrier layer because their size(0.153nm) is only marginally greater than that of O^{2-} ions(0.14nm), according to the evidence of Wells.[48] The OH^- ions and electrolyte anions, such as borate and phosphate ions, are apparently enriched towards the film exterior and it would be reasonable to expect a reverse gradient of the aluminium ions. The incorporation of anions is influenced by the discharge rate of anions at the oxide film/electrolyte interface, as well as their size and charge. Presumably the electrolyte anions and O^{2-} ions remain unchanged in the film but some OH^- ions might be expected to be converted to O^{2-} ions and protons.

Hydroxide ions or protons trapped in the oxide film produce the well-known hydrogen-bonded structure, as demonstrated by Dorsey.[49] Brock and Wood[47] consider that the amount of OH^- ions is greater towards the film exterior due to the increased OH^- ion concentration in the electrolyte, allowing these ions to compete successfully with water molecules and the electrolyte anions for adsorption and subsequent entry into the oxide film.

The OH^- or O^{2-} ions participating in the film development could originate from the abundant water or possibly in some cases from the electrolyte anions.[15] Water molecules might be expected to adhere to the film surface, with the negatively charged oxygen atom adjacent to the oxide surface. Trivalent or divalent ions could

adsorb much more easily than monovalent ions on the positively charged aluminium surfaces, especially at high fields. Discharge of large electrolyte anions would be favored at higher fields, incorporation of such anions possibly affecting the size of the film microcrystallites and thus modifying the overall film properties and structure.

3.1 Formation of the oxide film

The formation of anodic oxide film could result from the movements of oxygen vacancy and aluminium vacancy through the oxide film. The oxide film formation reaction resulting from the movement of oxygen vacancy is obtained by combining Eq. (2) and Eq. (5), and that due to the movement of aluminium vacancy is given by adding Eq. (1) and Eq. (6)

$$2Al_{Al}(m) + 3H_2O = Al_2O_3 + 6H^+(aq) + 6e \quad (8)$$
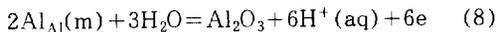
In general, the formation of anodic oxide film is known to proceed from the movement of oxygen vacancy in acidic, neutral and alkaline solutions.[29,31] However, the movement of metal vacancy was suggested also to produce anodic oxide film on aluminium in alkaline solution.[34]

The generation of aluminium vacancy due to reaction (4) hardly occurs in alkaline solutions [34] in which aluminate ions rather than aluminium ions are formed as a result of the dissolution of the oxide film.[50] So, first rapid annihilation of oxygen vacancy via reaction (5) will occur and then quick generation of aluminium vacancy via reaction (6) ensues on this in alkaline solutions. This gives why the movement of aluminium vacancy could result in the formation of aluminium oxide film in alkaline solu-

tions, as suggested by Moon and Pyun.[34]

In reaction (8), it is noted that the formation of each molecule of oxide is accompanied by liberation of six protons and this appears to affect the growth and dissolution of the oxide layer during anodizing. Three sinks of hydrogen ion are follows : the reaction with the oxide ; the association with the anion in the electrolyte ; the molecular(convective) diffusion into the electrolyte.

3.2 Dissolution of the oxide film

The dissolution of the oxide film is classified into electrochemical and chemical processes. The electrochemical oxide dissolution reaction (4), which involves the direct ejection of aluminium ions from the oxide film into the electrolyte at the oxide film/electrolyte interface, is a field-assisted process and it occurs just only in acidic solution.[34] It was suggested that the electrochemical oxide dissolution is controlled by anion-removal rate at the oxide film/electrolyte interface, depending upon pH of the electrolyte.[1] Otherwise, Kim et al.[29] showed that the rate of aluminium ion removal according to reaction (4) crucially determines the electrochemical dissolution rate of the oxide film.

The chemical dissolution of the oxide film is divided into the attack by hydrogen ion in acidic solutions

$$Al_2O_3 + 6H^+(aq) = 2Al^{3+}(aq) + 3H_2O \quad (9)$$
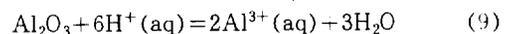
and the attack by hydroxide ion in alkaline solutions

$$Al_2O_3 + 2OH^-(aq) = 2AlO_2^-(aq) + H_2O \quad (10)$$

where OH^-(aq) is the hydroxide ion in aqueous solution and AlO_2^-(aq) represents the aluminate ion in aqueous solution.

Chemical dissolution of aluminium oxide film in acidic solutions is likely to be primarily the protonation(hydration) reaction leading to formation of some soluble complex ions which diffuse toward the bulk of the electrolyte. Hence, this produces a mechanism for dissolving and thinning of the oxide film, and the rate of this process should be some function of the hydrogen ion concentration in the electrolyte.

3.3 Coulombic efficiency

As a measure of the efficiency of oxide film formation, some investigators[7,9] used the coating ratio which is defined as the ratio of the weight of the oxide film to the weight of aluminium reacting. If all the reacting aluminium atoms were converted to aluminium oxide and none of oxide film were dissolved by the electrolyte, the coating ratio would be about 1.89.[7] When the oxide film contains 14% SO_3, the theoretical coating ratio would be about 2.2. But, because of solvent action of the electrolyte on the oxide film, the coating ratio scarcely reaches its theoretical value. The highest coating ratio values were found where the conditions of the film formation were adjusted to give the minimum rate of oxide dissolution.[7] When high the current density and low temperature were employed, higher coating ratio values appeared. The higher current density causes a decrease in the dissolution rate of the oxide film by the rapid formation of dissolution products in the pores.

The coulombic efficiency is defined by the ratio of coulombs necessary to oxidize aluminium to the trivalent state, to the total coulombs passed through the oxide film. The coulombic efficiency varies greatly with the thickness of the film and anodizing time. It was observed that no oxygen is evolved from the anode until there is a voltage drop of 15-20V across the film.[51] So the current efficiency of the aluminium anode is close to 100% before oxygen gas evolves. As the film thickens, a continuously higher percentage of the total current appears as oxygen gas evolution and the efficiency drops.

The current passing through the oxide film during anodizing of aluminium is accounted for quantitatively by the oxidation of aluminium to the trivalent ion and the liberation of oxygen gas at the anode surface. Plumb[51] reported that the current loss of about 80% after the oxide film reaches its maximum thickness for a given applied voltage, could be accounted for in terms of oxygen gas liberation at the anode surface. In general, aqueous solutions are characterized by poor current efficiency of oxide formation as a result of oxygen evolution and anodic dissolution of aluminium metal. Bernard and Cook[52] observed a linear rise in the formation voltage of the oxide film with time and no apparent evolution of oxygen gas up to 150V in glycol-borate electrolyte at 25℃, leading to 100% current efficiency of the oxide formation.

3.4 Pore and cell nucleation

Electron micrographs show very few pores in the films during the initial decline of the current at an applied anodic potential, but the porous system is virtually completed by the time when the current has risen and steadied out.[3] According to Hoar and Yahalom[53], pore initiation can

occur only when the current and the field have dropped sufficiently low to allow thermally activated protons to enter the oxide film, caus- ing locally high solubility areas to be formed at randomly distributed defect sites, rather than at regions of different crystallinity. Local Joule heating is said to ensure the continuous exis- tence of the pores.

The presence of an Al^{3+} ion space charge in the film around pore, due to the greater mobility of Al^{3+} ion in the film compared with that of OH^- or O^{2-} ions, inhibits excessive radial spread of the pore by further proton uptake and ensures that the next pore to be nucleated forms at an appropriate distance away. The third pore in the vicinity must also develop at an appropri- ate distance from both its predecessors, and so on until an approximately close packed hexago- nal distribution is arrived out. Such a mecha- nism would predict a voltage-dependent pore distribution.

On the other hand, pores may be initiated by preferential attack at randomly located defects in the original oxide film, where the current first concentrates. Any local thickening could be due to easier transport of ions through the oxide film if bulk transport control is rate-determin- ing, or to easier entry of ions into the film at lattice defects if control is at the metal/oxide in- terface. As the film thickness increases, sub- strate effects become less pronounced and the regions between the main pores become more regular. The degree of crystallinity and composi- tion of the initial oxide film vary locally, which would affect its local growth rate and dissolu- tion rate of the oxide film.

4. Summary

This article reviewed the structural character- istics and growth kinetics of anodic oxide films on aluminium in aqueous solutions. The struc- ture of anodic oxide film was shown to depend strongly on the electrolyte type and concentra- tion and electrolyte temperature, and the anodic oxide film was divided into thin barrier-type oxide film and thick porous-type oxide film. The growth kinetics of anodic oxide film were de- scribed by electrochemical reactions occurring at the aluminium/oxide film and oxide film/elec- trolyte interfaces based upon point defect model. The formation and dissolution mechanisms of anodic oxide film were discussed in terms of the transports of aluminium vacancy and oxygen vacancy through the oxide film. In addition, coulombic efficiency of oxide film formation and pore nucleation mechanism during anodizing of aluminium, were detailed.

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