

양극산화피막 형성에 관한 연구(IV)

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Anodic Film Formation on Aluminum(IV)

—Theories of Ionic Conduction and Ionic Migration—

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양극산화 피막의 형성 반응에 대한 연구는 1930년대 부터 되어 왔으며, 특히 High Field Conduction에 대한 물리학자들의 관심도는 아주 높았었다. 1960년대에 이르러 비정질 구조에 대한 심도 있는 연구가 진행되면서, 여러가지 이론적으로 풀지 못하는 실험실적 결과 들에 대한 제안들이 나오게 되었고, Ionic Migration Process에 대한 Kinetics는 많은 발전을 보게 되었다. 최근 까지의 연구 결과, Ionic Conduction Mechanism은 Anodic Film의 미세 결정 구조와 밀접한 연관성을 가진다는 결론에 도달하였고, 비정질 구조의 High Field하에서의 거동에 대한 새로운 분야의 연구가 진행되고 있다. 본 고에서는 반응 Mechanism에 관한 연구결과들을 1930년대 이후 어떻게 진행되어 설명 되었는가를 조명하므로써 실제 실험 결과의 해석에 도움이 되었으면 하는 바램이다.

1. Introduction

Anodic films have a low electronic conductivity and a high ionic conductivity and hence, at a high electric field strength, ionic conduction is the predominant mode of charge transport. If barrier films can be assumed to be completely non-porous, the films continue to grow as long as ionic currents continue to flow, the ionic current being dependent on the electric field strength present across the anodic film, i.e., the voltage drop across the film divided by its thickness, the metal, and the anodic film parameters, e.g., the activation energy for ion motion. The ratio of

the thickness of the anodic film to the voltage drop across the film, is usually quoted to as the 'formation ratio'. This ratio depends upon the value of the certain electric field E , i.e., the value of the minimum ionic current, to which the films are formed.

2. Theories of Ionic Conduction

Guntherschuitze and Betz⁽¹⁾ found that the ionic current density (i) was related to the electric field strength (E) according to equation (1), where A and B were temperature dependent constants.

$$i = A \exp (BE) \quad (1)$$

The mathematical form of equation (1) has been explained in terms of ionic transport through the anodic film, either via interstitial or vacancy defects. The mobile ions can be regarded as harmonic oscillators distributed amongst the positions of minimum potential energy in the anodic film lattice. The separation of adjacent minima is called the jump distance (2a), which corresponds to twice the activation distance (a) for ionic motion. On the application of an electric field (E), the height of the energy barrier (W) retarding ionic movement is considered to be lowered by an amount qaE, where q is the charge carried by a mobile ion. Thus, ionic transport in the direction of the applied field is enhanced and this induces a net ionic current in the field direction. In addition, the energy barrier for ionic motion against the field direction is increased by the same amount.

Ionic transport through the anodic film is referred to as high field conduction when the electric field strength is sufficient to make ionic jumps against the field unlikely; this occurs at field strengths of 10^6 to 10^7 V cm⁻¹. Alternatively, in low field conduction, ionic motion against the electric field is significant, leading to the development of space charges in the film. This accumulation of charged ions in the anodic film tends to cause a net reduction of the applied field. The ionic current density (i) during high field ionic conduction is given ⁽²⁾ by;

$$i = 2 n \nu q \exp [-(W - qaE)/kT] \quad (2)$$

where n is the concentration of mobile ions at the metal side of the metal/film interface, ν is the vibration frequency of a surface metal atom

about a mean position, k is the Boltzman constant, T is the absolute temperature (K), and W is the energy barrier at the metal/film interface⁽³⁾.

Comparing with equation (1) gives;

$$A = 2 n \nu q \exp [-W/kT] \quad (3)$$

$$\text{and } B = qa/kT \quad (4)$$

The assumptions of this model are;

- (a) Film growth is due to the transport of metal cations across the anodic interface where they react with electrolyte species;
- (b) The rate-limiting step for film growth is the emission of metal cations from the metal into the film at the metal/film interface;
- (c) Negligible amount of ions are moving against the direction of the electric field. The implication of these assumption is that the number of ions in transit through the film is very small, and hence the space charge is negligible.

Verwey ⁽⁴⁾ considered that the energy barrier for ion movement through the bulk anodic film, which is assumed to be electrically neutral, is the rate-determining step. The relationship between the ionic current density and the electric field strength is similar to (1) to (4), but the meaning of parameters in Verwey's equations are related to bulk anodic film properties instead of metal/film interface properties. In both cases, the ionic current density is given by equation (2), and (W - qaE) is the activation energy for the rate controlling process. However, equation (2) has been found in some cases to provide an inadequate description of the dependence of the ionic current density on the electric field strength; plots of $\ln i$ versus E were found ⁽⁵⁾ to be non-linear, indicating that the parameter B is field dependent. This was explained by postulat-

ing that the activation distance (a) decreased as the applied field was raised. Furthermore, the value of B has been reported to be either independent of temperature ^(6,7), to increase with temperature ⁽⁸⁾, or to vary in an ill-defined manner with temperature ⁽⁹⁾.

Dewald ^(10,11) considered that these changes in the activation distance (a) were due to a transition in the rate determining step for anodic film growth, from metal/film interface control to bulk film control. If the activation energies for ionic transport at the metal/film interface and in the bulk film at zero field are W and U , respectively, then these are lowered to $(W - qaE)$ and $(U - qa'E)$ on application of the electric field, where a and a' are the activation distances in each case. Clearly, if a and a' are not equal, each energy barrier will vary in a different manner with the field, such that a dual-barrier control mechanism could exist. As the film grows, the transition from metal/film interface to bulk film control would be expected when $(U - qa'E) < (W - qaE)$. However, since the energy barrier at the metal-film interface is then lower than that in the bulk film, ionic movement against the applied field is possible and a space charge layer may be established.

The Dewald dual-barrier control model has been found to apply in several anodizing systems including tantalum ⁽¹²⁾ in 40% sulphuric acid (up to 423K), zirconium ⁽¹³⁾ in 0.25M sodium sulphate, and niobium ⁽¹⁴⁾ in aqueous borate electrolyte. However, neither this theory nor those of Cabrera-Mott and Verwey, can adequately account for the 'overshoot' phenomena observed on ionic current ^(15,16) or voltage transients ⁽¹⁷⁾.

Bean, Fisher and Vermilyea ⁽¹⁸⁾ suggested

that the concentration of mobile ions is field-dependent. The model proposed by these authors involved the removal of metal ions from network forming sites in the amorphous anodic film by ordinary field-assisted thermal activation. Each such event would create an interstitial metal ion and a vacant cation site, i.e., a Frenkel defect, and the cation vacancies were supposed to be negatively charged. This was expected for a neutral oxide before the creation of the vacancy-interstitial pair. The interstitial ions were assumed to be mobile unlike the vacancies. Bean et al. ⁽¹⁸⁾ tacitly assumed that the two components of the Frenkel defects would remain in equal concentrations. Dewald ⁽¹⁹⁾ showed explicitly that this would occur on the assumption of electron neutrality and equal charges on the two components of the Frenkel defects. Interstitial ions were supposed to be destroyed through capture by vacancies. A steady state concentration of mobile ions would exist for any given electrostatic field. When the field was changed, the concentration of the mobile interstitials would not immediately jump to its new value and, consequently, various transient phenomena would be expected for step changes in either field or current.

However, it was later found by Young ⁽⁵⁾ that a relatively large and constant field is applied to films prepared in such a way. If the theory is correct, they would contain a low concentration defects but the ion current increases in accelerating fashion. The results were first observed by Young ⁽⁵⁾ for tantalum, but similar experiments on aluminium by Dignam and Ryan ⁽¹⁹⁾ yielded similar results.

Dignam ⁽²⁰⁾ originally proposed a set of equa-

tions for ionic conduction in an electrically neutral film, but later modified them to describe rate control by the oxide/electrolyte interface^(21, 22). In the original version⁽²⁰⁾ the amorphous oxide was considered to be composed of relatively small crystallites or polymeric units (dielectric mosaic model), with the principal rate-controlling step being ion transport between such units. The field strength in such regions is a function of the polarization of the oxide. Dielectric relaxation processes can accordingly give rise to ion-current transients. In order to account quantitatively for the transients, it was assumed that the dielectric polarization relaxes to its equilibrium steady-state value at a rate that is proportional to the ion current density (provided that $i = 0$). This assumption was rationalized in terms of the large amount of energy dissipated per ion jump, this energy effectively bringing about local polarization equilibrium. The model on which the equations were developed must be rejected, since it cannot possibly be valid for films only a few tens of angstroms in thickness. However, Dignam^(21, 22) recast the same equations in terms of a model involving interfacial control, retaining the essential features of the earlier model, namely, that ion-current transients arise as a result of dielectric relaxation processes in the film. The basic physical idea of this model was that the motion of the ions sweeps out a volume in which the oxide approach to an equilibrium polarization is expedited. In order to complete the model Dignam has to assume that the activation energy for ionic transport is non-linear in the effective field.

Dignam's theory has been questioned⁽²³⁾ because the large increase in current in constant

field transients could be explained only by postulating an unreasonably large amount of slow polarization. Young⁽⁵⁾ suggested that a momentum transfer process causes moving ions to generate further Frenkel defects (a sort of ionic avalanche effect) and, under constant field conditions, the number of mobile defects increases toward its steady-state value at a rate proportional to i^2 . A further observation of Young, that plots of the electric field strength against the log ionic current density were slightly non-linear, led him to propose that the results could be explained by taking the activation distance as $a = \alpha \beta E$, where α and β are both positive constants and E is an electric field strength.

Recently, Young^(24, 25) has reported that anodic films have usually been considered to be glassy in nature; therefore, such a structure would appear to have ample possibilities of showing history effects of the kind observed. These history effects might be conveniently described in terms of variations in the concentrations of mobile species or variations in activation energies. The basic physical idea was that the extent of the variation of the ionic current, which is produced by a given field in the film, is so large that to attribute it entirely to a variation in the concentration of some mobile species could be questionable. Because of this, Young has stressed the need to take a general approach by assuming that the structure of the oxide is characterized by some parameter S , the nature of which need not be specified. Young proposed that the activation energy (W) for ionic transport is then a function of S as well as an electric field strength (E). The ionic current density (i) is at all times given by

$$i = i_0 \exp [- (W(S,E)/kT)] \quad (5)$$

In addition, Young has assumed a linear dependence of S on E in the steady state and this would correspond to the simplest linearization approach for the variation of W . He stressed that the dependence on current density implied that each moving ion catalyzed the adjustment of the structure as it swept out a volume determined by some area of influence attached to the ion.

All the above theories for the growth of amorphous barrier films may be criticized because they are theoretically based upon the transport of ions through their assumed lattice structure and by their assumed ionic motion without any clear evidence. Particularly, it is not entirely clear whether the film material is amorphous, glassy, or consists of microcrystallites held together by relatively diffuse intercrystallite regions and whether such regions may coexist. Thus, this information, coupled with knowledge of the precise nature of ionic transport in barrier-type films and the barrier layers of porous films may aid the development of a universally valid theory for ionic conduction in oxide films.

3. The Nature of the Migration Processes

Two basic questions arise in connection with the atomic migrations leading to anodic film formation on a metal surface. First, how much do the cations and anions move during anodizing (i.e. the determination of cationic and anionic transport numbers)? Secondly, what is the nature of the transport step (e.g. a step-by-step movement "or" movement across the total film thickness)?

To answer the first question, a marker experiment is required, in which the relative

migration of cations and anions is determined from the position of an inert immobile marker. The principle of this technique is shown schematically in Figure 1. To answer the second question, tracer experiments are required, in which the nature of the migration process is determined from changes in the concentration profile of the tracer.

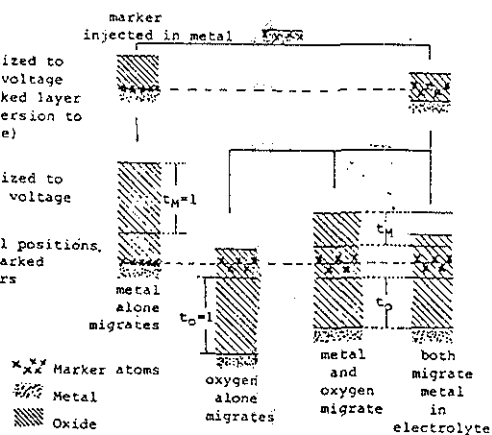


Fig. 1 Schematic representation of final positions of inert markers in anodic oxides caused by the effect of metal ion and/or oxygen ion migration during anodizing⁽²⁶⁾

The determination of cationic or anionic transport numbers in the anodic oxidation of metals has widely used implantation of noble gases near in the surface regions of the material. Locating the final position of the marker after anodization and thus extracting transport numbers can be achieved either by using radio emitters^(26,27) or stable isotopes^(29,30,31). The first case, which is often associated with chemical sectioning, has the advantage of requiring low implantation doses (typically 10^{13} atoms cm^{-2}) while the second, which is based on Rutherford backscattering analysis (RBS), needs at least a ten times larger value. All these experiments are

interpreted by assuming that the noble gas markers are immobile during anodic oxidation, whereby transport numbers for metal and oxygen can be derived. Evidence for immobility of noble gas markers, in experiments on anodic oxidation of tantalum, has been discussed in detail by Pringle⁽²⁶⁾. Inert gases, such as Xe and Rn, are usually chosen as the ideal marker which should be (a) uncharged, so that it does not migrate under the influence of the applied electric field; (b) large in size, so that they do not diffuse significantly within the oxide lattice; (c) present in trace amounts, so that the macroscopic properties of the tagged oxide remain unaltered; and (d) such that their depth beneath the surface can be determined in situ, without damaging or destroying the oxide layer.

Early experiments on the anodic oxidation of aluminium and tantalum in aqueous solution by Davies, Pringle, Graham and Brown⁽²⁸⁾ reported that the Xe¹²⁵ markers in anodic Al₂O₃ remained very close to the outer surface. They also noted that an appreciable amount of aluminium went into solution during anodizing, which suggested that aluminium ions might be mobile but were not building oxide at the outer surface. Subsequent experiments^(30,31) showed that the final location of the marker atoms within the aluminium oxide layer depended markedly on the current density used and also on the nature of the electrolyte. Later research by Davies, Domeij, Pringle and Brown⁽³²⁾, using beta-ray spectroscopy and radiotracer techniques, proved that in most cases both oxygen and metal ions are mobile during oxide film growth on the Al, Nb, Ta, and W, but in Zr and Hf only oxygen transport is observed. Radiotracer measurements showed that the amount of metal dis-

solving in the electrolyte was usually less than 1% of the total oxidized, but that for Al it could be as high as 40%, depending on the current density and electrolyte used.

The values of the transport number of oxygen-containing species, t_{O_2} , and aluminium, t_{Al} , obtained so far are variable. The reported t_{Al} varies from 0.24⁽³³⁾, 0.33⁽³⁴⁾, 0.42⁽³⁵⁾ in boric acid and borate electrolytes; 0.54 to 0.63⁽³²⁾ in a mixture of 50g/l sodium tetraborate in 95% ethylene glycol and 5% water; 0.38 - 0.42 in ammonium pentaborate electrolytes⁽³⁶⁾, 0.46 - 0.68⁽³⁶⁾ in ethylene glycol electrolyte. It has been claimed that the transport number is current density dependent, e.g. in 3% aqueous ammonium citrate electrolyte, t_{Al} increases with the current density, changing from 0.33 - 0.41 at 1 Am⁻² to 0.72 at 100 Am⁻²⁽³²⁾.

Recently, transmission electron microscopy of ultramicrotomed sections of an aluminium substrate and the attached anodic film has been employed to reveal clearly an implanted xenon marker layer within the film⁽³⁷⁾. The position of the marker layer can be determined directly and relatively precisely, without the need for any indirect analytical techniques. From the position of the xenon marker layer in the preformed and final 300V films, a value of about 0.44 was obtained for the apparent transport number of aluminium. This value showed good agreement with the transport number of aluminium, 0.41 ± 0.04 , obtained by Brown and Mackintosh⁽³⁶⁾ using the Rutherford backscattering technique.

Marker experiments require careful xenon implantation in the specimen. The larger doses must impart greater radiation damage to the outer layer and inevitably interfere with the anodizing process. The dose of the radioactive

species can be as low as 10^{12} to 10^{13} atoms cm^{-2} , equivalent to an atomic fraction of 20 to 200 ppm⁽³²⁾. Thomas, Fallavier, Spender and Francois⁽³⁸⁾ found anomalous behaviour, including the formation of xenon bubbles and the detection of two xenon peaks, for influences of about 10^{15} atoms cm^{-2} at a cal energy of 30 KeV. Anomalous behaviour was also observed in the distribution of the implanted xenon atoms within the anodic film in the case of implantation into the metal⁽³⁷⁾. These were the extensively flawed film development over the area and the anomalous distribution of the xenon bubbles in the lower regions of the anodic film.

Only one type of tracer can be used in tracer experiments, and that is an isotope of the species being traced. In the first such experiment reported for anodic oxides, Amsel and Samuel⁽³⁹⁾ used ^{18}O as a tracer for oxygen during the formation of barrier layers on aluminium, and were able to show that the oxygen order is largely conserved, i.e., the oxygen atoms incorporated later remain nearer the oxide surface than those incorporated earlier. They then tried the corresponding experiment for metal migration, by depositing a layer of aluminium on a tantalum substrate. In effect, this was an attempt to use one metal, aluminium, as a tracer for another, tantalum, but that is logically impossible. If the migration of the metal being traced is unknown, there is no way of proving that the metal used as tracer migrates in the same way.

Some years later, however, Rigo and Siejka⁽⁴⁰⁾ performed a similar experiment with niobium and tantalum. Using Rutherford back-scattering, they were able to show that the metallic order was conserved during the anodization of a niobium layer deposited on a tantalum

substrate, i.e., the anodic niobium oxide formed first remained superimposed over the anodic tantalum oxide formed later. They then proceeded to the reverse experiment, the anodization of a tantalum layer deposited on a niobium substrate, and found that the order was not conserved; instead, it was partially inverted. Later work by Perriere, Siejka and Croset⁽⁴¹⁾ showed that it is possible to anodize metallic substrates such as Al, Ta, or Nb covered with calcia stabilized zirconia (CSZ) thin films. They suggested that if oxygen and cation transport events are not distinct, there would be only one transport event implying the simultaneous movement of cations and anions. The other extreme assumption is that the oxygen and cation transport events are distinct, oxygen transport events have to exist in the whole oxide and the current continuity, and the continuity of oxygen fluxes imply that a cationic charge M^+ has to be created at CSZ/oxide interface. Most recently, Perrier and Siejka^(42,43) used ^{18}O as a tracer for investigation oxygen and cation movements during the anodization of Nb on Ta and Ta on Nb superimposed layers. They reported that all results were consistent with a short-range migration for oxygen, as well as for cation transport, and a strong correlation appears between oxygen and cation migration.

One concept of a correlated motion of cations and anions has been proposed by Sato and Cohen⁽⁴⁴⁾ to explain their experimental observations of the logarithmic growth of anodic oxide films on iron. They visualized simultaneous place exchanges of this type along an entire line of atoms extending through a three dimensional layer. The activation energy for individual place-exchange events deduced by comparison of

this model with experimental data was about 0.15 eV. Later Basic⁽⁴⁵⁾ pointed out that this is probably too low by about an order of magnitude. Recently, Fromhold⁽⁴⁶⁾ proposed that there was an alternative to the simultaneous place-exchange mechanism of Sato and Cohen which led to a more realistic value for the activation energy. This alternative was a non-simultaneous place-exchange (or hop-on) mechanism, in which individual place-exchange events occur sequentially in time along a chain of dipoles extending through the medium. Conservation mechanisms for the growth of amorphous barrier films may be criticized because they are ideally based upon the transport of ions through an essentially crystalline lattice, and can not explain the 'overshoot' phenomena observed on ionic current or voltage transients.

Recently, the growth mechanisms suggested by Thompson et al.⁽⁴⁷⁾ have been refined in light of results obtained by Shimizu et al.^(48,49,37), using ultramicrotomy allied with both ion implanted xenon marker layers and electron beam induced crystallization, and Skeldon et al.^(50,51,52) using RBS. Films formed in a range of buffered electrolytes developed at nearly 100% current efficiency, with Al^{3+} egress and $\text{O}^{2-}/\text{OH}^-$ ingress to produce new film at the film/solution and metal/air formed film interfaces. There is no doubt on the previously described dissolution/precipitation model for their conditions, with solid film growth by the Al^{3+} egress occurring at the film/solution interface being preferred. The results pointed to a real cationic transport number of about 0.4. Interesting results concerning incorporated anion mobilities were also pre-

sented. Borate was found to be essentially immobile, phosphate mobile inwards, and tungstate and molybdate or their transformation products were mobile outwards.

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