

양극산화피막 형성에 관한 연구 (Ⅲ)

한 성 호

한국기계연구소 표면공학연구소

Anodic Film Formation on Aluminum(Ⅲ)

SEONG-HO HAN

Surface Engineering Laboratory, Korea Institute of Machinery and Metals,
Changwon, Kyung nam, Korea

양극산화 피막의 결정구조에 관한 연구는 1960년대 부터 반응 Mechanism의 연구와 병행하여 많은 논란이 되어 왔다. 결정구조의 정확한 Model 이 아직까지 확립되어 있지 않은 상태에서, 여러 가지 접근방식으로 연구되고 있는 실정이다. 최근에는 HRTEM, MAS - NMR 등의 고정밀 장비의 응용에 의한 결정구조의 분석이 활발히 진행이 되고 있으며, 이론 물리학의 응용 또한 이곳까지 확산되고 있는 상태이다. 본 고에서는 반응 Mechanism을 연구하는데 가장 밀접한 분야인 양극산화 피막 결정 구조에 관해 1950년대 이후 이렇게 연구되고 설명되었는가를 조망하기로 한다.

1. Introduction

It has long been recognized that anodic films are amorphous or consist of microcrystalline γ - Al_2O_3 or γ' - Al_2O_3 ^(1,2), the relative extent of the crystalline material depending on the formation conditions. However, a considerable amount of work has been undertaken to elucidate the precise microstructure of anodic films, since further insight into the growth mechanisms and likely chemical behaviour of such films. The presence of crystalline alumina in porous anodic films has been suggested over the years, but recent direct observation of the real film material in cross-section tends to suggest otherwise^(3,4,5) It has also been shown, a discussed in conjunction with barrier films, that crystalline γ or γ' -

Al_2O_3 can be promoted by electron beam heating of the film material^(4,5).

Crystalline alumina has at least 17 allotropes⁽⁶⁾, due to different arrangements of the aluminium and oxygen ions.

Structural studies using electron diffraction and X-ray diffraction techniques are of only limited value for amorphous solids. There has been speculation about the structure based on such measurements.

2. Microstructure of Anodic Films

Harrington and Nelson⁽⁷⁾ in an electron diffraction study of anodic films formed in a wide variety of electrolytes found the films

to be amorphous alumina of random structure. Wilsdorf⁽⁸⁾ found that he could relate the diffuse haloes observed in the transmission electron diffraction pattern with a possible structure composed of Al_4O_6 molecular units consisting of an octahedron of O^{2-} ions with Al^{3+} ions bonded to four of the octahedral faces. Taylor, Toker and Edwards⁽⁹⁾ suggested that the crystalline proportion of the film is not related to the type of electrolyte and is favoured by increasing film thickness, high temperature, high formation voltages, dilute electrolytes and ac current, which were thought to be related to high electrostatic stresses within thick films. This increase in the crystalline γ - Al_2O_3 proportion with increasing thickness was confirmed by Stirland and Bicknell⁽¹⁰⁾, using a dissolution technique involving the measurement of the oxide solubility in a mixture of phosphoric and chromic acids. Altenpohl⁽¹¹⁾, in a study of barrier-type films, also using a chemical dissolution technique, reported that the outer layer of such films which was assumed to be amorphous was soluble and the inner layer, which was assumed to be γ - Al_2O_3 , was insoluble.

Franklin⁽¹²⁾ suggested that anodic films formed in boric acid-borax electrolyte have at least three types of oxide. He reported that a hydrated oxide exists at the oxide-electrolyte interface resulting from the incorporation of water, leading to a gradual formation of monohydrate from amorphous oxide, and the inner layer is composed of patches of γ -alumina and amorphous alumina. Dorsey^(13,14) has examined film formed in a variety of electrolytes by infrared spectroscopy and found that adsorption peaks differ between porous and barrier

regions. The barrier layer was considered to be a strongly hydrogen-bonded polymer of cyclic aluminic acid trihydrate units, which was depolymerized as pores formed. Later work by Dorsey^(15,16) examined the effect of anodizing conditions on the Al-O-Al linkages, a structural feature which showed in the far infrared spectrum. A cross-linked Al-O-Al network in the form of helical fibres has been speculatively proposed for the porous layer, together with a similar model showing how sulphur in films formed in sulphuric acid could be chemically incorporated. A secondary barrier phase has been suggested where polymeric primary barrier material is decyclised before becoming incorporated into the cross-linked porous layer.

Oka et al.⁽¹⁷⁾ have attempted to account for the various peaks in X-ray scattering patterns in terms of a disordered structure derived from γ -alumina. There is support for such a structure from X-ray fluorescence spectra study by Takahashi et al.⁽¹⁸⁾ which have been interpreted on the basis that the Al^{3+} ions occur in both tetrahedral (four fold) and octahedral (six fold) coordination with O^{2-} ions, as in the case of crystalline γ -alumina.

A more direct approach has been made by El-Mashri et al.⁽¹⁹⁾ using high-resolution electron microscopy. They studied the structure of very thin films (< 10 nm thick) formed in sodium tartrate and stripped from the aluminium metal in mercuric chloride solution. This showed that, whilst the oxide is almost completely composed of a truly amorphous phase, there are small domains of quasi-crystalline structure. These contain a small number of regular 'lattice plane fringes' which suggests a tendency for the amor-

phous structure to be layer-like. Recently, El-Mashri et al. ⁽²⁰⁾ have investigated the molecular structure of the amorphous films formed on pure aluminium by anodic oxidation in sodium tartrate and phosphoric acid electrolyte, which are known to give different oxide morphologies using the technique of electron-yield EXAFS (extended X-ray absorption fine structure). They showed that the Al-O 'bond-length' derived from the EXAFS spectra to be different for the two types of film, which suggested different states of aluminium-oxygen co-ordination. It was further reported that the tartrate-formed film showed only slight morphological change and a correspondingly small change in Al-O bond length, whereas the phosphoric acid formed film undergoes an extensive change of morphology and bond length. They proposed that the amorphous structure is simply a bimodal distribution of octahedral $[\text{AlO}_6]$ and tetrahedral $[\text{AlO}_4]$ bonding; it is possible to derive the fractions, a and b, of these two co-ordination states from the average co-ordination number. Crystalline α -alumina, with 100% octahedral co-ordination is known not to hydrate. Therefore, they concluded that the ability to undergo amorphous nature of anodic film is related in some way to the existence of tetrahedrally bonded Al^{3+} . Popova ⁽²¹⁾, using transmission electron diffraction, found a bond length of 0.182 nm for borate-formed films, which corresponds to 100% tetrahedral co-ordination. Oka et al. ⁽¹⁷⁾ quoted $[\text{AlO}_6]/[\text{AlO}_4]$ ratios of 30 : 70 and 40 : 60, derived from X-ray fluorescence spectroscopy, for films formed in sulphuric acid using ac and dc polarizing voltages respectively. Normal et al. ⁽²²⁾ reported a bond length of 0.185 nm for an ano-

dized aluminium sample of unknown origin. This corresponded to a ratio of $[\text{AlO}_6]/[\text{AlO}_4]$ of about 30 : 70.

The studies using EXAFS suggest that the microstructure of anodic films consists mainly of both crystalline alumina and amorphous alumina. The relative proportions of these components are thought to depend on the anodizing conditions. The incorporation of anions and water from anodizing electrolytes makes consideration of the structural situation even more complicated. Recent direct observation of ultramicrotomed sections of anodic films, formed over wide range of conditions, does not show the presence of crystalline alumina ^(3,4), although crystallization of the film to γ' and γ -alumina can be induced in the electron microscope by electron beam heating. ^(4,5)

Several studies have quoted microcrystallite diameters or 'grain sizes' of the film material, with values ranging from 1 to 9.5 nm; Harrington and Nelson ⁽⁷⁾, from electron diffraction studies of films formed in sulphuric, oxalic and phosphoric acids determined a grain size of 1.2 nm; Philips ⁽²³⁾ quoted a value of 0.5–1.0 nm. Baker and Pearson ⁽²⁴⁾, using gas adsorption and wide-line nmr spectroscopy, claimed a microcrystallite radius of 2.4 nm. Alvey ⁽²⁵⁾, using a low angle X-ray scattering technique, reported microcrystallite dimensions of about 9.0, 9.5 and 4.0 nm for films formed in oxalic, phosphoric and chromic acids respectively. Electron microscopy of ion beam thinned porous anodic films by Thompson et al. ⁽²⁶⁾ revealed a texture in the cell material which related to a microcrystallite size of about 2 ~ 2.5 nm. Again, direct observation would appear to contradict values at the

higher end of this range, and, in reality, doubt exists as to whether the films are truly amorphous, exhibiting no electron diffraction, microcrystalline, or glassy in nature, the last denoting a lack of long range order.

However, from the data of the kind given earlier, some attempts have been made to elucidate the microstructural model of anodic films. Murphy and Michelson⁽²⁷⁾ proposed a model of the microstructure of porous anodic films which was based on colloidal chemistry concepts. A schematic diagram illustrating their model is shown in Figure 1. They considered anodic films to be an agglomeration of sub-microcrystalline particles, probably of anhydrous Al_2O_3 , surrounded and held together by submicroscopic regions, the intercrystalline regions, containing electrolyte anions, water molecules, hydroxyl and hydrogen ions in a relatively complex hydrogen-bonded system. They also proposed an outer porous region in anodic films formed in highly acidic electrolytes containing physically distinguishable pores and regions of differing hydration and density of film material.

O'Sullivan, Hockey and Wood⁽²⁸⁾, using infrared spectroscopic methods including isotopic exchange techniques, proposed a microstructural model for both unsealed and sealed films. They suggested that unsealed films were a relatively open array consisting of amorphous alumina crystallites and were permeated by molecular water, the surfaces of the crystallites carrying hydroxyl groups or ions. Hydrothermal treatment caused the structure to re-arrange by an agglomeration process into a more closely packed configuration, limiting the removal of molecular water and the extent of deuterium exchange. A

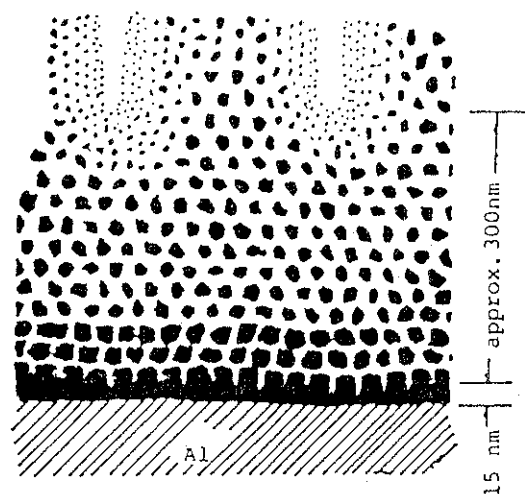


Fig. 1 Schematic representation of the porous anodic film as suggested by Michelson²⁷⁾, showing the pores, which were considered to be of secondary importance, near the outer surface of the film.

recent proposal by Thompson and Wood⁽²⁹⁾, refining earlier thinking, was that the film material consists of an open array of alumina microcrystallites typically in the range 2.5 ~ 10 μm , with indistinct boundaries between them comprising of a hydrogen bonded magma of alumina, the acid anion and water.

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