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On the Nature of "Easy Paths" for the Diffusion of Oxygen in Thermal Oxide Films on Aluminum

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Thermal oxide films grown on electropolished aluminum specimens have been investigated by transmission electron microscopy of stripped oxide films and ultramicrotomed sections. Particular attention has been focused on the nucleation sites of γ-Al_2O_3 *crystals and the relationship of such sites to surface features on the electropolished aluminum surface. It is evident that "easy paths" for the diffusion of oxygen, or the nucleation sites of* γ-Al_2O_3 *crystals, are not distributed randomly over the electropolished aluminum surface, but form preferentially in the amorphous oxide layer grown over preexisting metal ridges. Thus, the diffusion of molecular oxygen through cracks in the amorphous oxide layer represents the most realistic and acceptable basis for explaining the local growth of the* γ-Al_2O_3 *crystals in thermal oxide films on aluminum, although the cracks have not yet been observed directly.*

KEY WORDS: easy diffusion paths; Al_2O_3 films; γ-Al_2O_3 nucleation sites; amorphous film.

INTRODUCTION

The high affinity of aluminum for oxygen ensures that the aluminum surface is always covered with an amorphous oxide layer, 2–3 nm thick, which is generally called an "air-formed" film. If aluminum supporting an air-formed film is heated in air or oxygen, varied behavior is evident which depends

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on the oxidation temperature. For oxidation temperatures up to 350°C, the oxidation kinetics have been represented by an inverse logarithmic law,[1,2] whereas between 350–425°C the oxide thickens according to a parabolic law.[3,4] At higher oxidation temperatures, complex oxidation kinetics have been observed.[5–8]

At oxidation temperatures below about 425°C, the amorphous air-formed film thickens to values of about 20 nm. To explain the oxidation kinetics, it has been proposed that at oxidation temperatures up to 300°C, the amorphous film growth is controlled by the migration of aluminum ions through the film under the influence of a high electric field created by oxygen ions on the outer amorphous oxide surface.[1] Beck *et al.*[8] have noted the similarity between this model and anodic oxidation of aluminum at ambient temperatures in aqueous electrolytes. However, more recent studies have shown that anodic oxidation of aluminum under high field conditions always involves the simultaneous, possibly cooperative, migration of Al^{3+} and O^{2-} ions.[9]

For oxidation of aluminum at temperatures in the range 300–425°C, the parabolic rate law is explained by outward diffusion of Al^{3+} ions controlling the oxidation rate.[8] At higher oxidation temperatures, the oxidation behavior is explained by two processes: the growth of amorphous alumina and the eventual development of crystalline γ-alumina at the amorphous alumina/metal interface.[5–8,10] For example, if aluminum supporting an air-formed film is heated in air or oxygen at temperatures above 450°C, thickening of the amorphous oxide layer is observed initially but, after some induction period, γ-alumina crystals start to grow at the amorphous oxide–metal interface. The growth of γ-alumina does not proceed by crystallization of the initially formed amorphous oxide layer, but by the inward diffusion of oxygen through "easy paths" in the amorphous oxide layer. Although this has been demonstrated clearly by transmission electron microscopy of shadowed carbon replicas taken from the oxide–air and oxide–metal interfaces,[8,11] and more recently by O^{16}/O^{18} SIMS analysis,[12] the nature of the "easy paths" for the diffusion of oxygen still remains uncertain.

In the present paper, electropolished aluminum specimens were thermally oxidized in air at 515°C for various periods of time. The thermal oxide films were then stripped from the aluminum substrate and examined thoroughly in the transmission electron microscope, with particular attention directed at the sites at which γ-alumina crystals nucleate and the relationship of such sites to surface features on the aluminum substrate. Furthermore, ultramicrotomed sections of the aluminum substrate and its thermal oxide film were also prepared, enabling observation by transmission electron microscopy to gain further insight into the structure of the thermal oxide.

EXPERIMENTAL

Annealed aluminum foil of 99.99% purity and 0.1 mm thickness was used for all experiments. This foil is polycrystalline, with grain sizes around a few hundred microns, but exhibits a preferred (100) orientation. About 90% of the surface is covered with grains of (100) orientation, with the rest having orientations close to (110) or (311), as determined by the etch pit method.

The foil was cut into small pieces of dimensions 10 × 50 mm. They were then electropolished individually in a perchloric acid-ethanol bath at temperatures lower than 10°C using a constant current density of 100 mA/cm^2. After electropolishing, the specimens were rinsed thoroughly in absolute ethanol and, finally, dried in a warm air stream. Prior to thermal oxidation, the electropolished foils were given a brief etch in a solution consisting of 1.5 ml of HF, 10 ml of H_2SO_4, and 90 ml of H_2O for 30 sec, rinsed thoroughly in distilled water, and then dried in a warm air stream.

Thermal oxidation was carried out in air at 515°C for various periods of time using an electric furnace. Thermal oxide films were stripped from the aluminum substrate using a mercuric chloride/methanol solution and rinsed thoroughly in absolute ethanol before being collected on copper grids for electronoptical examination.

Ultramicrotomed sections of the aluminum substrate and its thermal oxide film were prepared in the usual way[13] using a DuPont Sorvall MT 5000 ultramicrotome. The encapsulated specimens were trimmed with a glass knife, and suitably thin sections, between 5 and 10 nm thick, were prepared by sectioning in a direction approximately parallel to the oxide-metal interface with a diamond knife.

The stripped films and ultramicrotomed sections were examined in a JEM 2000 FX II transmission electron microscope operated at 100 kV.

RESULTS AND DISCUSSION

Figure 1 shows transmission electron micrographs of the stripped oxide films grown on the (100) and (110) faces of aluminum by heating in air at 515°C for 30 min. The thermal oxide film grown on the (100) face is amorphous and appears relatively featureless. On the other hand, a characteristic furrowed pattern is observed in the thermal oxide film grown on the (110) face; relatively long, straight furrows, spaced about 870 nm, are observed clearly. Gamma-alumina crystals with sizes up to about 0.1 μm are also observed in the thermal oxide film grown on the (110) face. The crystals are rod-shaped, with their long axes aligned perpendicular to the straight furrows. Electron diffraction analysis reveals an epitaxial relationship between the aluminum substrate and the γ-Al_2O_3 crystals in such a way that $(100)_{ox}/\!/(100)_{Al}$, as evident from the essentially single-crystal diffraction pattern (inset, Fig. 1b). Direct counting of the number of crystals gives an average nucleation density of $2.2 \times 10^{10}/cm^2$.

An important correlation is readily noted between the nucleation sites of the γ-Al_2O_3 crystals and the furrowed background contrast observed in the amorphous oxide film. It appears that the γ-Al_2O_3 crystals are not distributed randomly over the surface, but are sited along the straight furrows. More specifically, the γ-Al_2O_3 crystals are present along the relatively straight and fine bands of darker contrast in the furrowed background pattern. No crystals are readily observed in the wider bands of lighter contrast between the darker bands.

Figure 2 shows transmission electron micrographs of the stripped thermal oxide films, formed in air at 515°C for 30 min, on other unspecified faces of aluminum. Darker corrugation patterns are observed clearly in the amorphous region of these films. Gamma-alumina crystals are also observed and are of pentagonal (Fig. 2a) or rod-shaped (Fig. 2b). The average nucleation density of the γ-Al_2O_3 crystals is estimated to be 3.2×10^9 and $1.0 \times 10^{-10}/cm^2$ for the films shown in Fig. 2a and b, respectively. Electron diffraction analysis has shown an expitaxial relationship between the aluminum substrate and the γ-Al_2O_3 crystals in these films. However, no further attempts were made to determine the orientation of these aluminum

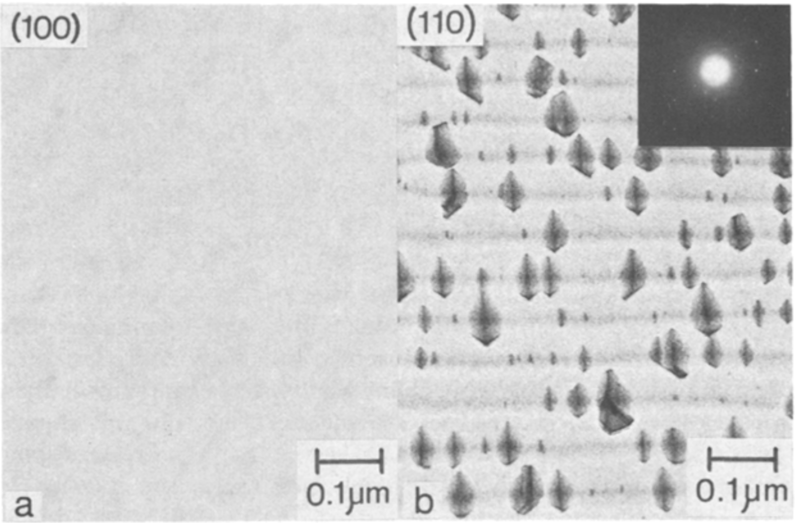

Fig. 1. Transmission electron micrographs of the stripped thermal oxide films grown on aluminum in air at 515°C for 30 min: (a) (100) grain orientation; (b) (110) grain orientation.

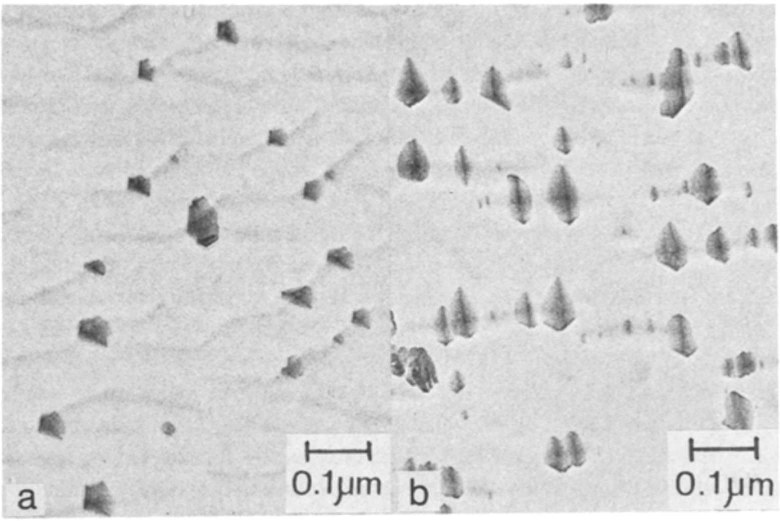

Fig. 2. Transmission electron micrographs of the stripped thermal oxide films grown on grains of non (100) orientations, showing the preferential nucleation of γ-Al_2O_3 crystals along the darker corrugation patterns.

substrates. It is readily noted that the γ-Al_2O_3 crystals are again not distributed uniformly over the surface, but are present along the darker corrugation patterns as observed in the (100) face. Figure 2a also indicated clearly that the triple points in the darker corrugation pattern, where three furrows meet, are the most favorable sites for the nucleation of the γ-Al_2O_3 crystals.

Figure 3 shows a transmission electron micrograph of the stripped thermal oxide film grown on the (100) face of aluminum in air at 515°C for 1 hr. After 1 hr oxidation, the growth of discrete γ-Al_2O_3 crystals is observed in the thermal oxide films grown on the (100) face. The crystals are of sizes up to about 0.1 μm and exhibit very irregular shapes. No specific shape can be assigned for the crystals and, hence, no "characteristic shape" exists for γ-Al_2O_3 crystals grown on the (100) face of aluminum. Furthermore, a network of fine cracks is observed in each γ-Al_2O_3 island. The electron diffraction pattern (inset, Fig. 3) indicates a random orientation of the γ-Al_2O_3 crystals as evident from the diffraction rings, which are characteristic for polycrystalline materials. From Fig. 3, the average nucleation density of the γ-Al_2O_3 crystals is estimated to be about $7.7\times 10^9/cm^2$. A close comparison between Figs. 1a and 3 also indicates that the γ-Al_2O_3 crystals are not distributed randomly over the surface, but are present along the hexagonal cell pattern observed only faintly in the amorphous oxide film.

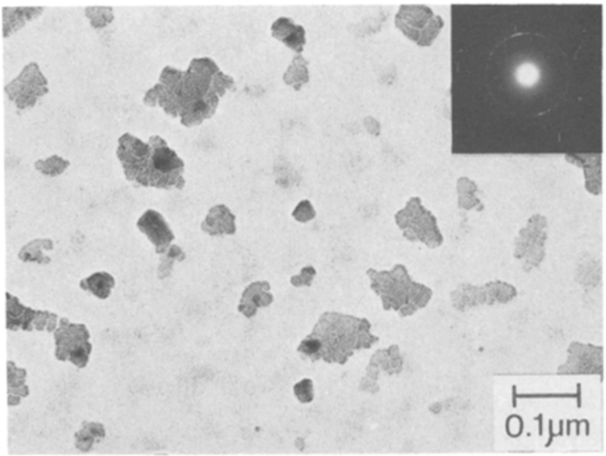

Fig. 3. Transmission electron micrograph of the stripped thermal oxide film growth on the (100) aluminum grain orientation in air at 515°C for 1 hr.

Thermal oxide films on aluminum have been examined in the transmission electron microscopy by many workers.[8,11,12,14,15] Some of the results presented above are, therefore, by no means new. Thus, the epitaxial relationship between the aluminum substrate and γ-Al_2O_3 crystals developed on the (100) orientation and the random orientation of γ-Al_2O_3 crystals for the (100) orientation have already been found in 1963 by Doherty and Davis.[11] However, the present work has revealed clearly, for the first time, an important correlation between the nucleation sites of γ-Al_2O_3 crystals and the background contrast observed in the amorphous oxide layer. It is readily evident that the nucleation sites of the γ-Al_2O_3 crystals are not distributed randomly over the surface as suggested by Beck *et al.*,[8] but preferential nucleation sites are apparent. In turn, this indicates the existence of preferential sites in the amorphous oxide layer for the formation of the "easy paths" for the inward diffusion of oxygen. Evidently, such sites are the narrow, relatively dark bands in the furrowed or corrugation patterns observed in the amorphous region of the stripped thermal oxide films.

In order to gain further insight into the nature of these darker bands, ultramicrotomed sections of the aluminum substrate and its air-formed oxide film or thermal oxide film were prepared and examined by transmission electron microscopy.

Figure 4 shows a transmission electron micrograph of an ultramicrotomed section of the aluminum substrate and its air-formed oxide film or,

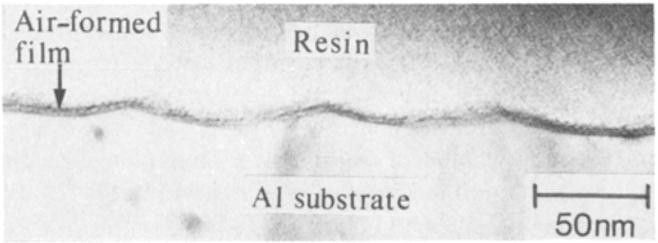

Fig. 4. Transmission electron micrograph of an ultramicrotomed section of the aluminum substrate and its air-formed oxide film, showing the presence of ridges on the electropolished surfaces.

more strictly, the air-formed film developed on the electropolished aluminum surface. The aluminum substrate is observed at the bottom of the micrograph and exhibits a scalloped or ridged surface. It is evident, therefore, that the electropolished aluminum surfaces are considerably different from the ideal crystal planes represented by models based on the packing of hard spheres. The embedding resin is observed at the top of the micrograph. The air-formed oxide film, about 3 nm thick, is observed between the aluminum substrate and the embedding resin. The thickness of the air-formed oxide film appears uniform, with no local regions of thicker film formation readily evident.

Figure 5 shows a transmission electron micrograph of an ultramicrotomed section of the aluminum substrate and its thermal oxide film grown in air at 515°C for 30 min. Only a ridged surface region is presented here at a relatively high magnification. The aluminum substrate is observed at the bottom of the micrograph. The embedding resin, which became detached

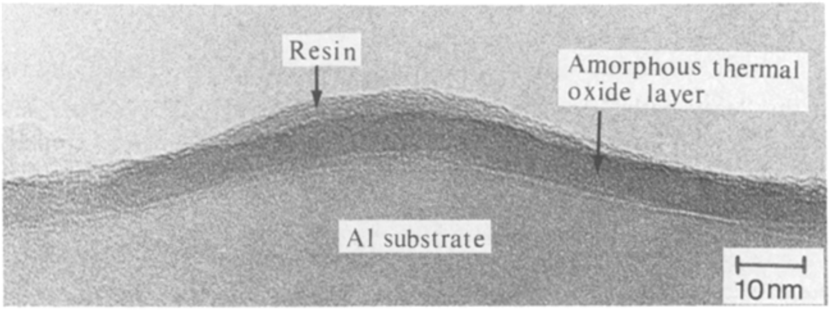

Fig. 5. Transmission electron micrograph of an ultramicrotomed section of the aluminum substrate and thermal oxide film grown in air at 515°C for 30 min, showing the uniformity in the film thickness.

from the oxide surface during sectioning, is not observed in the micrograph. The thermal oxide film is observed over the ridged aluminum substrate. The oxide film is uniform in thickness, which is about 5.5 nm, and appears amorphous. No local regions of thicker film formation nor periodic variations in film thickness, as suggested by Doherty and Davis,[11] are observed. It is noted here that the present observations were made using an annealed polycrystalline aluminum foil of 99.99% purity with more than 95% of the surface grains having the non-(100) orientations.

Given these observations, it is now evident that the background contrast observed in the amorphous region of the stripped thermal oxide film is not due to the local variation in film thickness, but rather to the presence, in the electropolished aluminum surfaces, of a network of ridges whose pattern is dependent on the grain orientation of the aluminum surface and the initial electropolishing treatment. The amorphous thermal oxide film is of uniform thickness perpendicular to the local metal surface (Fig. 5). However, when the amorphous thermal oxide films grown on the ridged aluminum surfaces are stripped from the substrate and are examined in plan in the transmission electron microscope (i.e., normal to the plane of the entire film), the film grown over the ridges is viewed obliquely, thus giving rise to the relatively dark local contrast in the image.

This interpretation of the origin of the background contrast observed in the amorphous region of the stripped thermal oxide films leads to an important conclusion concerning the sites for the "easy paths" for the diffusion of oxygen. Such sites form preferentially in the amorphous oxide layer covering the metal ridges. The preferential nucleation of the γ-Al_2O_3 crystals at the metal ridges was also confirmed by transmission electron microscopy of ultramicrotomed sections, as shown in Fig. 6. Here, the aluminum surface exhibits a ridged appearance and supports an amorphous oxide layer about 6 nm thick. A fine γ-Al_2O_3 crystal is observed clearly at the top of the metal ridge and beneath the amorphous film, as indicated by the arrow in the micrograph.

These observations suggest strongly that the "easy paths" for the diffusion of oxygen are cracks which develop in the initially developed amorphous oxide layer. During specimen heating up, the amorphous thermal oxide layer is subjected to tensile stresses due to the difference in the thermal expansion coefficient between the oxide and aluminum. These stresses would add to any tensile growth stresses preexisting in the amorphous alumina, or would likely exceed any such compressive stresses. Bubar and Vermilyea[16] have indicated that thin alumina films have some ductility while thicker films (greater than about 5 nm) appear to be entirely brittle. Cracking of the amorphous oxide layer represents a route through which the stresses are relieved. There is little doubt that the ridges or the triple

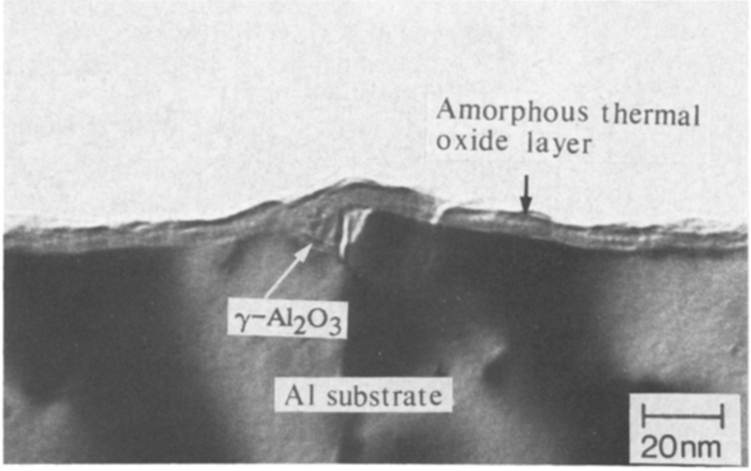

Fig. 6. Transmission electron micrograph of an ultramicrotomed section of the aluminum substrate and the thermal oxide film, showing the nucleation of a γ-Al_2O_3 crystal at the metal ridge beneath the amorphous oxide layer.

points of the ridges, where high local stresses are expected, are the most preferable sites for the film cracking. Once cracks develop in the amorphous oxide layer, molecular oxygen has ready access to the metal-oxide interface. The direct reaction between the molecular oxygen diffusing through the cracks and the exposed bare aluminum surface leads to the growth of γ-Al_2O_3 crystals at the amorphous oxide-metal interface as indicated by Henry *et al.*[17] and by Eldridge *et al.*[12] The precise reason why γ-Al_2O_3 nucleates, rather than the more amorphous alumina, is not totally understood. Because of the combination of epitaxy and stress conditions on the ridges, this may favor crystal development. Additionally, or alternatively, nucleation on bare metal at high temperatures may favor this process. Furthermore, the volume expansion associated with crystalline alumina formation leads to the development of high local strains in the amorphous oxide layer, particularly at the peripheries of the crystals, which would, in turn, contribute to enhanced cracking of the amorphous oxide layer. The densities[18] of aluminum and γ-Al_2O_3 are $2.7 \times 10^3\,\mathrm{kg\,m^{-3}}$ and $3.2 \times 10^3\,\mathrm{kg\,m^{-3}}$, respectively, leading to a volume increase from aluminum transforming to γ-Al_2O_3 of about 19%. The peripheral feeding of the molecular oxygen through such cracks allows the lateral and continuous growth of the γ-Al_2O_3 crystals, since new cracks are always being formed at the peripheries of the expanding crystal boundaries, as shown schematically in Fig. 7.

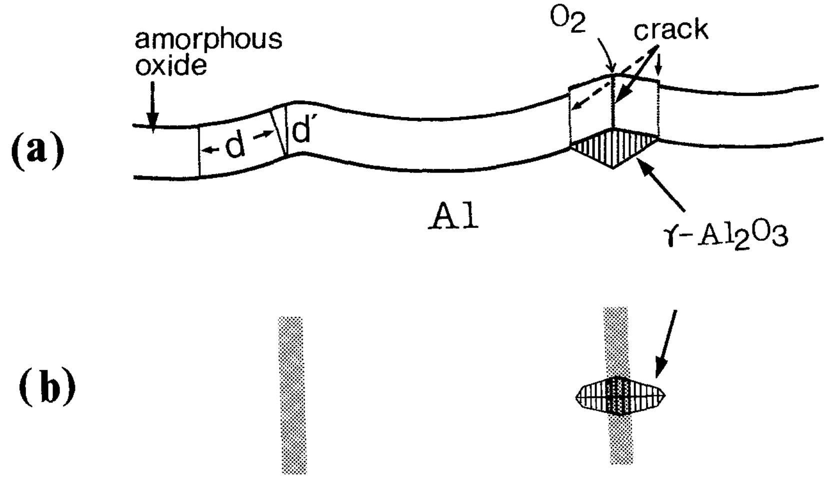

Fig. 7. Schematic diagram representing the growth of the γ-Al_2O_3 crystals during thermal oxidation of aluminum: (a) cross-sectional view; (b) plan view. The likely initial cracks develop in the amorphous oxide layer covering the metal ridges due to the development of tensile stresses. Molecular oxygen then diffuses through the cracks to react with the exposed bare aluminum surface, forming γ-Al_2O_3 crystals at the amorphous oxide-metal interface. Thereafter, the volume expansion during crystal formation probably leads to the formation of new cracks at the peripheries of the crystal. The peripheral feeding of the molecular oxygen through such cracks allows lateral and continuous growth of the γ-Al_2O_3 crystals. Also shown is the origin of the darker contrast in the image in the transmission electron microscope. Thus, parts of the film grown over the ridges are viewed obliquely, giving rise to the locally darker contrast in the image. Note that the thickness d' is greater than d.

The present view that the "easy paths" for the diffusion of oxygen are associated with cracks which develop in the amorphous oxide layer during heating is reinforced further by the following experimental observation. Here, the electropolished aluminum foils were etched in the solution consisting of 1.5 ml of HF, 10 ml of H_2SO_4, and 90 ml of H_2O for 60 sec (instead of the previously used 30 sec). A longer etching in the solution produced etch tunnels extending deep into the metal. The etched tunnels are bounded by the orthogonal (100) faces and form preferentially over grains of non-(100) orientations.

Figure 8 shows a transmission electron micrography of the stripped thermal oxide film, grown in air at 515°C for 30 min, on a grain with penetrating etch tunnels. An examination of the micrograph reveals immediately that the edges of the tunnels, sited where the orthogonal (100) faces meet, are the most preferential sites for the nucleation of the γ-Al_2O_3 crystals; at such locations, the crystals line up along the edges as shown by the arrows in the micrograph. No crystals are readily observed on the walls

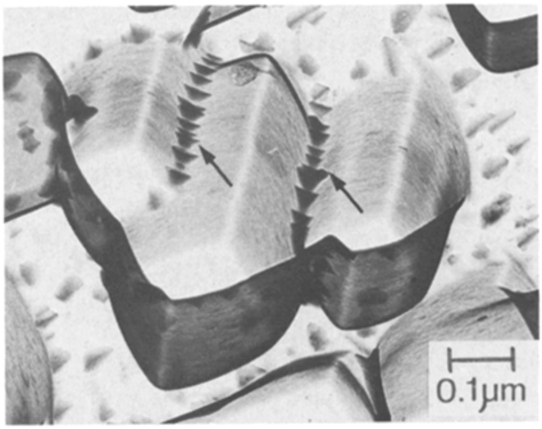

Fig. 8. Transmission electron micrograph of the stripped thermal oxide film grown on an aluminum grain with the previously developed etch tunnels. Thermal oxidation reveals the preferential nucleation of γ-Al_2O_3 crystals at the edges of the etch tunnels, which are formed where orthogonal (100) faces meet.

of the tunnels, which are of (100) orientation and appear relatively smooth. This observation, together with the results presented previously, indicates a crucial role played by the microscopic surface roughness of the substrate in the formation of "easy paths" for the diffusion of oxygen through the amorphous oxide layer. A further interesting feature (Fig. 1) is that when new γ-Al_2O_3 crystallites develop between preexisting ions—they occupy half-way positions. This may well reflect the initial cracking pattern of the amorphous oxide. Thus, Riley[19] and Edeleanu and Law[20] have shown that when anodic films on aluminum are extended in tension, new cracks develop progressively mid-way between existing cracks; however, in this case, the anodic films were thicker than the amorphous oxide developed at 515°C.

SUMMARY AND CONCLUSIONS

Previous studies[8,11] have established that the growth of γ-Al_2O_3 crystals occurs at the amorphous oxide-metal interface by the inward diffusion of oxygen through the highly localized "easy paths" in the initially formed amorphous oxide layer. However, the nature of the "easy paths" and the transport mechanism of oxygen through these "easy paths" has remained the subject of discussion. Randall and Bernard[14] found that the growth of γ-Al_2O_3 crystals at 600°C occurs at the amorphous oxide-metal interface even in the presence of an initially developed amorphous anodic film of thickness about 360 nm. It was suggested that γ-Al_2O_3 crystals grow by the inward diffusion of molecular oxygen through the cracks or fissures which develop in the amorphous anodic oxide layer during heating, since the anionic diffusion of oxygen through such thick amorphous anodic oxide layer seems totally unlikely even at 600°C. More recently, Eldridge *et al.*[12] have employed an O^{18}/SIMS technique to specify the transport mechanism of oxygen through the "easy paths" in the amorphous oxide layer. It was suggested that the anionic diffusion of oxygen through the "easy paths" in the amorphous oxide layer is responsible for the growth of γ-Al_2O_3 crystals in the thermal oxide films on aluminum. However, the nature of the "easy paths" for the diffusion of oxygen was not specified.

The present work has revealed clearly that the "easy paths" for the diffusion of oxygen, or the nucleation sites of γ-Al_2O_3 crystals, are not distributed randomly over the surface, but form preferentially in the amorphous oxide layer covering the unavoidable metal ridges associated with metal treatment prior to oxidation. Preferential nucleation of γ-Al_2O_3 crystals was also found along the orthogonal edges of the etch tunnels. If anionic diffusion of oxygen is assumed, it is difficult to understand why the "easy paths" for the diffusion of oxygen should form preferentially in the amorphous oxide layer covering the metal ridges. One possibility, other than cracks, is that they are regions of less dense amorphous oxide, as suggested by one of the referees; however, the nature of such material, or how it would grow preferentially over metal ridges is not clear. Thus, the diffusion of molecular oxygen through the cracks which develop during thermal oxidation in the amorphous oxide layer covering the metal ridges seems the most expected and realistic basis for explaining the local growth of the γ-Al_2O_3 crystals in the thermal oxide films on aluminum.

In a later paper, the nature of the induction period, when the authors believe fine crystal development proceeds, will be explored further. Also, the effect of rate of heating to the oxidation temperature and for a constant oxidation time, the effect of isothermal treatment and thermal cycling on the nucleation of γ-Al_2O_3 and the development of "easy paths" will be discussed.

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