MODEL OF OXIDE FILM GROWTH DURING ANODIZATION OF ALUMINUM

V. Yu. Izotov, Yu. A. Maletin, L. B. Koval', A. A. Mironova, S. G. Kozachkov, and V. P. Nezdorovin

A theoretical model is proposed for describing the growth of an amorphous or polycrystalline oxide film on an aluminum surface during its anodization. An example of anodization in electrolytes based on salts of dicarboxylic acids is used to illustrate a satisfactory agreement of the model with the experimental data.

Anodic oxidation of aluminum results in the formation on its surface of a polycrystalline or amorphous oxide film that protects the metal from further dissolution [1, 2]. The structural characteristics of the film in turn determine its physical and chemical properties. Known theoretical models [3-5] for describing the growth of the oxide film on the surface of aluminum and other rectifier metals ignore the structure of the film and do not consider the influence of electrolyte composition on the anodization process.

They assume that only water molecules can act as the source of oxygen. Therefore, the purpose of the present work was to develop a theoretical model of the formation of an amorphous or polycrystalline oxide film on aluminum and to answer the question of how the oxide film structure on the surface of aluminum changes during its anodization and what it depends on. In the modelling of the film growth process, the electrochemical reactions at the oxide—electrolyte boundary are examined, and it is assumed that in addition to water, other oxygen-containing particles present in the electrolyte can act as oxygen sources.

The following data indicate that water is not the only source of oxygen atoms in the formation of anodic oxide film. During galvanostatic anodization of aluminum in thoroughly dried solutions (water concentration < 10^{-2}% ) of dicarboxylic acids in propylene carbonate and γ-butyrolactone, the anodization voltage, 50-100 V, is easily reached (see Table 1). This corresponds to the formation of a barrier layer 0.12-0.15 μm thick [1]. Attempts at anodization in lithium or tetraethylammonium tetrafluoroborate solutions in acetonitrile with the same moisture content showed that no barrier film is formed if oxygen-containing compounds are not added. On the other hand, as is evident from Fig. 2, the anodization voltage and hence, the thickness of the aluminum oxide barrier film depend on the number of methylene links in the dicarboxylic acid and consequently, on the size of the corresponding anion.

On the basis of these data, we will construct a model of the process taking place at the oxide—electrolyte boundary. According to [5], the anodization process begins with the coordination of HO^- anion (or RO^m- anion in our more general case) with an aluminum atom in the surface layer of the oxide:
TABLE 1. Maximum Voltage \(U_{\text{max}}\) and Time of Aluminum Anodization in Dehydrated Electrolytes at a Current Density of 5 mA/cm\(^2\)

<table>
<thead>
<tr>
<th>Electrolyte composition</th>
<th>U(\text{max}), V</th>
<th>Time necessary to reach U(\text{max}), min</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-Butyrolactone</td>
<td>50</td>
<td>1.0</td>
</tr>
<tr>
<td>Dimethylformamide</td>
<td>52</td>
<td>1.0</td>
</tr>
<tr>
<td>N-Methylacetamide</td>
<td>88</td>
<td>1.0</td>
</tr>
<tr>
<td>3-Methoxypropionitrile</td>
<td>80</td>
<td>1.6</td>
</tr>
<tr>
<td>Propylene carbonate</td>
<td>105</td>
<td>2.5</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>0</td>
<td>—</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>0</td>
<td>—</td>
</tr>
</tbody>
</table>

The second step may include dissociation of \(R-O\) bonds with the formation of oxygen-rich quasi-ions on the surface. Subsequent steps are usually represented in the form of various processes of charge transfer: migration of the quasi-ions to the metal–oxide boundary, transfer of electrons across this boundary, and migration of aluminum ions from the metal surface to the oxide–electrolyte boundary [4].

It will be assumed that as film growth takes place, both polycrystalline and amorphous regions can exist on the oxide surface. Discharge of oxygen-containing anions in the polycrystalline region leads to growth of a polycrystalline layer, and in the amorphous region, of an amorphous layer. The probability of an electrochemical reaction on the oxide surface may be represented in the form

\[
W = c_i \exp(-E_i/k_B T),
\]

where \(c_i\) is the concentration of discharging ions on the Helmholtz inner plane (HIP), and the index \(i\) takes on the values 1 and 2, corresponding to the polycrystalline and amorphous regions; \(E_i\) is the size of the barrier characterizing the migration of oxygen atoms from the electrolyte to the oxide surface with the formation of a quasi-ion. The value of \(E_i\) is chiefly determined by the difference between the binding energies of oxygen in the discharging ion and in the adsorbed state on the oxide surface. These interactions are brief and may be assumed independent of the oxide structure.

The quantity \(c_i\) is related to the volume concentration \(c_0\) by the equation

\[
c_i = c_0 \exp\left(-\frac{E_i + z\psi_i}{k_B T}\right),
\]

where \(E_i\) is the energy of the image forces of the oxygen-containing anion on the HIP; \(z\) is the charge of the oxygen-containing anion; \(\psi_i\) is the potential on the HIP.

To answer the question of what oxide film will grow as the anodization takes place, let us consider the ratio of the probabilities of the electrochemical reaction on active centers pertaining to the polycrystalline and amorphous regions. This ratio is

\[
\frac{W_1}{W_2} = \exp\left[\frac{E_2 - E_1 + z(\psi_2 - \psi_1)}{k_B T}\right].
\]

When \(W_1/W_2 > 1\), the predominant growth will be that of the polycrystalline film, and when \(W_1/W_2 < 1\), the predominant growth will be that of the amorphous film.

Figure 1 shows the model of a film on an aluminum surface. The film is characterized by two dielectric constants which correspond to the polycrystalline \((\varepsilon_1 \approx 10)\) and amorphous \((\varepsilon_2 \approx 20)\) portions of the oxide. To describe the dielectric properties of the metal, the Thomas–Fermi model was used. The metal–oxide and oxide–electrolyte boundaries were assumed to be sharp, and the surface, homogeneous.