THE USE OF NUCLEAR REACTIONS TO TRACE THE SOURCE OF OXYGEN IN ANODIZATION

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Summary

In cases where the anodization of metals involves the use of chemical solutions, the oxidation mechanism is frequently uncertain. In such cases it is usually possible to make oxygen bearing solutions from oxygen which is enriched in isotope-18. After use in anodization, the oxide films can be analyzed by the method of nuclear microanalysis which separates profiles the 16O and 18O. In this way the depth distribution of the 18O can be compared quantitatively with that of the 16O arising from all other oxygen bearing chemicals in solution. We have applied this method to the case of the anodization of vanadium and zirconium. The results indicate an unconventional anodization mechanism for the vanadium case.

Introduction

In the usual process of anodization of a metal negatively charged hydroxyl ions (anions), OH−, migrate to the positively charged metal, M+, by action of the electric field in an electrically conducting solution. At the anode an oxidation process takes place and an oxide layer MxOy forms on the metal surface. After an oxide layer forms on the surface, the oxidation process cannot readily continue unless the oxygen bearing anions can migrate through the oxide layer. This is usually accomplished by increasing the electric field or anode voltage. Since pure water is low in hydroxyl ions and is a poor electrical conductor, a small amount of KOH can be dissolved in solution to raise the OH− concentration several orders of magnitude:

\[ \text{KOH} + \text{HOH} \rightarrow \text{K}^+ + \text{OH}^- + \text{HOH} \quad (1) \]

In this case of only one type of anion, the source of oxygen in the anodization is understood.

However, in some anodization techniques, water based solutions are not used. In the case we discuss below, the anodization of vanadium, vanadium oxide is known to be water soluble so that precise thicknesses of oxide films cannot be made with water based electrolytic solutions. For this reason Keil and Salomon devised a technique using an almost nonaqueous solution of acetic acid, CH₃COOH, 2.0 M in water and 0.02 M in sodium tetraborate, Na₂B₄O₇. While they have suggested that the oxygen in the resulting oxide film is provided by the water, the anodization mechanism here is clearly more complex with three oxygen bearing compounds in solution. Not only is the initial source of oxygen in the oxide film of interest, but also whether the anodization mechanism changes after the initial passivation. We show below that it is possible to answer these questions by using oxygen isotopes to form the oxygen bearing compounds and by examining the resulting oxide films by the method of depth profiling using nuclear reactions.

Experimental

A. Anodization

Single crystal vanadium disks were used for the anodization; the faces were (110) planes of the crystal. To prepare a face for anodization, the specimen was polished through 3/0 emery paper, lapped with 6-µm diamond paste, fine polished with 0.3 µm Al₂O₃ suspension, and etched with a 70% (by volume) tretic acid-30% nitric acid solution. The anodization was performed in the solution suggested by Keil and Salomon at a formation potential of 20 to 50 V. The resulting oxide film, when formed at 21 V, was goldish in appearance and had to be immediately dried with compressed air in order to stabilize it.

In order to determine the source of oxygen in the oxide, 16O was used to label some of the oxygen containing species in the anodizing solution. Water enriched to 90% 18O was added to the solution to determine if the water was the oxygen source. To determine if the oxide comes from the acetic acid, acetic anhydride and H₂O (90% 18O) were reacted to form acetic acid. The anodizing solution was then made, as previously described, and similar anodization procedures were then used for each solution. The oxygen, which was an integral part of the sodium tetraborate molecule, was not labeled.

A specimen of zirconium was anodized in 1 wt % KOH solution (90% 18O enriched H₂O) to form an oxide layer which contained 18O. This specimen was used to compare with the vanadium measurements. The specimen was anodized at 100 V, an oxide layer approximately 2900 A thick being produced. ³

B. Analysis

The ion scattering analytical technique, such as that described by Ansel, is a sensitive probe for measuring isotope concentrations and concentration profiles in various substrates. We use the method here to measure the 18O/16O ratio near the surface of anodized vanadium and zirconium targets. Our particular approach is as follows.

As shown in Fig. 1, incident deuterium ions with energy 0.450 MeV penetrate through the oxide surface. Occasionally a nuclear reaction such as 16O(d,p) or 18O(d,p) occurs, and the proton penetrates back through to the target surface. The energy and count rate of these protons are carefully measured. Their values determine the depth of oxygen isotope below the surface and its density in the substrate. A similar result takes place with an incident beam of protons and the 18O(p,a) reaction ensues. This latter method complements the former by being more sensitive to the 18O isotope. Experimental details are given elsewhere. ⁶

Results

A. The (d,p) Reaction

Typical spectra from the 16O, 18O(d,p) reaction are shown in Fig. 2. The anodized Zircaloy specimens yielded spectra like that at the top of Fig. 2, whereas the analogous anodized vanadium specimens are shown at the bottom. The peaks are labeled by the specific nuclear

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Fig. 1. Schematic illustration of the ion beam and target. The energy loss of ions $a$ and $b$ as they penetrate the surface layer broadens the reaction $A(a,b)$ spectrum as shown.

Fig. 2. Typical nuclear reaction spectra following 0.45 MeV deuteron bombardment of anodized zirconium (top) and vanadium (bottom) samples. Where the zirconium spectrum shows the presence of $^{18}$O (around channel 325), the vanadium sample does not (around channel 333). Peaks characterizing $^{16}$O can be readily seen in both spectra, but the $^{18}$O peaks are almost totally absent in the anodized vanadium. The subscripts (e.g., $p_0$ or $p_1$) refer to the fact that the final nucleus ($^{17}$O) is left in its ground or first excited state. Since the cross section for the $^{18}$O($d,p_0$) reaction is relatively small, the measurements were made for several hours, and a few monolayers of $^{14}$N were observed in all samples. In addition, some pulse pileup in the Zircaloy target may have caused slight peak broadening. The $V_0$ peak labeled $^{16}$O($d,p_1$) is analyzed in more detail in Fig. 3.

Fig. 3. Comparison of spectral shapes for the $^{16}$O($d,p_1$) and $^{18}$O($p,a$) reactions. Also shown are computer generated curves from convolution integrals discussed in the text.

B. The ($p,a$) Reaction

Since the cross section for the $^{18}$O($p,a$) reaction is much larger than the $^{16}$O($d,p$), we used the former to complement the information obtained above. The ($p,a$) spectra contained only one peak, that for $^{18}$O. An example of the peak shape from the $^{18}$O($p,a$) compared to $^{16}$O($d,p$) is shown in Fig. 3. As expected, both peaks have rather well-defined high- and low-energy edges which is characteristic of a uniform oxide layer. Very little diffusion of oxygen from the anodized layer through the substrate surface appears to have taken place at room temperature. On the other hand, the tops of the peaks are not simply flat but slope down toward the low-energy (channel) end of the spectrum. This characteristic is also expected even for uniform oxide layers because the nuclear cross section is strongly energy dependent at the rather low bombarding energies ($450$ keV) used in our case. For the present case we have used a computer code to evaluate the required convolution integrals. Details of the code are given elsewhere. Some of the results of the computation are given in Fig. 3. For simplicity, the oxygen profile was assumed to be uniform and to have the widths (chosen by trial and error) as shown in Fig. 3. In the case of the $^{16}$O($d,p$) we also used the measured cross sections and the peak area to evaluate the width, and this result ($2173$ Å) agrees to within $9\%$ of the peak width method ($1390$ Å). It is evident that the uniform distribution assumption is sufficient for the purpose here.
although some evidence for oxygen diffusion or a higher oxidation state can be seen by the existence of counts well above the calculated curve. For the $^{16}\text{O}(d,p)$ this discrepancy can be found at depth >1400 Å and for $^{16}\text{O}(p,a)$ in Zircaloy it occurs at depths >2000 Å.

**Discussion**

A summary of the measurements of the Zircaloy and vanadium oxide layers is presented in Table 1. The total amount of oxygen found in each vanadium sample was approximately as expected from the formula of Arora and Kelly:

$$t(\mu g/cm^2) = 2.0 + 1.14 V \cdot (2)$$

For the tetravalent state of vanadium this gives 1372 Å for vanadium (sample No. 2) and 603 Å for vanadium samples No. 3 in Table 1. Only the anodized Zircaloy contained mostly $^{16}\text{O}$ in its oxide. This was expected from the fact that an exchange (maximizing mixing entropy) of the oxygen-18 from the water and oxygen 16 from the KOH left most OH$^-$ anions bearing $^{18}\text{O}$.

Table 1. List of Targets on Which the Oxygen Isotope Concentration was Measured

<table>
<thead>
<tr>
<th>No.</th>
<th>Oxide</th>
<th>Thickness, Å</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Zr$^{16}\text{O}_2$</td>
<td>780</td>
<td>100 V; $H_2^{18}\text{O}$, 780 Å</td>
</tr>
<tr>
<td></td>
<td>Zr$^{18}\text{O}_2$</td>
<td>~2000</td>
<td>17 KOH</td>
</tr>
<tr>
<td>I</td>
<td>V$^{16}\text{O}_2$</td>
<td>277</td>
<td>Non-anodized</td>
</tr>
<tr>
<td></td>
<td>V$^{18}\text{O}_2$</td>
<td>~6</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>V$^{16}\text{O}_2$</td>
<td>1350</td>
<td>50 V; $H_2^{18}\text{O}$, 1350 Å</td>
</tr>
<tr>
<td></td>
<td>V$^{18}\text{O}_2$</td>
<td>~60</td>
<td>110 Na$_2$B$_4$O$_7$</td>
</tr>
<tr>
<td>3</td>
<td>V$^{18}\text{O}_2$</td>
<td>859</td>
<td>21 V; CH$<em>3$C0$</em>{18}$OH, 859 Å</td>
</tr>
<tr>
<td></td>
<td>V$^{16}\text{O}_2$</td>
<td>~64</td>
<td>62 H$_2$O, Na$_2$B$_4$O$_7$</td>
</tr>
</tbody>
</table>

A Assumed oxide form based upon references cited in the text. Thickness estimate assumes a uniform oxide layer.

All vanadium samples contained much more $^{16}\text{O}$ than $^{18}\text{O}$. When vanadium was anodized in acetic acid labeled with $^{18}$O, i.e., CH$_3$C0$_{18}$OH, approximately as much $^{18}$O was incorporated into the oxide as when the anodization was performed in $H_2^{18}\text{O}$ (cf., samples 2 and 3); in neither case was a significant quantity of $^{18}$O taken up into the oxide.

The results of the nuclear analysis have shown that when vanadium is anodized in acetic acid–2 N water-0.02 N sodium tetraborate solution, the oxygen which is incorporated into VO$_2$ film does not come from the water, or acetic acid. Therefore, the oxygen may come from the sodium tetraborate molecule. This conclusion is based on the idea that the sodium tetraborate is dissolved in the water and thus ionized:

$$Na_2B_4O_7 + 10 H_2O \rightarrow 2 Na^+ + B_4O_7^{2-} + 10 H_2O \cdot (3)$$

The borate ions are then free to move in the electric field. When borate ion reaches the anode it may then yield an oxygen atom to the vanadium, possibly by forming orthoboric acid:

$$12 H_2O + B_4O_7^{2-} + V \rightarrow WO_2 + 4e^- + 8 H_2B_3O_3 \cdot (4)$$

This reaction would then result in the formation of an oxide layer on the vanadium. However, it is known that $B_4O_7^{2-}$ is not stable in water but forms a weak base: