Ionic Conduction through Anodic Oxide Films Formed on Niobium in Oxalic Acid

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Anodic oxidation of niobium is carried out at different current densities and temperatures in 0.1 N oxalic acid solution by eliminating the difference of film growth caused by different surface conditions. Tafel slope is found to be independent of temperature, but decreases with increase in current density. Dewald's double barrier theory of ionic conduction has been examined critically and various parameters calculated for Nb$_2$O$_5$ films and compared with those of Ta$_2$O$_5$ films. A comparison of Nb$_2$O$_5$ and Ta$_2$O$_5$ film data shows that Dewald theory is applicable to both the systems. However, magnitudes of various parameters are quite different in both the cases. The large values of parameters $a$ and $b$ particularly at higher current density set, are difficult to visualize but these large half-distance values are not impossible in amorphous Nb$_2$O$_5$ film.

In our earlier work$^{1,2}$ on the kinetics of anodic oxidation of tantalum, it was established that Dewald's double barrier theory$^{3,4}$ explained the data more satisfactorily than any other single barrier theory. In order to check, if the anodic oxidation behaviour of tantalum and niobium is similar or not, the kinetics of growth of Nb$_2$O$_5$ films, has been presently studied using 0.1 N oxalic acid as contacting electrolyte. The data have been examined in terms of Dewald's theory$^{3,4}$.

Materials and Methods

The method of preparing niobium specimens (99.9% purity) with $2 \times 10^{-4}$ m$^2$ in area was the same as that described elsewhere$^1$. To eliminate the surface condition effects, the specimens were treated as described earlier$^2$ such that the Tafel slope was given by Eq. (1)

$$E_1 - E_2 = \frac{\tau}{2.303} \quad \cdots (1)$$

where $E_1$ and $E_2$ are the field strength at $i_1$ (upto a formation voltage of 30V) and $i_2$ (upto a formation voltage of 50V) current densities respectively. The values of $E_1$ and $E_2$ were calculated for the same formation voltage. The density of Nb$_2$O$_5$ film was taken as 4.36 kg dm$^{-3}$ as reported by Holtzberg et al.$^5$ Oxalic acid used for preparation of 0.1 N contacting electrolyte was of AR (BDH) grade.

Results and Discussion

The plot of voltage of formation versus time of anodization for the current density pair (100, 10 Am$^{-2}$) at 294.15K is presented in Fig. 1. Similar plots were obtained at other current density pairs (20, 2 and 60, 6 Am$^{-2}$) and also at other temperatures (294.15, 304.15, 314.15, 324.15 and 334.15K). Each set of observation was repeated five times and the values of field strengths, $E_1$ and $E_2$, at a particular current density pair and temperature
were calculated and the values are presented in Table 1. The reproducibility in the field values was ± 0.005 x 10^8 Vm⁻¹. The field strength increases with current density but decreases with temperature for all the current density pairs studied. As in case of tantalum the plots of E versus 1/T irrespective of current density employed are linear and parallel (Fig. 2) indicating that the difference of field at all temperatures for a given current density pair is constant and hence the Tafel slopes are independent of temperature. Now we examine our data in term of Dewald's theory. The expression for change in the field (ΔE), bringing about increase in current density ten times is given by Eq. (2)

$$\Delta E = \Delta E_0 - \frac{1}{\beta} \left[ F(\delta) - F(\delta/\theta) \right]$$ \hspace{1cm} (2)

Here ΔE₀ is the change in the field due to surface charge and its value is 2.303 kT/bq and F(δ) is a function dependent upon the space charge δ. Equation (2) can be written as

$$2.303 a/b - \beta \Delta E = F(\delta) - F(\delta/\theta)$$ \hspace{1cm} (3)

Tafel slope (τ) from Dewald's theory is given by Eq. (4)

$$\tau = \frac{kT}{aq} \left[ 1 + (a/b - 1) \ln \left( \frac{1 + \delta}{\delta} \right) \right]$$ \hspace{1cm} (4)

Using Equations (4) and (3), the parameters a and b were determined as under:

(i) The values of a and a/b were assumed and hence the value of θ was evaluated.
(ii) F(δ) - F(δ/θ) (r.h.s. of Eq. (3)) was represented graphically as a function of δ.
(iii) The values of 2.303 a/b - βΔE (l.h.s. of Eq. (3)) at different temperatures were evaluated.

(iv) From (i) and (iii) by interpolation, the value of δ(T) was determined.
(v) Using the values of δ, a and a/b, the theoretical value of Tafel slope (τ) was calculated.

Such a calculation was repeated until values of a and b were found such that an agreement with experimental values of Tafel slopes were obtained. There are two widely different values of a/b ratio which allow a quantitative fit to all the data available. The ratio a/b along with absolute values of a and b are presented in Table 2. Only for these values of a/b, it was possible to achieve a temperature-independent Tafel slope. The values of a and b increase with increase in current density; the ratio a/b increase slightly with increase in current density. The correct value of a/b (whether it is ≈ 1.35 or ≈ 0.820) is difficult to decide. Dewald used the values of a/b ratio, which gave minimum values of a and b. Using the same criterion we have chosen a/b ≈ 0.820, for further calculation of various parameters. The values of δ at different temperatures and for different current density sets, show that δ decreases with increase in temperature (Table 3). The effect of space charge is more clearly observed at a temperature when δ > 1. This effect becomes predominant as the temperature is lowered. The δ value depends mainly on exp[−W/kT] as shown in Eq. (5)

$$\delta = \frac{\beta I \cdot \Delta x}{2\pi q}$$

$$e^{\frac{-w}{2kT}}$$

$$= \frac{2\pi \alpha(2\pi q)^{1-\alpha}}{\nu kT}$$

... (5)
Table 2—Two Sets of Absolute Values of Parameters \(a\), \(b\) and \(a/b\)

<table>
<thead>
<tr>
<th>Current density (Am(^{-2}))</th>
<th>(a) (nm)</th>
<th>(b) (nm)</th>
<th>(a/b)</th>
<th>(a) (nm)</th>
<th>(b) (nm)</th>
<th>(a/b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-20</td>
<td>0.540</td>
<td>0.417</td>
<td>1.295</td>
<td>0.400</td>
<td>0.492</td>
<td>0.813</td>
</tr>
<tr>
<td>6-60</td>
<td>0.950</td>
<td>0.704</td>
<td>1.349</td>
<td>0.680</td>
<td>0.829</td>
<td>0.820</td>
</tr>
<tr>
<td>10-100</td>
<td>1.090</td>
<td>0.805</td>
<td>1.354</td>
<td>0.780</td>
<td>0.948</td>
<td>0.823</td>
</tr>
</tbody>
</table>

The values of \(W\) have been evaluated from the plot of \(\log \delta\) versus \(1/T\) (Fig. 3). These plots were linear for all the current density pairs and the values of \(W\) calculated at such current density pairs are given in Table 4. Knowing \(\delta\) and \(E\), the surface charge field \(E_o\) was evaluated using Eq. (6)

\[
E = E_o + \frac{1}{\beta} \left[ \left( 1 + \frac{1}{\beta \gamma n_0 \Delta x} \right) \ln(1 + \beta \gamma n_0 \Delta x) - 1 \right]
\]

\[\ldots (6)\]

The values of \(E_o/T\) were computed and plotted against \(1/T\) (Fig. 4). For each current density pair such plots were linear. \(E_o\), the field due to surface charge is given by Eq. (7)

\[
E_o = kT/bq \ln(i/N, \nu, q) + \phi/bq
\]

\[\ldots (7)\]

Here \(b\) is entrance half-jump distance, \(N_i\) is the concentration of ions on the surface, \(\nu\) is the vibrational frequency normal to the barrier and \(\phi\) is the entrance barrier energy. According to Eq. (7) such plots should be linear with a slope = \(\phi/bq\). From the slopes, the values of \(\phi\), the entrance barrier energy were obtained and are given in Table 4. Using the relation \(U = a\phi/b - W\) the value of \(U\), the diffusion barrier energy were calculated and these are reported in Table 4. Both \(\phi\) and \(U\) seem to increase with current density and magnitude of \(U\) is smaller than that of \(\phi\) at all the current density sets. This suggests that the rate-determining step would be ionic movement at the metal/oxide interface and not across the film. However, at high field the correct activation energies would be \((\phi - E bq)\) and \((U - Eaq)\) instead of \(\phi\) and \(U\). Therefore, using average value of field for each current density set, taking charge on each...
niobium atom in Nb$_2$O$_5$ film as 5e and using values of $\phi$, $U$, $b$ and $a$ from Table 4, the values of $(\phi - Ebq)$ and $(U - Eaq)$ were computed and are recorded in Table 4. The value of $(\phi - Ebq)$ is greater than that of $(U - Eaq)$ at each current density set and this again suggests that the rate-determining step would involve ionic movement at metal/oxide interface. Though there is a substantial contribution of space charge ($\delta > 1$) at low temperature yet the rate-controlling step is at the metal/oxide interface. This is a misleading conclusion. It seems that our choice of $a/b = 0.820$ is not correct. Next we assumed $a/b = 1.35$ and calculated the values of various parameters at different current densities and temperatures adopting the same procedure as given above, and the values of various parameters obtained are recorded in Table 4. The values of $W$ were obtained from the plots of log $\delta$ versus 1/$T$ for all the current density pairs. The values of $\phi$ were obtained from plots of $E_p/T$ versus 1/$T$ at each current density pair.

It can be seen from Table 4, that magnitude of $\phi$ is smaller than that of $U$ at all current density pairs, thus indicating that the rate-determining step for ionic movement would be within the film and not at the metal/oxide interface. The values of $(\phi - Ebq)$ and $(U - Eaq)$ are not much different from each other suggesting the metal/oxide interface barrier is important for the conduction of ions. With the increase in current density, the value of $(\phi - Ebq)$ is slightly less that of $(U - Eaq)$. This shows that the rate-controlling step also shifts from metal/oxide interface to the diffusion barrier within the film.

**Comparison of results of Ta$_2$O$_5$ and Nb$_2$O$_5$ films**

In our earlier work$^2$ on Ta$_2$O$_5$ films, it was found the value of Tafel slope increases with increase in current density. Contrastingly decreases for Nb$_2$O$_5$ films. In Ta$_2$O$_5$ films $a$ is constant at all current densities while $b$ decreases with increase in current density. In Nb$_2$O$_5$ film both $a$ and $b$ increase with increase in current density. The behaviour of $\phi$, $U$ and $W$ with current density is the same for Nb$_2$O$_5$ films, showing the dual barrier control of ionic movement. But the Ta$_2$O$_5$ film the value of $(U - Eaq)$ is considerably larger than that of $(\phi - Ebq)$, indicating that the space charge ($\phi$) plays a dominant role in the conduction of ions in Ta$_2$O$_5$ film.

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**References**