

ON THE MECHANISM OF ANODIC OXIDATION OF TANTALUM

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Summary

The mechanism of ionic transport during the anodic oxidation of tantalum is studied. A thin layer of radioactive tantalum is applied to a tantalum sheet. After oxidation the oxide layer is dissolved in successive stages and the activity distribution is measured. It is shown that the transport of Ta ions is neither governed by a pure vacancy mechanism, nor by a pure interstitial process.

Résumé

On a étudié le mécanisme du transport des ions pendant l'oxydation anodique du tantale. Une couche mince contenant le tantale radioactif a été appliquée sur une plaque de tantale. Après l'oxydation, la pellicule d'oxyde a été dissolue en quelques étapes et la distribution d'activité a été mesurée. On a trouvé que le transport des ions Ta n'est pas réglé par un mécanisme de vacatures ainsi que par un mouvement interstitiel pur.

Zusammenfassung

Der Mechanismus der Ionenbewegung während der anodische Oxydation von Tantal wurde untersucht. Ein Tantalblech wurde mit einer dünnen radioaktiven Tantalschicht bedeckt. Nach der Oxydation wurde die Schicht stufenweise gelöst und die Aktivitätsverteilung gemessen. Es wurde gezeigt, daß der Transport der Tantalionen weder durch reine Leerstellenbewegung noch durch reine Zwischen-gitteratombewegung beschrieben werden kann.

It has been demonstrated by the experiments of Vermilyea¹⁾ that during anodic oxidation of tantalum the oxide grows at the electrolyte/oxide interface. This means that the metal ions move through the oxide during its growth, whereas the oxygen ions are at rest. This was a priori very likely on account of the difference between the radii of tantalum and oxygen ions.

However, there exists no further information regarding the way of transport of the metal ions through the oxide. The distance l , traversed by a moving ion, may range from a (one atomic distance) to d (the total thickness of the layer). Now the effects of these two limiting cases should be different in a peculiar way. For, if we number the lattice planes of Ta in the metal starting at the surface, the sequence of these layers in the oxide will be the same after oxidation by a mechanism with $l = a$, whereas it will be reversed in the case $l = d$.

Vermilyea¹⁾ has reported a method for removing a Ta_2O_5 layer in successive parts by careful dissolution in HF. This method when tested by us worked perfectly. It would thus be possible to obtain information on the transport mechanism during anodic oxidation if one were able to apply radioactive Ta on a sheet of this metal.

Deuteron bombardment of Ta at energies just above the threshold energy of the $\text{Ta}^{181}(d,p)\text{Ta}^{182}$ reaction produced an active layer that was an order of magnitude too thick. Evaporated Ta films could be made, but difficulties were met in removing all the oxide from the metal sheet onto which the activity had to be applied.

Finally we tried to clean a Ta surface in a gas discharge by heating and ion bombardment. The other electrode in this discharge was a neutron-activated disc. A thin layer of radioactive tantalum was then sputtered onto the cleaned disc.

Now the sputtered layer was not sufficiently compact, since it dissolved very quickly in HF. However, owing to the heating of the electrodes during cleaning and sputtering some activity had apparently diffused into the sheet and the penetration depth was just convenient for our purpose.

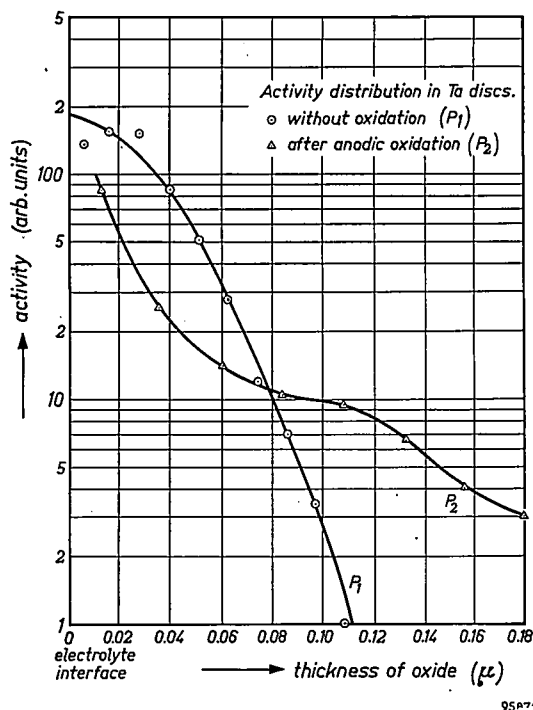


Fig. 1. Distribution of activity in tantalum discs. P_1 : without oxidation; P_2 : after anodic oxidation.

Two such discs were prepared and the distribution of activity was measured in the following way.

From both discs the loose sputtered layer was removed with HF. Then from one disc (P_1), without oxidizing it, successive thin layers were removed by etching with HF and the remaining activity was counted after each treatment. The other sheet (P_2) was oxidized anodically to 120 V ($\approx 0.25 \mu$ thick oxide layer) and the oxide was also removed in successive parts with HF. The remaining activity after each treatment was counted again.

As is shown in the figure the distribution of the activity was not the same in both cases, the original distribution being a pure diffusion pattern. It should be remarked that, as tests had shown that etching of Ta and Ta_2O_5 proceeded at different rates, these differences in dissolution rate have been accounted for in the figure. For easy comparison the penetration depths in the metal were converted to the corresponding oxide thicknesses.

The result shows that some reversal in the sequence of the Ta ions must have taken place during oxidation. This would imply $a < l < d$. Apparently a pure vacancy mechanism (with $l = a$) or a pure interstitial process (with $l = d$) are not the governing processes. On the other hand, the condition $a < l < d$ is fulfilled in the case of a transport mechanism as proposed by Bean, Fisher and Vermilyea²⁾. The present preliminary results are not sufficiently accurate, however, to analyse the process in more detail.

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