Galvanostatic Breakdown Voltages of Anodic Oxide Films Formed on Tantalum in Aqueous Electrolytes

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The breakdown voltage \( V_B \) is found to be independent of current density used for film formation, field strength, topography of the specimen and pH of the electrolyte solution. However, it depends upon the nature of the electrolyte, concentration of the solution and temperature employed. Only anions of the electrolyte influence the \( V_B \). It appears that during anodic polarization the electrons from the anions of the electrolyte get injected into the conduction bands of the film. Due to high field strength the electrons acquire very high energy and cause release of secondary electrons, resulting in the multiplication of avalanches and hence breaking the film. Of the various methods of identifying \( V_B \), the appearance of sparking is found to be a superior method.

The anodic oxide film on a valve metal can be formed upto a certain maximum value of voltage designated as breakdown voltage \( V_B \) beyond which sparking appears and the film breaks down\(^1\) - \(^9\). The appearance of visible sparking\(^1\), slowing down of voltage\(^2\), attainment of maximum voltage\(^3\), occurrence of audible cracking\(^4\) and rapid voltage fluctuation\(^5\) have been variously used by different workers to identify \( V_B \). Burger and Young\(^6\) reported that the electrical breakdown was triggered by conduction through electrolyte-filled fissures and flaws in the oxide film. Yahalom and Hoar\(^7\) suggested that the breakdown resulted by the incorporating of ions into the film from the electrolyte. Alwitt and Vijh\(^5\) expressed the view that the breakdown was controlled by the electrochemical reactions at the electrolyte/oxide interface and also depended on the solid state properties of the oxides. Ikonopisov\(^8\) suggested a theoretical model to explain breakdown.

It appears that the results obtained and the mechanisms suggested for electrical breakdown are at variance. There is no uniform criterion for identifying breakdown voltage \( V_B \). Further, the behaviour of \( V_B \) in the presence of an electrolyte is different from that in the presence of a dry dielectric\(^9\). This is of value in the capacitor technology and other anodization phenomena. These observations suggest the imperative need for further research in this area and hence the title investigation.

Materials and Methods

Samples of tantalum (99.9% purity) of \( 2 \times 10^{-4} \text{ m}^2 \) area were prepared as described in an earlier communication\(^10\). The experimental set-up and the procedure for anodic polarization have been reported elsewhere\(^10\). The voltage at which sparking appeared was taken as the breakdown voltage \( V_B \). All the chemicals used were of AR (BDH) grade. The solutions were prepared in conductivity water and their electrolytic resistivities were measured using a digital conductivity meter, type NDC 732 (Naina Electronics, India).

Results and Discussion

The plots of voltage at which the oxide film on tantalum was formed versus the time for which anodic polarization was carried out in 0.1 mol dm\(^{-3}\) aqueous oxalic acid solution at varying current densities (5, 10, 50, 100, 500, 1000 Am\(^{-2}\)) and 298 K are shown in Fig. 1. At low current densities (5 and 10 Am\(^{-2}\)), increase in the charge passed increases the voltage of formation up to a certain value (maximum value) thereafter any further increase in charge does not lead
to change in voltage of formation. This maximum voltage has been used as one of the criteria to measure \( V_B \). However, at higher current densities no such maximum voltage is reached at least in the vicinity of reported breakdown values. Hence this criterion cannot be accepted as a measure of \( V_B \). Slowing down of voltage which is also one of the criteria to measure \( V_B \) has not been found useful because the rate of slowing down \( \frac{dV}{dt} \) decreases as the current density increases and ultimately it reaches almost a zero value (as indicated by the curvature in the plot) in the region of voltage of interest. Further, at each current density sparking occurred. The voltages at which sparking occurred are shown on each curve in Fig. 1 by a horizontal line. Since the appearance of sparking occurred at all current densities in the same region and further at low current densities (5 and 10 Am\(^{-2}\)) the sparking voltages were close to the maximum voltage, the appearance of sparking was taken as a measure of \( V_B \). Audible cracking occurred at current densities > 10 Am\(^{-2}\) and was not easily detectable at low current densities. Rapid voltage fluctuation was only occasionally observed. Gas evolution preceded sparking but at low current densities gas evolution took place for a very long time before sparking started. Hence at low current densities gas evolution is also not better than sparking as a criterion for identifying \( V_B \). The order of sequence of events which took place during the process of breakdown is summarised as under:

At low current densities (5 and 10 Am\(^{-2}\))

- Slowing down of voltage; reaching of maximum voltage; gas evolution staying for a longer period and sparking.

At moderate current densities (50 and 100 Am\(^{-2}\))

- Slowing down with much less rate; gas evolution staying for a smaller period; sparking and audible cracking.

At high current densities (500 and 1000 Am\(^{-2}\))

- Gas evolution instantaneously leading to sparking; audible cracking.

The plots of breakdown voltage \( (V_B) \) versus current density for 0.1 mol dm\(^{-3}\) aqueous solutions of oxalic, citric, tartaric and acetic acids are shown in Fig. 2. The linear plots (Fig. 2) with zero slopes indicate non-dependence of \( V_B \) on current density. However, the values of \( V_B \) are not constant for various electrolytes used. The results of breakdown voltages obtained at varying concentrations of aqueous oxalic, citric and acetic acids are shown in Fig. 3. In each case \( V_B \) shows a linear decrease with increase in electrolyte concentration up to 0.1 mol dm\(^{-3}\). Thereafter, with further increase in electrolyte concentration only small decrease in the values of \( V_B \) is obtained and it tends to acquire a certain minimum value. These observations point to an exponential decrease of \( V_B \) with increase in electrolyte concentration and, therefore, to check it further the values of \( V_B \) were plotted against log[electrolyte]\(^{-1}\) (Fig. 4). Linear plots in Fig. 4 confirm this conclusion and hence the effect of concentration of
The effect of electrolytic resistivity ($\rho$) on $V_B$ was checked more directly by measuring the resistivities of aqueous solutions. It was found that $V_B$ did not vary linearly with $\rho$. However, when the values of $V_B$ were plotted against $\log (\rho)$, linear plots were obtained and hence a relation between $V_B$ and $\rho$ can be represented by Eq. (2).

$$V_B = a + b \log \rho$$

(2)

where $a$ and $b$ are constants with positive sign. The values of $a$ for acetic, citric and oxalic acids were obtained from the intercepts of the linear plots ($V_B$ versus $\log (\rho)$), as 246, 278 and 332 V respectively. The corresponding values of $b$ were found to be 187, 171 and 169 respectively.

The effect of field strength on $V_B$ was studied. The values of field strength at 298 K (current density 50 $\text{Am}^{-2}$) for 0.1 mol dm$^{-3}$ oxalic and citric acids were found to be $6.46 \times 10^8$ and $6.36 \times 10^8\text{Vm}^{-1}$, respectively. The corresponding values of $V_B$ were 280 and 365 V. This clearly showed non-dependence of field strength on $V_B$. Further, though the values of field strength at 298 K for oxalic acid at current densities 5,
10, 50 and 100 Am\(^{-2}\) were 5.77, 5.98, 6.46 and 6.68 \(\times 10^4\) \text{Vm}^{-1}, respectively the values of \(V_B\) did not change as the current density increased. This again confirmed non-dependence of field on \(V_B\), atleast in the range of present study.

Ten samples of tantalum with varying degrees of topography were prepared and the breakdown voltages in 0.1 mol dm\(^{-3}\) aqueous solution of oxalic acid measured. It was found that \(V_B\) did not change with the change in topography of the specimen. Since the samples with varying topography would have varying degrees of flaws and fissures and since \(V_B\) is independent of the topography, the suggestion\(^{6}\) that \(V_B\) is triggered by conduction through fissures and flaws cannot be accepted.

The \(V_B\) values in 0.1 mol dm\(^{-3}\) solutions of oxalic acid and its sodium salt were found to be 280 and 290, respectively (Table 1). This showed that only anions affected \(V_B\). However, the values of \(V_B\) for citric and acetic acids decreased from 365 to 240 and from 460 to 310 V respectively when their sodium salts were used (Table 1). The decrease in \(V_B\) values was not due to the change of cations but due to the decrease in the values of resistivity when the acids were changed into their sodium salts, e.g. in the case of citric acid the value of resistivity decreased from 3.25 to 0.62 while the corresponding value for acetic acid decreased from 16.57 to 2.13 \(\Omega\)m. Using the values of resistivity of sodium oxalate, sodium citrate and sodium acetate, the \(V_B\) values were computed from the linear plots of \(V_B\) versus log \(\rho\) and the values obtained were 296, 244 and 305 V respectively. These computed values are very close to the experimental values of \(V_B\) in the presence of sodium oxalate (290 V), sodium citrate (240 V) and sodium acetate (310 V). Hence it may be concluded that only anions (and not the cations) influence the \(V_B\) value.

It appears that the breakdown voltage results because of the conduction of avalanching in the bulk of anodic film. During anodic polarization the anions of the electrolytes provide electrons which are injected into the conduction bands of the film. Due to high field strength the electrons acquire very high energy and cause release of secondary electrons by impact ionization, resulting in the multiplication of avalanches and breaking of the film. This view is close to the view expressed earlier\(^{8}\).

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References