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# Anodization of molybdenum. II. Electrical breakdown

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The breakdown phenomenon during galvanostatic anodization of molybdenum has been investigated. The effect of current density and the electrolyte composition and concentration on the breakdown voltage, $E_B$, was studied. $E_B$ was found to depend on the electrolyte composition and resistivity and not on the anodizing current density. The empirical relation between $E_B$ and the logarithm of electrolyte resistivity, $\varrho$

$$E_B = a_B + b_B \log \varrho$$

was fairly valid. Post-breakdown anodization experiments showed that the breakdown characteristics are independent of the history of the anodic film formation. Also, an increase of sparking time, $T_B$, leads to: (i) shift of the zero time potential in the second electrolyte, $E_2^0$, towards higher values; and (ii) decrease of the electrode capacitance. Such findings may be taken as evidence for the covering of the breakdown spots with thicker films.

## 1. Introduction

Electrical breakdown during the anodization of valve metals is a well-known phenomenon since the early work of Güntherschulze and Betz [1] and has been recently reviewed [2–5]. Since the breakdown terminates the anodic film formation, it is important from the technical point of view to study the factors affecting such a phenomenon. The breakdown occurs when the formation voltage reaches a certain value called the 'breakdown voltage', $E_B$, and it can be detected by the appearance of visible sparks [1, 6], sound effects [1, 7, 8] and a descending voltage oscillation [1, 8]. The value of $E_B$ was found to depend on the nature of the anodized metal [1, 7, 9], the electrolyte composition [3, 6, 10] and electrolyte resistivity, $\varrho$, according to the empirical equation [1, 3, 7, 11]:

$$E_B = a_B + b_B \log \varrho \qquad (1)$$

where $a_B$ and $b_B$ are constants which depend on the nature of the anodized metal and the electrolyte composition. $E_B$ seems to be independent of the anodizing current density [1, 11–13], temperature [7, 13, 14], topography and method of preparation of the metal surface [8], stirring conditions of the electrolyte [6] and history of anodic film formation [6, 11, 15]. Ikonopisov [16] attributed the breakdown to the avalanche of the injected electrons at the oxide–electrolyte interface. Also, Klein and co-workers [17, 18] studied the rate of the breakdown as a function of the film thickness and explained the breakdown by the theory of stochastic succession of avalanches. Recently, and based on the Ikonopisov model, Albella *et al.* explained the curvature of the potential–time curve during anodization [19–21] and the dependence of $E_B$ on the electrolyte concentration [22]. Most of the recent studies in this respect are restricted to the typical valve metals and it seems that a metal like molybdenum, the anodization of which is not yet clarified, was not subjected to such studies. Although Ikonopisov [16] expected that metals which anodize with the appearance of induction periods (e.g. molybdenum [23]) were excluded from his theory, our present investigation shows that such expectation is not correct.

## 2. Experimental details

A molybdenum disc electrode of apparent surface, ~0.125 cm$^2$, was cut from spec. pure molybdenum rod (Johnson–Matthey, London).

*Table 1. Breakdown characteristics of anodization of molybdenum at 8.0 mA cm$^{-2}$*

| *Electrolyte* | $T_B$ *(S)* | $E_B$ *(V)* | $C_B$ *(μF/electrode)* | *Colour and notes* |
|---|---|---|---|---|
| 95% $H_2SO_4$ | 42 | 66 | 0.030 | yellowish red; attacked |
| 0.2 M $H_2SO_4$ | 42 | 99 | 0.025 | pink |
| 98% $H_3PO_4$ | – | 98 | 0.023 | yellow |
| 0.2 M $H_3PO_4$ | 81 | 152 | 0.018 | green |
| 0.2 M HCl | 95 | 105 | 0.035 | pink |
| 0.2 M HBr | 25 | 20 | 0.120 | yellow; attacked |
| 0.2 M HI | 125 | 183 | 0.013 | faint pink |
| 0.2 M $HNO_3$ | 72 | 106 | 0.023 | pink |
| 0.2 M $H_3BO_3$ | 72 | 178 | 0.013 | pink |
| 0.2 M malonic acid | 82 | 202 | 0.012 | faint pink |
| 0.2 M acetic acid | 145 | 220 | 0.008 | faint pink |
| 0.2 M $ClCH_2COOH$ | 400 | 248 | 0.020 | faint pink |
| 0.2 M glycine | 100 | 250 | – | faint pink |
| 0.2 M $NaHCO_3$ | 380 | 252 | 0.009 | faint pink |
| 0.2 M $Na_2B_4O_7$ | 240 | 234 | 0.010 | faint pink |
| 0.2 M $Na_3PO_4$ | 160 | 190 | 0.013 | pink |
| 0.2 M $Na_2SO_4$ | 60 | 153 | 0.016 | green |
| 0.2 M $Na_2SO_3$ | 80 | 179 | 0.013 | pink |
| 0.2 M $NaNO_3$ | 125 | 161 | 0.015 | pink |
| 0.2 M $NaNO_2$ | 320 | 230 | 0.011 | faint pink |
| 0.2 M NaCl | 82 | 137 | 0.017 | green |
| 0.2 MNaBr | 14 | 20 | 0.087 | pink |
| 0.2 M NaF | 75 | 155 | 0.400 | green; attacked |
| 0.2 M $K_2CrO_4$ | 45 | 76 | 0.030 | yellow |

The electrode preparation, electrolytic cell, electrical circuit and the experimental procedure have been described previously [24, 25]. All experiments were carried out in an air thermostat at 30 ± 0.2° C. The electrode capacitance, $C_m$, and the electrolyte resistivity, $\varrho$, were measured at 1 kHz. All solutions used were prepared from AnalaR grade chemicals and triply distilled water. Each experiment was carried out three to five times and the mean value was used in constructing the curves.

## 3. Results and discussion

Molybdenum was anodized at a constant current density of 8.0 mA cm$^{-2}$ in various solutions. The appearance of a chain of sparks was taken as an indication of the arrival of the breakdown voltage, $E_B$, where such method showed a high reproducibility. Table 1 shows the anodization time needed to reach the breakdown voltage, $T_B$, the electrode capacitance, $C_B$, at $T_B$, the colour

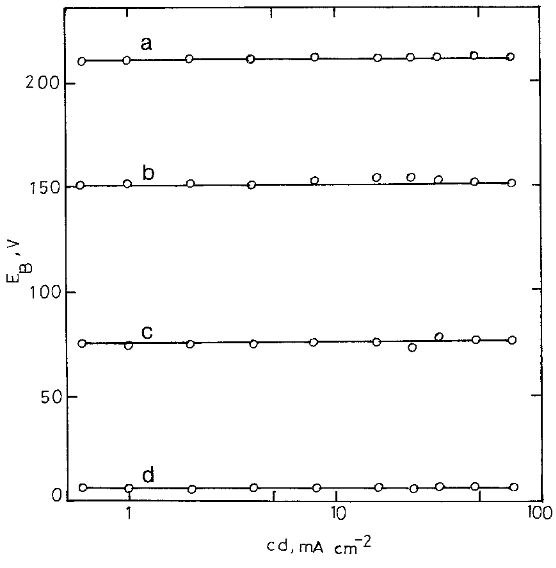

Fig. 1. Breakdown voltage as a function of current density (cd) on anodizing molybdenum in various electrolytes (mean values are plotted). (a) 0.1 M $CH_3COOH$; (b) 1.0 M NaCl; (c) 0.2 M $K_2CrO_4$; (d) 3.0 M NaBr.

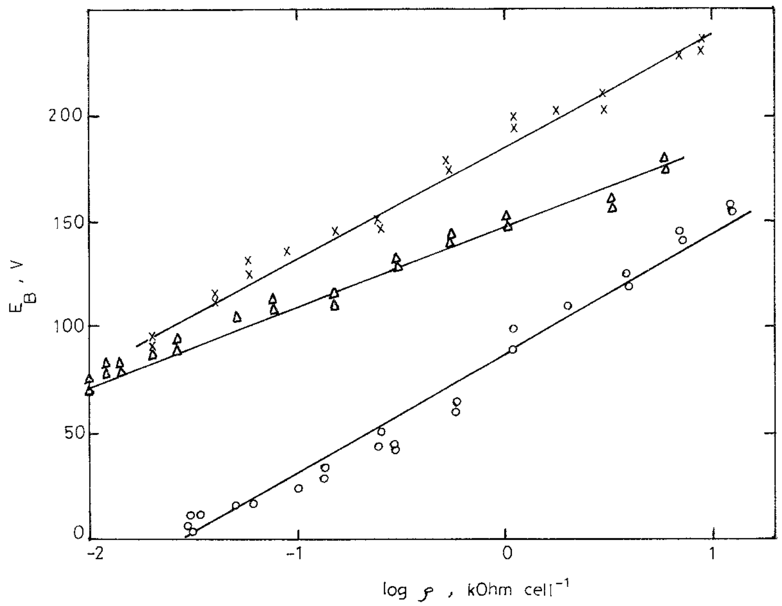

Fig. 2. Breakdown voltage during galvanostatic anodization of molybdenum at 8.0 mA cm$^{-2}$ plotted as a function of resistivity of electrolytes: (△) HCl; (×) NaCl; (○)NaBr.

of the electrode surface and $E_B$ in various electrolytes. The highest values of $E_B$ are found in organic acids and alkaline solutions. In solutions of halides, the order of $E_B$ is as follows: $I^- > F^- > Cl^- > Br^-$. In oxidizing solutions, e.g. $K_2CrO_4$ and $K_2Cr_2O_7$, $E_B$ values are much lower than those in reducing solutions, e.g. $NaNO_2$ and $Na_2SO_3$.

The effect of the anodizing current density on $E_B$ was investigated over about two orders of magnitude (0.6–70.0 mA cm$^{-2}$) in various electrolytes. As can be seen from Fig. 1, the current density has no effect on the $E_B$ value as generally found for many valve metals [1, 10, 12].

Equation 1 was tested for molybdenum in many electrolytes. For simplicity, $\varrho$ was measured for all solutions in units of kOhm cell$^{-1}$. The validity of Equation 1 is shown in Figs 2 and 3. The values of the constants $a_B$ and $b_B$ in the tested electrolytes are given in Table 2. As can be

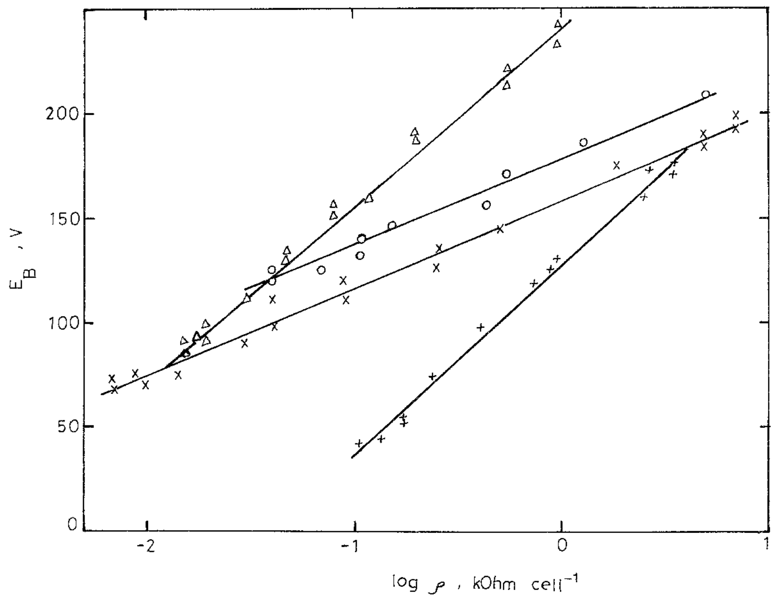

Fig. 3. Breakdown voltage during anodization of molybdenum at 8.0 mA cm$^{-2}$ as a function of resistivity of electrolytes: △, $H_3PO_4$; ×, $H_2SO_4$; ○, $Na_2SO_4$; + $K_2CrO_4$.

*Table 2. The constants* $a_B$ *and* $b_B$ *for molybdenum in various electrolytes*

| *Electrolyte* | $a_B$ | $b_B$ |
|---|---|---|
| $H_2SO_4$ | 158 | 41 |
| $Na_2SO_4$ | 178 | 43 |
| HCl | 150 | 40 |
| NaCl | 185 | 53 |
| NaBr | 86 | 56 |
| $NaNO_3$ | 200 | 74 |
| $K_2CrO_4$ | 127 | 93 |
| $H_3PO_4$ | 240 | 84 |

seen, both $a_B$ and $b_B$ are dependent on the electrolyte composition especially the anion type. It seems that a dependency of $E_B$ on the solution pH cannot be neglected as it has been in previous work [11]. In general, for one and the same anion and resistivity, $E_B$ values in acid media are lower than in neutral ones.

According to the recent theories of electrical breakdown [16, 17], the effect of the electrolyte takes place via its ability to inject electrons and its resistivity. The constant $a_B$ can be taken, for one and the same metal, as a measure of the ability of the anion to inject electrons and, hence, the ability of $Br^-$, $CrO_4^{2-}$ and $Cr_2O_7^{2-}$ anions is much higher than that of $PO_4^{3-}$, $SO_4^{2-}$ and $Cl^-$. Based on the fact that the outer layers of anodic films on many valve metals incorporate electrolyte anions [26, 27], Albella *et al.* [20–22] explained the dependency of $E_B$ on the electrolyte concentration via an increase of the incorporated anions with increase of electrolyte concentration. Although the increase of the anodizing current density was found to increase the amount of incorporated anions [26, 27], it is known that the anodizing current density has no effect on $E_B$ and, hence, it seems that the dependence of $E_B$ on the anion concentration is in doubt.

To test the dependence of the electrical breakdown characteristics of the history of the anodic film formation, some post-breakdown anodization experiments were carried out. Initially, molybdenum was anodized in 0.2 M $K_2CrO_4$ ($E_B$ = 76 V) until $E_B$ was attained, then the electrode was left to spark for a time interval, $T_B$,

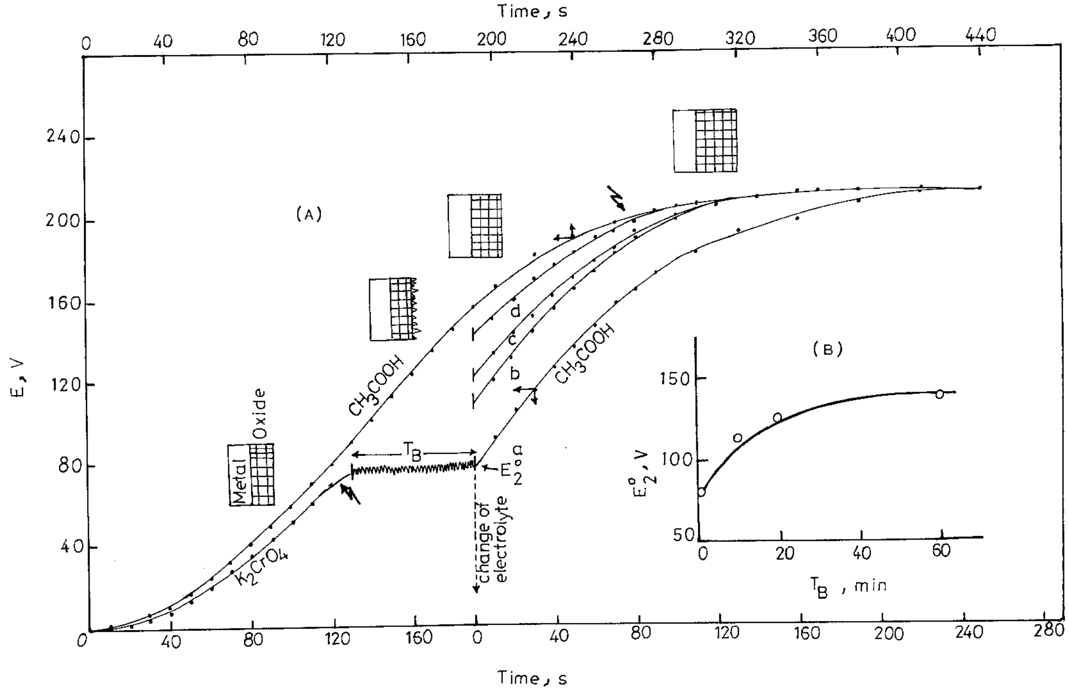

Fig. 4. Curves of anodization of molybdenum at 4.0 mA cm$^{-2}$ in 0.1 M acetic acid with and without preliminary sparking in a solution of 0.2 M $K_2CrO_4$ for (a) 1, (b) 5, (c) 20 and (d) 60 min. Sparking potentials are marked with danger arrows. For explanation of the model see text. (B) Zero time voltage of anodization in the second electrolyte, $E_2^0$, as a function of the breakdown time.

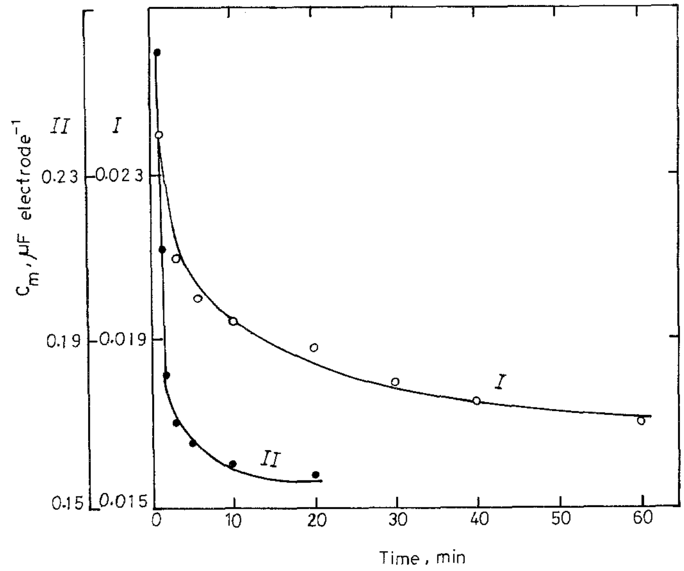

Fig. 5. Variation of capacitance of molybdenum electrode with the time of sparking at 8.0 mA cm$^{-2}$ in solutions of: ○, 0.2 M $K_2CrO_4$; ●, 3 M NaBr.

before changing the electrolyte by another one of higher $E_B$ (for example 0.1 M acetic acid, $E_B = 220$ V). The results of a post-breakdown anodization experiment are shown in Fig. 4. As can be seen the $E_B$ value of the second electrolyte was not affected by the previous sparking in the first electrolyte.

An interesting observation can be made from Fig. 4: the zero time potential of anodization in the second electrolyte, $E_2^0$ (taken during the first few seconds) was found to jump towards higher values with increase of $T_B$. A similar observation was also made by using 0.05 M $H_3PO_4$ as the second electrolyte. During the sparking, the anodization was interrupted and the electrode capacitance, $C_m$ was measured immediately as a function of $T_B$ in 0.2 M $K_2CrO_4$ and 3 M NaBr solutions. As can be seen in Fig. 5, $C_m$ decreases with $T_B$ increase probably due to film thickening. According to Ikonopisov [16], the electron avalanche causes an evaporation of the anodic film at the breakdown point and, hence, the breakdown spot loses its oxide coating. The constant current will pass through that spot, because of the high resistance of the remaining part of the film. Owing to the extremely high current density at the bare spot, the anodic film formed is thicker and possesses improved insulating properties. The shift of $E_2^0$ towards higher values with increase of $T_B$ may be attributed to the formation of thicker films. During the first few seconds of anodization in the second electrolyte the whole surface is assumed to be covered with a film of thickness corresponding to $E_B^0$ and thereafter the anodization kinetics proceed normally. The model illustrating this explanation is shown in Fig. 4. Accordingly, the rate of the oxide formation in the second electrolyte was not affected by the sparking time as was also found for niobium and tantalum [3, 6, 15].

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