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Kinetics of the dissolution behaviour of anodic oxide films on niobium in NaOH solutions

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The dissolution behaviour of the anodized niobium electrode in NaOH solutions was investigated as a function of alkali concentration, formation voltage, formation current density and temperature using potential and impedance measurements. The rate of dissolution is dependent on the alkali concentration. In dilute NaOH solutions (1 N) the anodic oxide film formed in 0.5 M H_2SO_4 is reasonably stable. On the other hand, at higher concentrations of NaOH ($\geqslant 2$ M), the anodized electrode is subject to continuous dissolution depending on the alkali concentration. Also, the dissolution process is considerably affected by temperature; at temperatures greater than 320 K the oxide film is destroyed in less than 30 min. The results show that the current density used during the formation of the oxide film has no effect on its dissolution rate.

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1. Introduction

Many investigations have been directed towards the production of corrosion-resistant materials to be used as efficient anodes in the manufacture of chlorine and caustic soda [1, 2]. Valve metals in general are known to form stable oxide films in aqueous media [3]. Niobium is one of these metals [4] and has been subjected to extensive studies, most of which were concerned with the kinetics of the oxide film on its surface [5–14]. Few studies have been directed towards the stability of these oxide films in aggressive media [15, 16]. Randall *et al.* [17] investigated the structure of the anodic oxide film formed on niobium using radioactive isotope techniques. The structure changes in the oxide film during the anodization of the metal were studied by Lakhiani and Shreir [18]. Stützle and Heusler [19] investigated the semiconducting properties of the anodic oxide film formed on niobium; they reported that the oxide film behaves as a weakly dissociated extrinsic semiconductor.

This present study reports on the stability of the anodic oxide film formed on niobium in NaOH solution. The impedance and potential measurements were employed to study the kinetic parameters controlling the rate and mechanism of the anodized niobium electrode.

2. Experimental details

Massive cylindrical spectroscopically pure niobium rod (Johnson Matthey, London) was used as electrode. A stout copper wire was employed as the electrical contact. The electrode was fitted into glass tubing of appropriate internal diameter, by an epoxy resin leaving a surface area of 0.196 cm^2 to contact the solution. The electrolytic solutions were prepared using Analar grade reagents and triply distilled water. Sodium hydroxide solutions were prepared from carbonate-free sodium hydroxide solution by appropriate dilution.

Before each experiment the electrode surface was abraded using successively finer grades of metallographic emery papers, down to 4/0, until a mirror-bright surface was attained. The circuit and the electrolytic cell were as described elsewhere [20, 21]. The open-circuit potential (E_h) was measured with the aid of high input voltage follower coupled to a valve voltmeter (Heathkit, Model 1M-180D). The electrode potentials are reported with reference to the standard hydrogen electrode (SHE). The components, C_m and R_m, of the impedance of the anodized niobium were measured at 1000 Hz. The measurements were carried out in an electrically controlled air thermostat at the desired temperature (30 ± 0.1° C).

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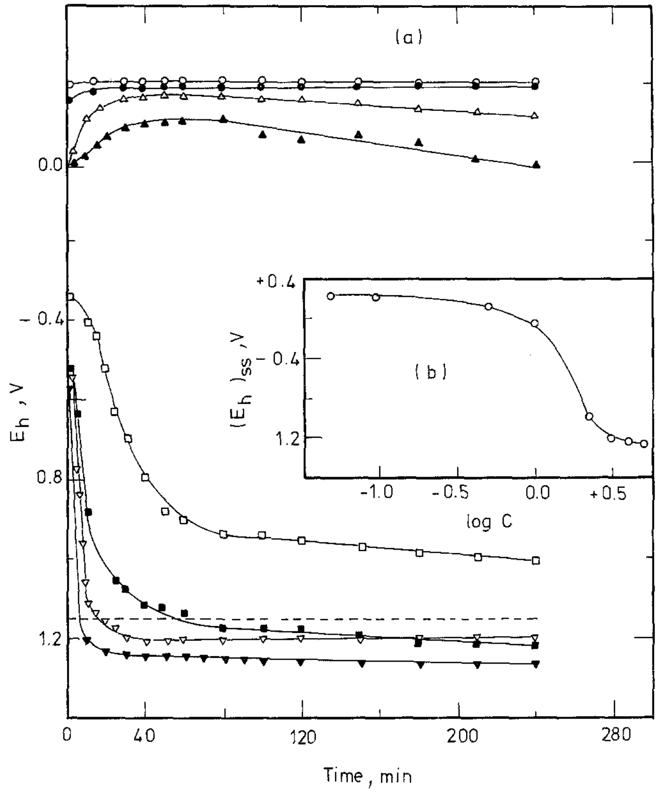

Fig. 1. (a) Variation of anodized niobium electrode potential with time in NaOH solutions of different concentrations: ○, 0.05 N; ●, 0.1 N; △, 0.5 N; ▲, 1.0 N; □, 2.0 N; ■, 3.0 N; ▽, 4.0 N; ▼, 5.0 N. ---, Abraded surface in 3.0 N solution. (b) Variation of steady-state electrode potential with the logarithm of NaOH concentration.

3. Results and discussion

3.1. *Effect of NaOH concentration on the stability of the anodic oxide film formed on niobium*

An anodic oxide film was formed on niobium at a current density of $0.501\,\mathrm{mA\,cm^{-2}}$ up to a formation voltage of 25 V versus SCE in naturally aerated 0.5 M H_2SO_4 solution. After the formation of the oxide film, the electrode was washed with triply distilled water and transferred quickly to the sodium hydroxide solution, taking the immersion moment as zero time. Values of E_h, C_m and R_m were monitored with time up to about 4 h (until a steady-state was reached). The variation of the electrode potential with time in NaOH solutions is illustrated in Fig. 1. For NaOH concentrations less than 1 M, the steady-state potential of the anodized electrode after the 4 h measurement period was not very different from the initial potential, indicating that the oxide film is stable up to this concentration. At higher concentrations of NaOH ($C_{NaOH} \geqslant 2\,M$) the electrode potential becomes more negative with time, indicating that the oxide film is subject to a continuous dissolution. The steady-state potential obtained in these solutions ($\sim -1.2\,V$) is about the same as that of the abraded electrode ($-1.15\,V$) (see Fig. 1a). Consequently, the most probable dissolution reaction for the anodic oxide film in the aggressive NaOH solutions ($C_{NaOH} \geqslant 2\,M$) may be written as

$$3Nb_2O_5 + 6OH^- = 6NbO_3^- + 3H_2O \quad (1)$$

$$6NbO_3^- + 2OH^- = Nb_6O_{19}^{8-} + H_2O \quad (2)$$

$$3Nb_2O_5 + 8OH^- = Nb_6O_{19}^{8-} + 4H_2O \quad (3)$$

The plots of reciprocal capacitance, C_m^{-1}, against time (Fig. 2) are in good agreement with the potential measurements. The plot of steady-state potential, $(E_h)_{ss}$, versus the logarithm of the concentration of NaOH shown in Fig. 1b illustrates clearly the two concentration regions; i.e. below a concentration of 1 M NaOH a very good

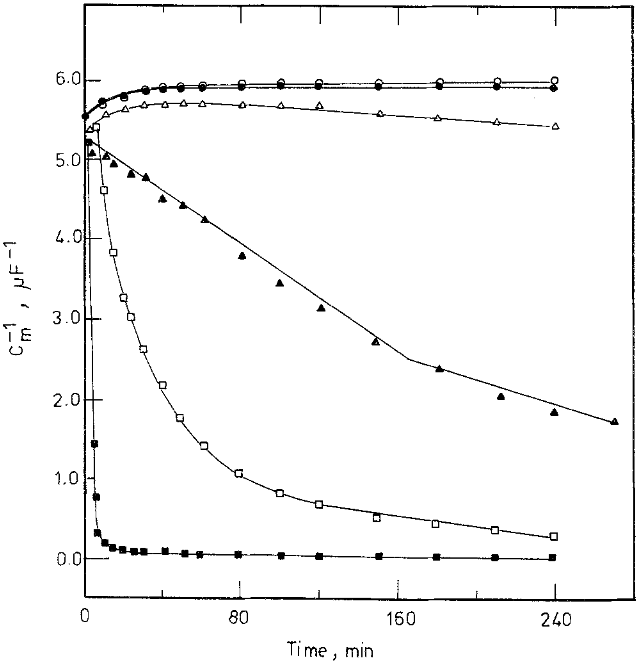

Fig. 2. Variation of reciprocal capacitance of anodized niobium electrode with time in NaOH solutions of different concentrations: ○, 0.05 N; ●, 0.1 N; △, 1.0 N; ▲, 2.0 N; □, 3.0 N; ■, 4.0 N.

stability of the anodic oxide film is achieved, whereas at concentrations above 1.0 M the oxide film dissolves. The rate of dissolution is proportional to the concentration of the dissolving medium, the formation voltage and the conditions of the surface [22]. As the OH^- ion concentration increases, the probability of its incorporation within the oxide film increases and hence the structure of the film is affected. The incorporation of species into the oxide film was observed by Randall *et al.* [17] to increase with increase of the electrolyte concentration. This remarkable effect is reflected in the measured capacitance, potential and resistance of the electrode. The change in the interference colour of the surface observed during film dissolution is an indication of the variation of the thickness of the oxide film during measurement [23]. A similar behaviour of film thinning in NaOH ($C_{NaOH} >$ 1 M) was also observed for anodized zirconium [22]. The slight shift of potential towards more positive values together with the increase of C_m^{-1} with time at lower concentrations of OH^- ions ($C_{NaOH} <$ 1 M) may be attributed to the film thickening due to adsorption of OH^- ions as was observed for anodized zirconium [22].

3.2. *Effect of formation voltage on the dissolution behaviour of the anodic oxide film on niobium*

The oxide films were formed as previously described at a current density of 0.501 mA cm^{-2} in 0.5 M H_2SO_4 up to polarizations of 2, 25, 40 and 60 V versus SCE. After each polarization interval the electrode was rinsed with triply distilled water and transferred immediately to the impedance cell containing the dissolution medium (3 M NaOH solution). The potential, capacitance and resistance of the electrode were measured during the dissolution process over a period of more than 4 h until a steady-state was reached. The relations between C_m^{-1} and E_h against time are illustrated in Figs 3 and 4. Fig. 3a shows that the capacitance of the oxide film increases with time, and since the values of C_m^{-1} could be taken as a measure of the oxide film thickness [24, 25], the extrapolation of C_m^{-1} versus time gives $1/C_m^0$, corresponding to the initial film thickness at the specified formation voltage. The initial oxide film thickness, $1/C_m^0$, depends on the formation voltage, whereas the steady-state reciprocal capacitance, $(1/C_m)_{ss}$,

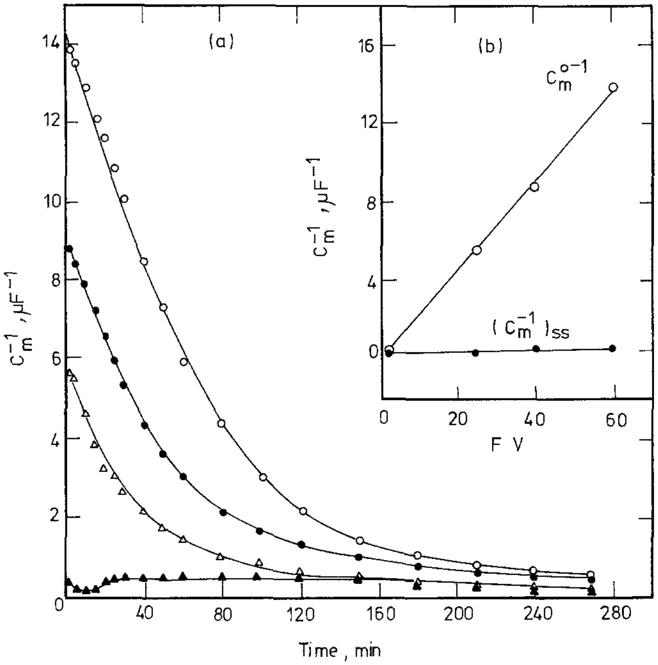

Fig. 3. (a) Variation of reciprocal capacitance of anodized niobium electrode at different formation voltages with time in 3.0 N NaOH solution: ○, 60 V; ●, 40 V; △, 25 V; ▲, 2 V. (b) Initial and steady-state reciprocal capacitance as a function of formation voltage (FV).

measured after 4 h from immersion is less dependent. The variation of $1/C_m^0$ and $1(1/C_m)_{ss}$ with formation voltage is illustrated in Fig. 3b. As can be seen, $1/C_m^0$ varies linearly with formation voltage as previously reported [3], which means that the thickness of the film formed on niobium in 0.5 M H_2SO_4 at the specified conditions is a linear function of the formation voltage used. This linear variation may be represented as

$$1/C_m^0 = \alpha V_F + \beta$$

where α represents the rate of variation of the initial film thickness with the formation voltage and β is a constant depending on the electrolyte and its concentration (representing the thickness of the naturally formed oxide film on niobium).

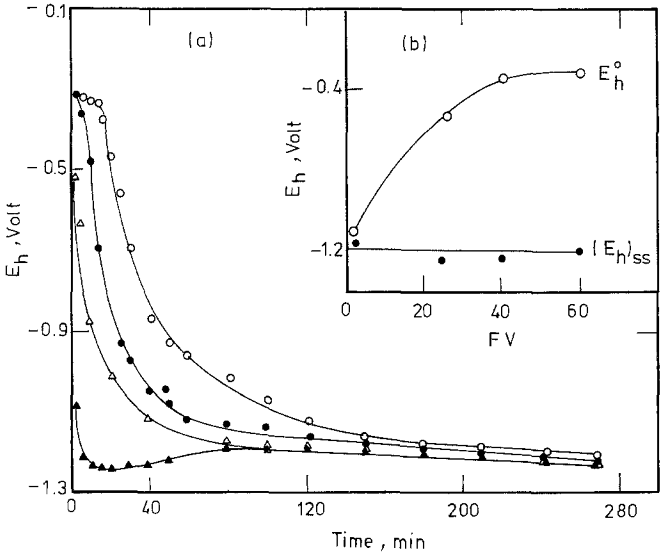

Fig. 4. (a) Variation of anodized niobium electrode potential at different formation voltages with time in 3.0 N NaOH solution: ○, 60 V; ●, 40 V; △, 25 V; ▲, 2 V. (b) Initial and steady-state potential as a function of formation voltage (FV).

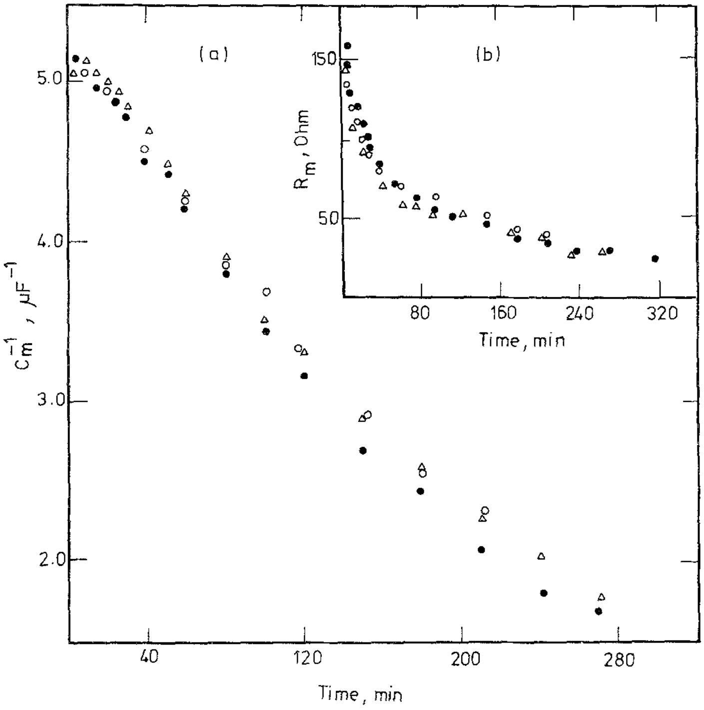

Fig. 5. (a) Variation of reciprocal capacitance of anodized niobium electrode with time at different current densities in 2.0 N NaOH solution: ○, 0.0501 mA cm^{-2}; ●, 0.501 mA cm^{-2}; △, 5.01 mA cm^{-2}. (b) Variation of resistance with time.

In the present measurements α, i.e. $d(1/C_m^0)/dV_F$, was found to be $0.23\,\mu F^{-1} V^{-1}$, whereas β was $-0.4\,\mu F^{-1}$.

The constancy of the values of $(1/C_m)_{ss}$ obtained, whatever the formation voltages used, indicates that the steady-state capacitance is independent of the formation voltage. The values obtained were identical to those measured on an abraded niobium electrode. This indicates that the nature of the remaining surface at the steady-state is more or less the same whatever the formation voltage used, and it behaves as if it were a newly abraded surface. The same conclusion may be obtained from the potential measurements shown in Fig. 4a and 4b. These results indicate that the dielectric properties of the anodic oxide film formed on niobium are greatly influenced if the anodized electrode is left in concentrated NaOH solution ($C_{NaOH} > 1$ M). Resistance measurements are consistent with those of the capacitance and potential and are shown in Figs 3 and 4. These results are in good agreement with those reported earlier for anodized niobium in HCl solutions [4].

3.3. *Effect of formation current density on the dissolution behaviour of the oxide film*

The effect of formation current density on the rate of dissolution of the oxide film formed in 2 N NaOH solution is presented in Fig. 5a and 5b. As can be seen from these results there is a shift over a wide range of magnitudes (from 0.0501 to 5.01 mA cm^{-2}). The measurements of C_m (Fig. 5a) and those of R_m, (Fig. 5b) are consistent. This behaviour is in contrast to the behaviour of some other related valve metals, e.g. tungsten in H_2SO_4 solution [21]. It is well known that increase of the formation current density increases the number of defects in the anodic oxide films formed on most valve metals [3, 26]. In the present measurements the use of high current density has no effect on the rate of oxide film dissolution, (cf. Fig. 5a, 5b). This means that the increased current density has no pronounced effect on the rate of dissolution of the anodic oxide film formed on niobium. The rate of dissolution depends considerably on the aggressiveness and active chemical attack of the NaOH solution ($C_{NaOH} > 1$ M) to the oxide film (cf. Figs 1, 2).

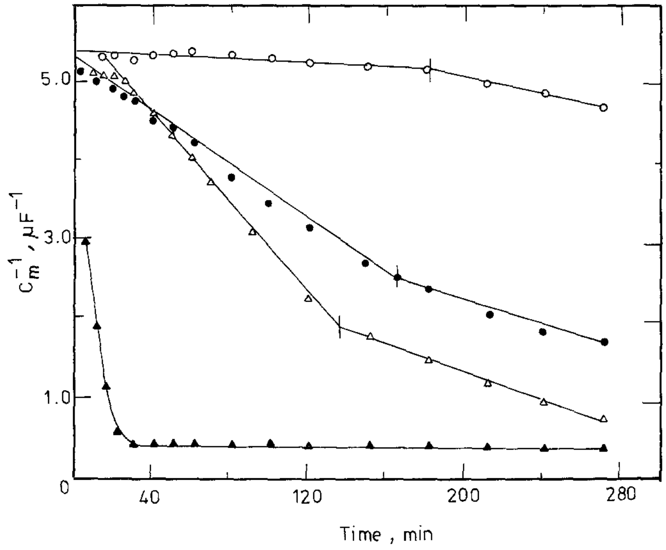

Fig. 6. Variation of reciprocal capacitance of anodized niobium electrode with time at different temperatures in 2.0 N NaOH solution: ○, 293 K; ●, 303 K; △, 313 K; ▲, 323 K.

3.4. *Effect of temperature on the rate of dissolution of the oxide film formed on niobium*

A niobium electrode was anodized as previously described up to a formation voltage of 25 V versus SCE. The rate of dissolution of the formed oxide films was recorded at different temperatures via capacitance and resistance measurements in 2 N NaOH solution. The effect of temperature on the dissolution behaviour of the anodized niobium electrode is illustrated in Figs 6 and 7. As shown in Fig. 6, C_m^{-1} decreases as the temperature increases. At low temperatures ($T \leqslant 293$ K) the rate of dissolution of the oxide film is very low (cf. Table 1). As the temperature increases the rate of dissolution increases. For each temperature in all measurements an inflection in the C_m^{-1} versus time relation is obtained. The inflection time decreases as the temperature increases. At higher temperatures (more than 320 K) the oxide film dissolves completely in less than 30 min and the second segment of the relation becomes parallel to the time axis. The values of C_m^{-1} are comparable with those obtained for the abraded niobium surface in the same solution. The relation between the rate of dissolution represented by $d(1/C_m/dt)$ and $1/T$ gives straight lines (Arrhenius plots) corresponding to the first and the second segments of the $1/C_m$ versus time relations at different temperatures (Fig. 8). From the slopes of these lines the activation energy of the dissolution process may be calculated as

Table 1. Variation of the dissolution rate with temperature in 2 M NaOH solution

T *(K)*	$\beta_1 \times 10^3$ *($\mu F^{-1} min^{-1}$)*	$\beta_2 \times 10^3$ *($\mu F^{-1} min^{-1}$)*
293	2.50	5.01
303	15.00	6.25
313	26.20	8.12
323	150.00	—

$$2.303R[d(\log \beta_1)/d(1/T)] = 114.8\,\mathrm{kJ\,mol^{-1}}$$

and

$$2.303R[d(\log \beta_2)/d(1/T)] = 19.1\,\mathrm{kJ\,mol^{-1}}$$

The two different values obtained from the two segments indicate that the effect of temperature on the dissolution of anodized niobium is a complicated parameter which needs further investigation.

4. Conclusion

The anodic oxide films formed on niobium in 0.5 M H_2SO_4 are stable in dilute NaOH solutions ($C_{NaOH} \leqslant 1$ M). At higher concentrations of NaOH ($C_{NaOH} \geqslant 2$ M) the oxide film is subject to continuous dissolution, the rate being

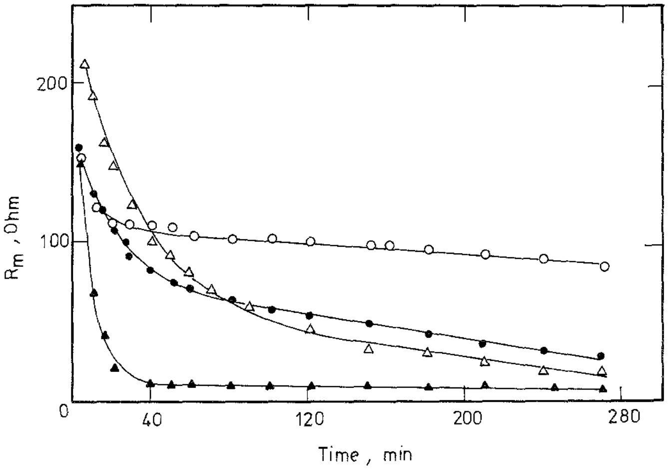

Fig. 7. Variation of resistance of anodized niobium electrode with time at different temperatures in 2.0 N NaOH solution: ○, 293 K; ●, 303 K; △, 313 K; ▲, 323 K.

dependent on the alkali concentration. The thickness of the oxide film formed on niobium is dependent on the formation voltage, whereas the rate of its dissolution is independent of this factor. The current density used during the formation of the oxide film has no effect on its dissolution rate. The dissolution process is greatly affected by temperature and at temperatures more than 320 K the oxide film is destroyed in less than 30 min.

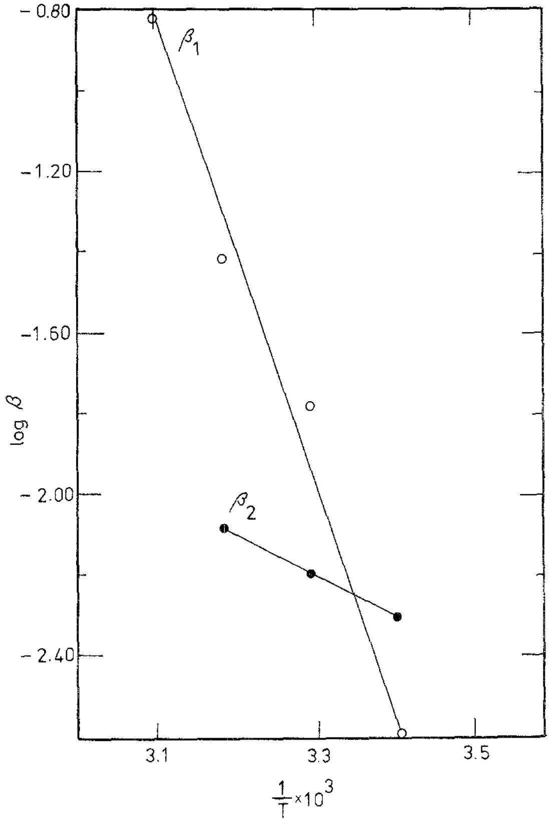

Fig. 8. Variation of the logarithm of the rate of dissolution of anodized niobium electrode with the reciprocal of the absolute temperature in 2.0 N NaOH solution.

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