NATURE AND STABILITY OF OXIDE FILMS FORMED ON NIOBIUM IN ACID BROMIDE SOLUTION

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The formation and stability of the anodic oxide films formed on niobium in acid bromide solutions were studied using polarization and impedance measurements. The charging curves in all concentrations display the same general trend. The steady-state potential was found to depend on HBr concentration. The efficiency of oxide building is diminished owing to preferential adsorption of Br^- ions on the oxide surface acting as depolarizer for the main anodic process. The dissolution behaviour of the anodized oxide niobium films is duplex in nature. The outer layer becomes more liable to dissolution with increasing film thickness or formation voltage. Also, the properties of the surface oxide film are greatly influenced by HBr concentration.

Valve metals are known to form stable oxides[1]. The stability and electrochemical activity of these oxides are essential for determining their stability as good anodic materials for many industrial application[2,3], e.g. for the manufacture of chlorine and caustic soda. Niobium is one of these metals[4]. Most studies on the electrochemical behaviour of niobium have been done on the kinetics of oxide film formation[5-10]. The nature and stability of the barrier films formed on niobium in different aggressive media have been received a little attention[11,12,14].

In the present investigation, the formation and stability of the anodic barrier oxide films on niobium in acid bromide solutions and the different factors affecting on it were studied.

EXPERIMENTAL

The electrode preparation for impedance and polarization measurements, the electrolytic cell, the electrical circuits and the experimental details were described elsewhere[15,16]. The capacitance and resistance were measured by using an alternating current (AC) bridge of the Wien type, in which the known arm is a capacitance in series with a resistance. The system was assumed to behave as the Raudles equivalent circuit[17].

The niobium electrodes used were cut from specpure niobium rod (Johnson and Matthey – London). A stout copper wire was made for the electrical contact. The electrodes was fitted into a glass tube of appropriate internal diameter by means of a thin layer of Araldite (Ciba, Switzerland), leaving a surface

area of 0.125 cm^2 to contact the test solutions. The acid bromide solutions of different concentrations were prepared from AnalaR grade HBr by appropriate dilution using triply distilled water, then standardized.

Before each experiment the electrode surface was mechanically polished using successively finer grades of metallographic emery papers, down to 4/0, until a mirror-bright surface was attained. The potential of the Nb electrode in open-circuit or during polarization was measured against SCE with the aid of a valve voltmeter (Electronic Instruments, Ltd., England). In polarization experiments, the current was supplied from a constant current unit source of range 5 μA – 100 mA. The AC bridge used for measuring the impedance components was a high precision standardized bridge, the known arm of which is a capacitor in series with a resistor. The input AC voltage was always 10 mV. All impedance measurements were carried out at frequency of 1 000 Hz. All measurements were carried out in naturally aerated solutions at 25 ± 1 °C in a double walled electrically controlled air thermostat.

RESULTS AND DISCUSSION

Galvanostatic Oxide Growth in Acid Bromide of Different Concentrations

Figure 1 shows galvanostatic anodic polarization of niobium electrode in HBr solutions of various concentrations. It is obvious that all curves display the same general trend; the potential increases very rapidly, then gradually and finally becomes steady. These observations are generally in agreement with those previously reported[4,18–20]. The first rapid increase of potential (few seconds) is connected with the charging of the electrical double layer as well as the deposition of chemisorbed oxygen. The gradual increase of potential is caused by oxide film formation which takes place with an efficiency of 100% (ref.[21]). After a certain period of time, the potential takes a value at which the rate of film formation is equal to the rate of film destroying. These steady value extends to a longer time with an increase of HBr concentration. Thus, for very dilute solutions, ≤ 0.10 mol l^{-1}, it is very finite and appears as a kink, where the rate of oxide film formation predominates and the potential shoot directly to higher positive values.

The steady-state potential E varies linearly with the logarithm of HBr concentration (Fig. 2) and obeys the following equation:

$$E = a - b \log [\text{HBr}], \tag{1}$$

where a is a constant depending on the nature of both metal and electrolyte[22,23] and slope b is an index for the shift of potential with HBr concentration. As shown in Fig. 2, the increase of HBr concentration shifts the potential to less positive value.

In the presence of Br$^-$ ions, the efficiency of the oxide formation is diminished, since a great part of the current is Faradaic, i.e. it does not involve oxide film formation. Consequently, instead of oxide formation another anodic process may occur, e.g. oxygen discharge, or liberation of Br$_2$ gas[24]. The Br$^-$ ions (as depassivating and aggressive anion) play their activating role through preferential adsorption on the oxide surface (assisted by the electric field at the oxide-solution interface). Under this condition Br$^-$ ions will act as depolarizer for the main anodic process of oxygen discharge,

thus destroying the main anodic process of oxide building. The niobium oxide surface, therefore, will posses a more open structure, i.e. not continuous and containing several active centers, in HBr solutions of higher concentrations. On the other hand, Lakhiani and Shreir[25] assumed that the steady-state in the E–time curves may be associated with the formation of discontinuities in the oxide caused by crystallization of the amorphous oxide.

In dilute HBr solutions, ≤ 0.10 mol l^{-1}, the depassivating action of Br^- ions become less important compared to the high affinity of the metal to oxygen[26]. The steady-state in this case appears to be finite and thickening of the oxide film will take place, consequently, the potential will gradually rise to attain higher positive values. The efficiency of the oxide formation process will increase again.

Effect of Formation Voltages on the Stability of the Anodically Nb Oxide Film in HBr Solution

The oxide films were formed on mechanically polished Nb at a current density of 10^{-4} A cm^{-2} in 0.5M H_2SO_4 solution up to 2, 5, 10, 20, 30 and 40 V vs SCE at 25 °C. After each formation voltage V, the applied current was interrupted and the electrode was washed with triply distilled water and transferred quickly to the acid 1M bromide solution. The measured open-circuit potential E_h, and the impedance of the pre-formed barrier oxide film, C_m and R_m, were followed with time. Figure 3 shows the variation of C_m^{-1} with the square root of time. The relation is a linear,
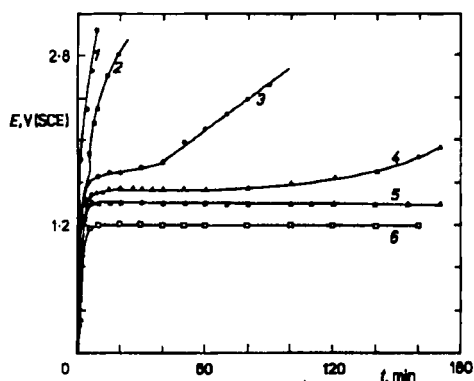

FIG. 1
Galvanostatic anodic polarization of niobium electrode in acid bromide solutions of different concentration (in mol l^{-1}: *1* 0.05, *2* 0.10, *3* 0.25, *4* 0.50, *5* 1.0, *6* 5.0), current density 10^{-4} A cm^{-2}
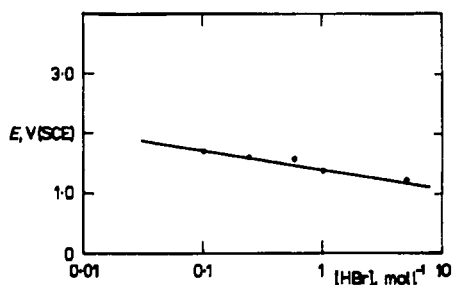
FIG. 2
Variation of the steady-state potential E with the logarithm of HBr concentration

$$C_m^{-1} = \alpha - \beta \sqrt{t},\qquad\qquad(2)$$

where α is the reciprocal capacitance at zero time, i.e. $(C_m^0)^{-1}$, and β is the slope which correspond to the rate of dissolution of barrier film. As can be seen from Fig. 3, the $C_m^{-1} - \sqrt{t}$ curves consist of two intersecting segments; the slope of the first segment β_1 is higher than that of the second segment β_2. The presence of two different dissolution rates led to the assumption that the barrier oxide film on niobium is duplex in nature. The outer layer seems to be more susceptible to chemical dissolution than the inner one as revealed from the higher β_1 (outer) than β_2 (inner) values. Similar results were found on Mo (ref.[27]), Zr (refs[28,29]), Ti (ref.[30]), Bi (ref.[31]), Ta (ref.[32]) and Al (ref.[33]).

Figure 4 shows the variation of the dissolution rate β_1 with the formation voltage. It is obvious that as the thickness of the anodic oxide film increases with the voltage V, the outer layer becomes more liable to dissolution, which may be attributed to the change in morphology of the oxide.

In this respect, Lakhiani and Shereir[25] found that the niobium oxide film is initially continuous and amorphous, however, with increasing formation voltage, the amorphous
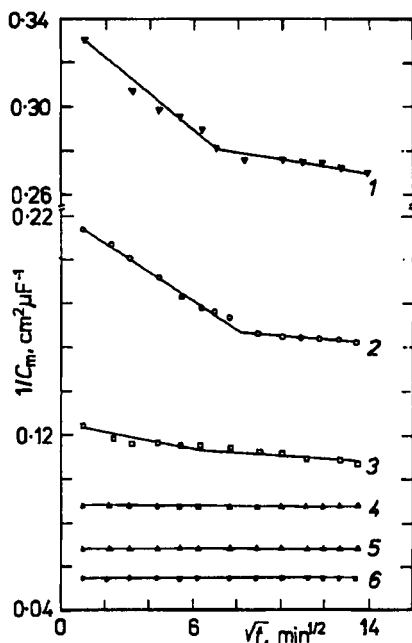

FIG. 3

Variation of the reciprocal capacitance, $(C_m)^{-1}$, of the oxide niobium films of different formation voltages (in V: *1* 40, *2* 30, *3* 20, *4* 10, *5* 5, *6* 2) with the square root of the time, $\sqrt{t}$, in acid bromide solutions (1 mol l^{-1})
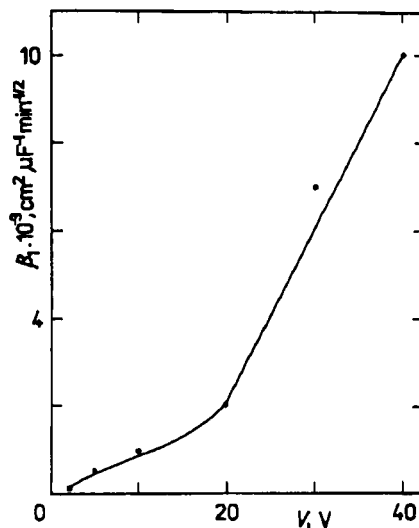
FIG. 4

Variation of the dissolution rate, β_1, with the formation voltage V

oxide may become discontinuous and crystalline. Also, the amorphous oxides are more, protective than the crystalline ones indicating the increase of dissolution may be due to crystallization. Also, the rate of anion penetration becomes pronounced with the increase of V (refs[34,35]).

Extrapolation of C_m^{-1} vs $t^{1/2}$ plots to zero time give $(C_m^0)^{-1}$, i.e. α, cf. Table I. As shown in Fig. 5, the $(C_m^0)^{-1} - V$ curve consists of two linear segments, the first segment shows gradual increase of thickness with increase of formation voltage up to a critical value ($V = 20$ V), then increases rapidly as shown in the second segment. This behaviour gives a further evidence for structure change during anodization. The anodic oxide growth occurs by high field ion migration in the film, both of metal ions outwards and oxygen ions inwards[1,36]. Such ions are injected at both metal/oxide and oxide/electrolyte interfaces, respectively. The $R_m - \sqrt{t}$ relations, Fig. 6, exhibit the same trend as that of capacitance.

On the other hand, the variation of the initial and final open-circuit potential E_h with the formation voltage V is shown in Fig. 7. It is obvious that for lower oxide film thickness, $V \le 20$ V, the potential becomes more positive with time. But for higher oxide films, $V > 20$ V, the potential becomes less positive with time. This may indicate that the corrosion potential of the barrier oxide film is complex in nature and depends
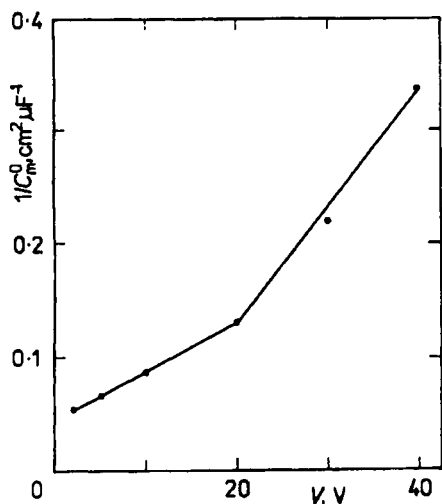

Fig. 5

Variation of the initial film thickness, $(C_m^0)^{-1}$, with the formation voltage V
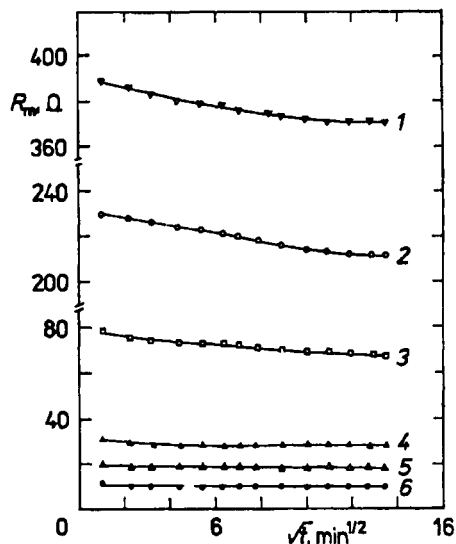

Fig. 6

Variation of R_m of the oxide niobium films at different voltages (in V: 1 40, 2 30, 3 20, 4 10, 5 5, 6 2) with $\sqrt{t}$ in acid bromide solutions (1 mol l^{-1})

on the voltage V. This behaviour can be explained by considering the occurence of two different opposing processes, the dissolution of the barrier film by the action of the aggressive Br^- ions, and the penetration of the film by traces of atmospheric oxygen. Thus, for oxide film formed till $V \le 20$ V thickness, the effect of dissolved oxygen seems to be pronounced, and the dissolution rate becomes very low and consequently the potential will be shifted, to more positive values, cf. Fig. 7. With increasing the preformed barrier film thickness, $V > 20$ V, the number of defects increase and the effect of dissolved oxygen is diminished, i.e. the corrosive action of Br^- is increased. Therefore, the open-circuit potential shifts to less positive values with time.

TABLE I
The film thickness at zero time α and the dissolution coefficients β_1 and β_2 as functions of formation voltage V measured in acid bromide solutions (1 mol l^{-1})

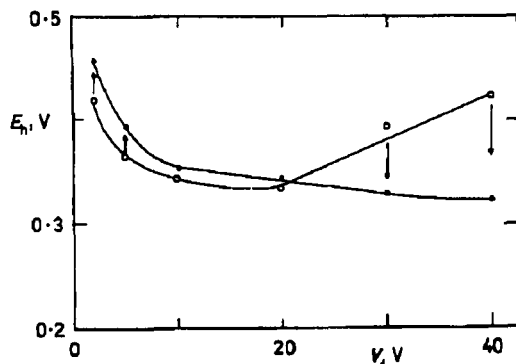| V V	α $cm^2\,\mu F^{-1}$	$\beta_1 \cdot 10^3$ $cm^2\,\mu F^{-1}\,min^{-1/2}$	$\beta_2 \cdot 10^3$ $cm^2\,\mu F^{-1}\,min^{-1/2}$
2	0.045	0.0	0
5	0.069	0.5	0
10	0.089	1.0	0
20	0.126	2.0	1
30	0.242	6.5	2
40	0.338	9.0	3

FIG. 7
Initial (○) and final (●) open-circuit potential of anodically formed niobium oxide film as a function of the formation voltage V

Effect of HBr Concentration on the Stability of the Anodic Oxide Film Formed on Niobium

An anodic oxide film was formed on niobium electrode at a current density of 10^{-4} A cm^{-2} up to a formation voltage of 20 V vs SCE in naturally aerated 0.5M H$_2$SO$_4$ solution. The current was then interrupted and the electrode was withdrawn from the cell, washed with triply distilled water and immediately immersed in acid bromide solutions of various concentrations. The open-circuit potential and impedance components of the electrode, C_m and R_m, at 1 000 Hz were followed with time. As shown in Fig. 8, for [HBr] $\geq$ 1 mol l^{-1}, the linear plots of C_m^{-1} vs $\sqrt{t}$, consist of two segments which indicate a duplex nature of the barrier oxide film. The observed inflection may be attributed to a change in the mechanism of film thinning. On the other hand, for HBr concentration lower than 1.0 mol l^{-1}, C_m^{-1} increases gradually to reach a limiting value, then falls down. This behaviour may be attributed to the competitive adsorption of aggressive Br$^-$ ions and oxygen on the oxide surface. It was assumed that adsorbed oxygen and/or metal oxide make up the passive film. At lower HBr concentration, oxygen has higher affinity than Br$^-$ for adsorption on the surface, the adsorbed oxygen may cause thickening of the oxide film as inferred from the increase of C_m^{-1} with $\sqrt{t}$. After a certain time corresponding to a critical oxide thickness and depending on electrolyte concentration, the adsorbed Br$^-$ ions succeed to destroy passivity by displacing the adsorbed oxygen and dissolving the oxide film, i.e. lowering of C_m^{-1} till reach a
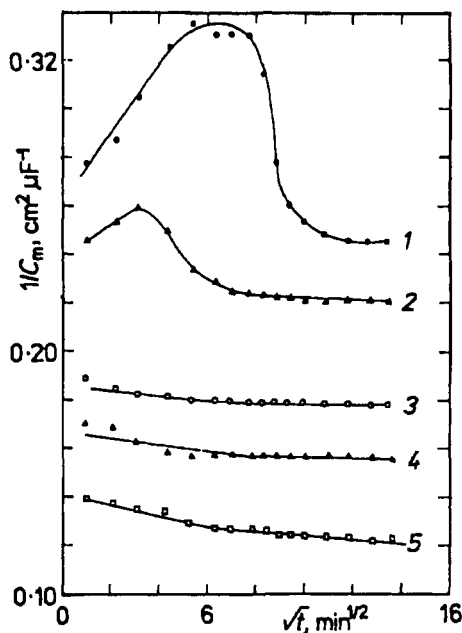

FIG. 8
Variation of reciprocal capacitance, $(C_m)^{-1}$, of the anodized niobium electrode ($V = 20$ V) in acid bromide solutions of various concentration (in mol l^{-1}: *1* 0.01, *2* 0.1, *3* 1.0, *4* 2.5, *5* 5.0) with the square root of time $\sqrt{t}$

limiting value. The vertical shift of the initial film thickness formed at 20 V, $(C_m^0)^{-1}$, with change of solution concentration, Fig. 8, is mainly due to the difference in the relative electrolytic conductance of the test solution[37]. Figure 9 shows the capacitance and resistance of the dissolving oxide at zero time, i.e. C_m^0 and R_m^0, as a function of square root of acid bromide concentration.

The variation of R_m with square root of time, Fig. 10, provides a further evidence for the dissolution process. Thus R_m decreases gradually with time, and the curves consist of two linear segments indicating a duplex nature of the oxide.

With respect to the open-circuit potential E_h of the dissolving oxide film, it would be interesting to demonstrate that for all HBr concentrations, the potential becomes less positive with time. The variation of the final steady-state value of E_h with HBr concentration is shown in Fig. 11. It is obvious that the steady state open-circuit potential increases by +35 mV per decade of HBr concentration. The positive shift of potential with increasing HBr concentrations may be attributed to the solution pH.

It is well known that on anodic polarization, the rate of film thickening is determined by the difference in the rate of film growth and film dissolution. The rate of change in thickness can be represented by the following equation[38]

$$\frac{\mathrm{d}D}{\mathrm{d}t} = (i_t - i_{corr})\frac{M}{z\,F\,\rho} \quad, \tag{3}$$

where i_t is the total oxidation current of oxide growth, i_{corr} is the dissolution rate expressed as corrosion current density, M is the molar mass of oxide, $z\,F$ is the number of Faraday's required for the formation of one mole of oxide and ρ is the density of the
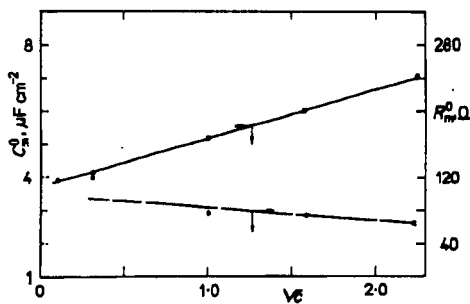

Fig. 9
Variation of $(C_m^0)^{-1}$ and R_m^0 of anodized niobium electrode (V = 20 V) with the square root of acid bromide concentration $\sqrt{[\mathrm{HBr}]}$
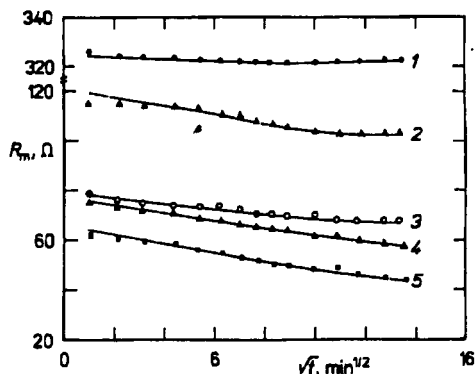
Fig. 10
Variation of R_m of anodized niobium electrode (V = 20 V) in acid bromide solutions of various concentration (in mol l^{-1}: *1* 0.01, *2* 0.1, *3* 1.0, *4* 2.5, *5* 5.0) with the square root of time $\sqrt{t}$

oxide. Definite thickness is obtained by applying the anodic cd for a certain period of time, when the current is interrupted and the electrode is transferred to the dissolution medium the oxidation current becomes negligible, and the oxide film may decay. Therefore, Eq. (3) takes the form:

$$- \frac{dD}{dt} = i_{corr} \frac{M}{zF\rho} \quad .$$

(4)

This equation agrees very well the results at higher HBr concentrations and formation voltages, respectively.

It is generally accepted that the rate of chemical dissolution of an inorganic solid, as the oxide film, is determined by its solid state and the concentration of defects within the solid. As the preformed barrier film thickness is increased, i.e. V, the number of defects seems to increase, particularly in the outer layer. The creation of structural and chemical defects in the solid markedly increases the rate of dissolution.

Draper and Harvey[38] showed that the incorporation of anions in the niobium oxide is an important in determining the rate of film growth. These ions are greatly affect the resistivity of the film and hence the ease of ions transport through the oxide. The amount of species incorporated into the film was found to increase with increasing electrolyte concentration[39].
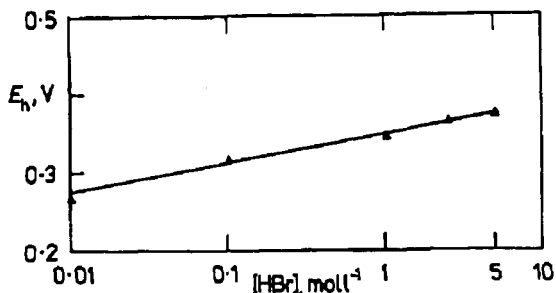
Fig. 11
Final open-circuit potential of anodized niobium electrode as a function of acid bromide concentration [HBr]

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