Anodic Polarization of Niobium in Various Oxyacid Media & in Sodium Hydroxide—Role of Prevailing Anion on Oxide-film Formation

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The anodic behaviour of mechanically polished and cathodically pretreated niobium electrodes has been examined at constant low c.d. in unstirred, N$_2$-deaerated IN solutions of H$_3$PO$_4$, HClO$_4$, H$_2$SO$_4$, HNO$_3$, and in NaOH solution. The results show a marked dependence of the anodic behaviour on the nature of the prevailing medium and pH. The effectiveness of the medium towards arresting the oxygen evolution process by anodic inhibition through the anion is found to follow the decreasing order: H$_3$PO$_4$ > HClO$_4$ > H$_2$SO$_4$ > HNO$_3$ > NaOH. This order in essence parallels that which is obtained by arranging the various anions according to their anodic inhibiting character. The dependence of anodic behaviour of niobium on the mode of preparation of surface has also been studied, and the results provide ample evidence in support of the existence of a layer of niobium hydride on the surface of the cathodically pretreated electrodes; further the hydride film is more inhibitive in character than the oxide.

In a previous paper$^1$ an attempt was made to elucidate (i) the significance of open-circuit potentials in terms of electrochemical reactions occurring at the electrode surface, (ii) nature of preimmersion film, and (iii) to determine pH of solution and extent of oxygen supply. For a further insight into the significance of such potential, and in order to evaluate the effectiveness of the various anions in inhibiting the anodic dissolution process, the anodic behaviour of niobium in oxyacid media and in NaOH solution has now been studied.

Not much work seems to have been done on the role of prevailing anions on the polarization behaviour of Nb. Most important contributions worth mentioning in this respect were made by Bondareva and Tsygankova$^2$, Shatalov$^3$, Bondareva and Nauchu$^4$, Piron and Kennobe$^5$ and Young$^6$. Their results indicated that the potential of Nb increased to higher positive values on anodic polarization with increasing current density due to formation of Nb$_2$O$_5$ film and that the structure of this film depended upon the electrolyte composition. Thus Bondareva and Tsygankova$^2$ reported that upon anodic polarization the potential of the niobium electrode increased with time and reached several tens of volts. These authors further claimed that an oxide film was formed on the metal surface even if no external current was applied due to localized corrosion currents. They assumed that the anodic oxidation of niobium is governed by interaction of the metal with water molecules, the only effect of the nature of the solution being that on the structure of the oxide film.

Shatalov et al.$^3$ reported that upon anodic oxidation of niobium the potential of the metal attained several tens of volts, after which it stabilized. The steepness of the polarization curves increased with current density. Bondareva and Nauchu$^4$ reported that at constant current density the potential ($\phi$) shifted linearly towards more positive values. This shift was greater at higher current densities and the rate of growth of the oxide film depended on the electrolyte composition. Young$^6$ studied the kinetics of formation of anodic oxide film on niobium and concluded that the anodic polarization of niobium produced interference-coloured oxide films similar to tantalum.

Materials and Methods

The electrodes used in this investigation were of spectroscopically pure niobium (Johnson and Matthey, England) of the massive type. Before each experiment the electrode was polished successively by 0.2/0 emery paper, rubbed with cotton wool, polished with smooth fine filter paper and finally rinsed with the test solution. The polarization cell consisted of two compartments sufficiently separated from each other to ensure equal distribution of current; an intermediate tap was always kept tightly closed during measurements to avoid contamination of catholyte and anolyte. A saturated calomel electrode was used as a reference unpolarizable electrode. Potentials were read directly on a valve voltmeter type U-719 which covered the range from 0-01 V to 300 V.

All the chemicals used were of AR grade. A carbonate-free solution of sodium hydroxide was prepared by proper dilution of a weight to weight concentrated solution as given in Vogel$^7$. 

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Fig. 1 — Anodic polarization of niobium in 1N H₃PO₄ acid [c.d. × 10⁻² (A/cm²) for curves 1-8; 6.6, 13.3, 26.6, 66.6, 133.3, 266.6, 400 and 666.6 respectively]

Fig. 2 — Anodic polarization of niobium in 1N HClO₄ acid [c.d. × 10⁻² (A/cm²) for curves 1-8; 6.6, 13.3, 26.6, 40.0, 66.6, 133.3, 266.6 and 666.6 respectively]

Fig. 3 — Anodic polarization of niobium at constant current densities in different oxy-anions [for set of curves I, c.d. = 13.3 × 10⁻⁴ A/cm²; for set of curves II, c.d. = 66.6 × 10⁻⁴ A/cm²]

Fig. 4 — Anodic polarization of niobium in 1N NaOH [c.d. × 10⁻⁶ (A/cm²) for curves 1-5; 6.6, 13.3, 20.0, 26.6 and 40.0 respectively]
Results and Discussion

Figs 1-4 represent potential (vs NHE)-time curves obtained on anodic polarization of niobium at various constant current densities in 1N solutions of H$_3$PO$_4$, HClO$_4$, H$_2$SO$_4$ and sodium hydroxide. The shape of these curves showed a marked dependence of the anodic behaviour of niobium on the nature of the prevailing anion and pH. In all acid media studied the general behaviour was the same at low and moderate current densities; the potential increased regularly with time to reach more or less stabilized positive values, in agreement with the observations of the earlier investigators. A close scrutiny of the potential-time curves (Figs 1-4) reveals the following features:

(i) In all the cases, an initial rise in potential is observed upon application of current. This is believed to be connected with the anodic removal of adsorbed surface hydrogen as well as the charging up of the electrical double layer at the metal solution interface.

(ii) The second linear segment of the potential-time curves may be due to film building and repair processes through blocking of the pores or cracks in the pre-immersion film with the formed oxide. At this stage the role of the prevailing anion can not be ignored. The higher degree of incorporation of the anion within the oxide leads to its greater inhibition character and, effectiveness to film repair, increased slope of the potential-time curves (Fig. 5), and higher degree of passivation. This, however, does not exclude the possibility that opposing processes such as chemical dissolution of the freshly formed oxide film — leading to surface uncovery — may not take place.

(iii) The rate of surface repair or oxide film perfection proceeds up to a certain limit where the second linear segment of the curve attains a stabilized potential. At this stage a state of equilibrium is reached, at which the two opposing rates (rate of thickening and dissolution) are equal and the potential does not change with time.

(iv) When the polarizing current density exceeds a certain limit, the potential of the niobium electrode jumps to reach higher potential values during the first two hours. Glow discharge is observed then the potential decreases, and hence a maximum appears on the potential-time curve (Fig. 2). This can be explained as due to continuous cracking and rehealing of the surface film resulting from internal stresses at the place where the oxide grows. Under such conditions heating effects of metal electrode surface and solution are expected which may result in convection currents and stirring of solutions, conditions which favour the dissolution of oxide film.

In spite of the resemblance in the general behaviour in different acid media, it is possible to differentiate between the effectiveness of the various anions in producing anodic insulating films on the metal. Such differences in behaviour can be expressed in terms of what may be defined as surface charging capacity $C_s = dq/dE$ (µF/cm$^2$), along the first linear segment of the potential-time curves. In Table 1 are presented the surface charging capacities for mechanically polished niobium surface in 1N solution of different anions at comparable current densities.

The values of $C_s$ obtained before the stabilized potential value is reached, show only a slight dependence on current density (Table 1). Such large surface charging capacities may be ascribed to an electrochemical reaction involving water or OH$^-$ ion (in alkaline solution), leading to progressive oxidation of the surface.

Based on the magnitude of $C_s$ at comparable current densities, the different anions can be arranged in order of their effectiveness in producing passivation as follows: $\text{H}_3\text{PO}_4 > \text{HClO}_4 > \text{H}_2\text{SO}_4 > \text{HNO}_3$. This order is the same as that obtained according to their anodic inhibiting character. The above order can also be arrived at by a consideration of the magnitude of the stabilized potentials at comparable constant current densities. The plots of the stabilized potential values obtained in the various acid media against the constant c.d. applied are shown in Fig. 5. The curves in Fig. 5 consist of two linear segments, with higher and lower slopes, respectively. The two segments intersect at nearly the same c.d. range (viz. 60-70 µA/cm$^2$). Below this c.d. range slopes (slope $E/I = R$ resistance of the film), are found to depend on the

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**Table 1 — Characteristic Polarization Data of Mechanically Polished Niobium Electrodes in Various Media**

<table>
<thead>
<tr>
<th>c.d.</th>
<th>$C_s \times 10^4$ (µF/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-6</td>
<td>0.08</td>
</tr>
<tr>
<td>13-3</td>
<td>0.42</td>
</tr>
<tr>
<td>26-6</td>
<td>0.41</td>
</tr>
<tr>
<td>66-6</td>
<td>0.40</td>
</tr>
</tbody>
</table>

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**Fig. 5 — Variation of stabilized potential values in different anions (1N) with c.d.**
At higher current densities the arrest, however, and the potential was found to be nearly constant. At very low current densities (6.6 × 10⁻⁴ A/cm²) the potential reached a definite formation voltage in H₃PO₄. The arrest was indefinite at the least quantity of electricity is needed to reach the same formation voltage. At a formation voltage of 60 V (210 m coul.) and a higher stabilized voltage (170 V) in H₃PO₄, another way of distinguishing the effectiveness of the various anions towards passivation is to compare the quantity of electricity passed (within the low c.d. range) in order to reach the same formation voltage. At a formation voltage of 60 V the quantity of electricity passed in the presence of H₃PO₄, HClO₄, H₂SO₄ and HNO₃ is 3050, 6000, 6400 and 8600 m coul. respectively. It is clear that the least quantity of electricity is needed to reach a definite formation voltage in H₃PO₄.

In sodium hydroxide solution general features similar to those in oxyacids are observed (Fig. 4). However, in this case the potentials were stabilized at ~1-0 V especially at low c.d. and during this arrest oxygen evolution was observed on the electrode surface. The arrest was indefinite at very low current densities (6.6 × 10⁻⁴ A/cm²), even though the measurements were extended for 6 hr, and the potential was found to be nearly constant. At higher current densities the arrest, however, terminated by itself with time, the time period being dependent on current density. In general the length of arrest was reduced with increase in current. The potential then changed more or less linearly to reach another stabilized, more positive value. At relatively high current densities, the nearly horizontal portion was found to be completely reduced and the two main linear segments of the potential-time curve merged with each other in a linear curve, which extended from the beginning to the end.

Along the arrest (b) of the potential-time curve, the current efficiency for oxide film build-up diminished. It may be due to the fact that a great proportion of the current will be electronic in character and involved in other anodic discharge processes, e.g. oxygen discharge. At low current density such electronic conduction may proceed to an indefinite extent, consequently the anodic polarization curve will not rise to higher positive potentials. As continuous oxygen evolution was expected to help the passivation process through progressive oxidative surface, and consequently leading to an increase in the effective current density, the arrest (b) became finite, thickening of the film took place and the potential increased regularly with increasing film thickness to attain higher positive values. It is noteworthy to mention that whereas the potential of oxygen evolution arrest did not change much with c.d., that of arrest (c) was found to be largely dependent on c.d., e.g. it increased from ~1-0 to 25 V for a 4-fold increase in c.d. These facts together with the decreasing capacity with c.d. substantiate the view that the behaviour of Nb in NaOH differs from that in oxyacids. Whereas a constant film thickness was reached in acids even at lower c.d. the thickness of the passive film of Nb in NaOH always increased with current density.

Based on the magnitude of surface charging capacity at comparable current densities one can arrange the different anions in the following order based on their effectiveness in producing passivation:

$PO_4^{3-} > ClO_4^- > SO_4^{2-} > NO_3^- > OH^-$

The position of phosphate at the top of the series runs parallel with the well established properties of this anion as anodic inhibitor in various systems. The position of perchlorate in the series as found in the present work, appears to be anomalous since it is known that this anion possesses low inhibition character. Most probably HClO₄ exerts its action

<table>
<thead>
<tr>
<th>Cathodic pretreatment</th>
<th>HClO₄</th>
<th>H₂PO₄</th>
<th>HNO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q coul/cm²</td>
<td>C₄ × 10⁴</td>
<td>q₄ × 10⁴</td>
<td>C₄ × 10⁴</td>
</tr>
<tr>
<td>c.d. = 1 mA/cm²</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>1.8</td>
<td>0.54</td>
<td>0.63</td>
</tr>
<tr>
<td>60</td>
<td>3.6</td>
<td>0.40</td>
<td>0.50</td>
</tr>
<tr>
<td>120</td>
<td>7.2</td>
<td>0.35</td>
<td>0.40</td>
</tr>
</tbody>
</table>

Table 2 — Data for Cathodically Pretreated Nb Electrode and Anodic Polarization in Different Oxyacid Media

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through oxidation rather than through its inhibition character. Although the OH\(^-\) ion is known to be a strong anodic inhibitor, its position in the above series also appears anomalous. The high electrochemical yield observed in this medium may be due to a depassivation effect resulting from the tendency of the passivating NbO\(_2\) film to dissolve on account of its amphoteric character, forming soluble pentaniobates.

Evidences for incorporation of anions and the dependence of properties of the surface oxide film on the nature of the electrolyte during formation were previously given by Vermilyea\(^19\), Dapper and coworkers\(^{20,21}\), Cheseldine\(^8\), Randall et al.\(^{12}\) and Dell Oca and Young\(^18\).

The dependence of anodic behaviour of niobium on the mode of preparation of surface can be revealed by comparing the results obtained with mechanically polished electrode in the same solution without previous cathodic pretreatment is also shown in Fig. 6. The data pertinent to the cathodic pretreatment and anodic polarization in different oxyacids are presented in Table 2.

From the shape of the polarization curves (Fig. 6) and the data included in Table 2, it is clear that cathodic pretreatment leads to increased passivation. This is judged from the marked decrease in the surface charging capacity, \(C_s\), along the first linear segment of the potential-time curve, and the quantity of electricity \(q_s\) passed before the stabilized potential is reached. Most probably, a layer of chemisorbed hydrogen atoms or niobium hydride film\(^21\) is produced on the electrode surface the presence of which initiates reactions capable of occurring at such high positive potentials, in which hydrogen atoms (or the metal hydride), and discharged oxygen are involved. The products of these reactions are of passivating character, since the potential is found to reach more positive values with time.

References