Growth Kinetics of Anodic Oxide Film on Titanium in Various Electrolytes

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The kinetics of anodic oxide film growth on titanium have been studied at various current densities in the electrolytes 0.1M KOH + 0.1M NaF, 0.05 M sodium oxalate and 95% glycolic solution of 0.1 M ammonium citrate. Formation rate (dv/dt) was calculated from the plots of formation voltage vs time drawn at each current density for these electrolytes. The plots of log. formation rate vs log. current density are fairly linear in agreement with the equation, $dv/dt = a(i)^b$.

Johansen et al[1] calculated the formation rates for the growth of the oxide films on titanium and other metals in borate solutions. Theoretical interpretations of these results were given by Van Rysselberghe and Johansen[2]. Amar and Kamal[3] reported the formation rates and reciprocal capacitance for the oxide film growth on titanium in acid media. Anjaneyulu[4] calculated the formation rates by carrying out anodization of titanium in 0.1 M propionic acid, 0.05 M H_2SO_4, and 9 % glycolic solution of 0.1 M KOH at various constant current densities.

In the present paper an attempt is made to find out the relationship between the formation rate and current density during anodization of titanium.

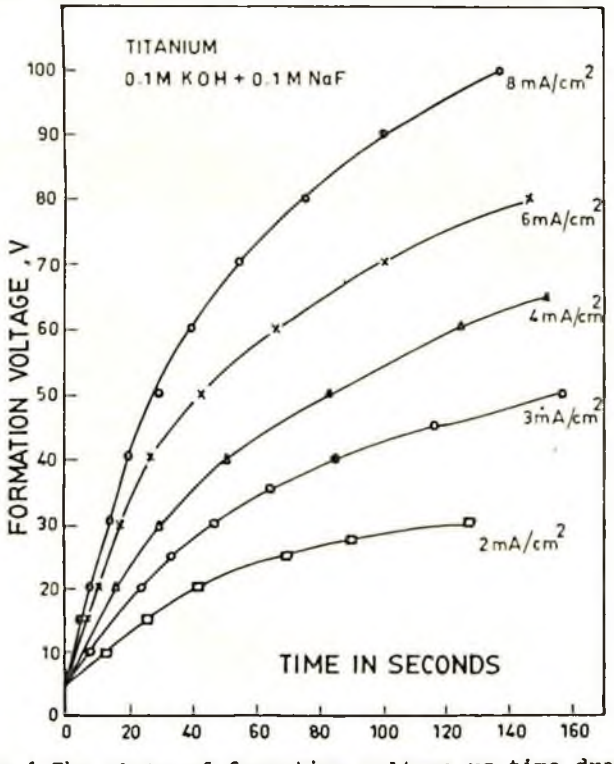


Fig.1 The plots of formation voltage vs time drawn at different current densities for Titanium in the electrolyte 0.1 M KOH + 0.1 M NaF

EXPERIMENTAL

Specimens were cut from .1 mm thick, annealed and rolled sheet of titanium of 99.7% purity. Main impurities were Carbon and Iron. All experiments were carried out at various constant current densities ranging from 2 to 12 mA/cm². The method of preparing the surface of the specimen and the constant current generator used were described in our previous paper [5].

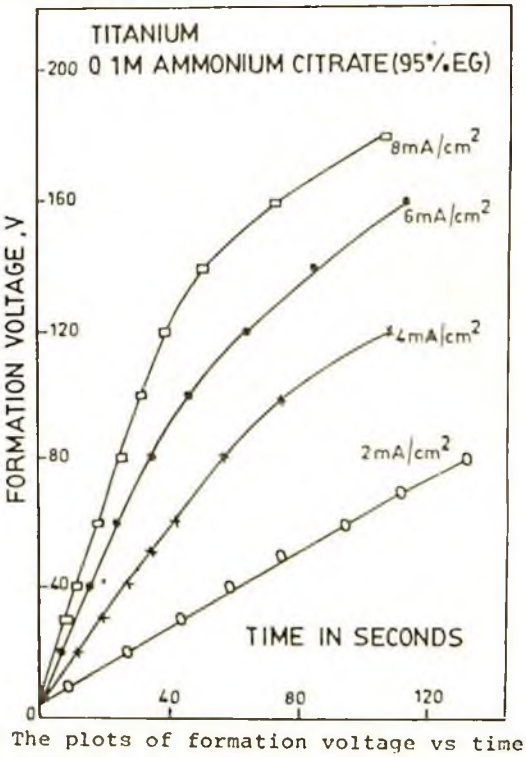


Fig.2 The plots of formation voltage vs time Titanium in the electrolyte 0.1 M Ammonium Citrate (95% glycol solution)

RESULTS AND DISCUSSION

Anodization of titanium was carried out at various current densities ranging from 2 to 12 mA/cm^2 in the electrolytes 0.1 M KOH + 0.1 M NaF, 0.1 M ammonium citrate (95% glycol solution) and 0.05 M sodium oxalate. The plots of formation voltage vs time drawn at each current density for the three electrolytes are shown in Figures 1,2,3. From these plots formation rate (dv/dt) was calculated at each current density in all the three electrolytes. The plots of log formation rate vs log current density are found to be fairly linear as shown in Figure 4. The slope and intercept values of these plots are given in Table-1, which the formation rate expressed in V/sec and the current density in A/cm^2 .

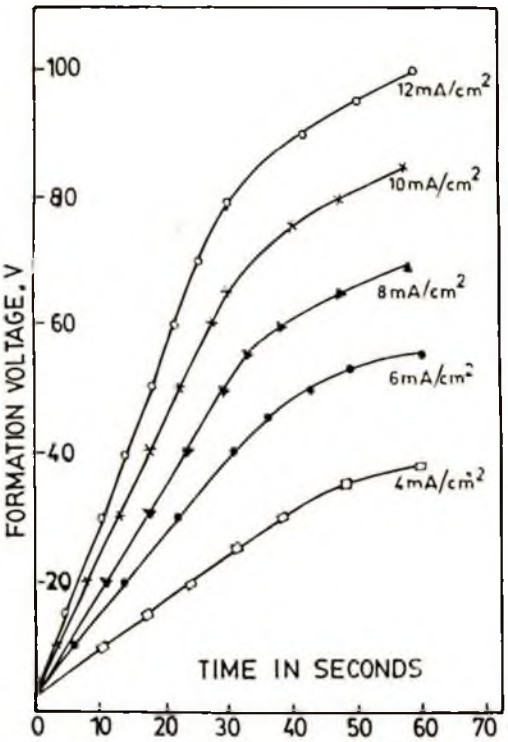


Fig.3 The plots of formation voltage vs time drawn at different current densities for Titanium in the electrolyte 0.05 M Sodium Oxalate

The linearity between log(dv/dt) and log I suggests the emperical relation.

$$dv/dt = a\ (I)^b \qquad \ldots\ (1)$$

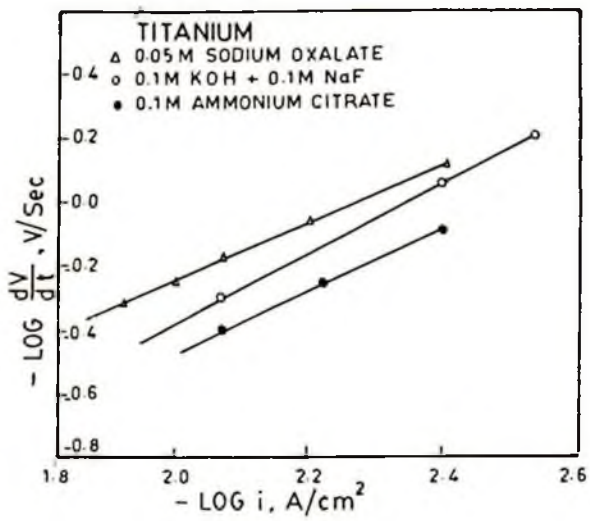


Fig. 4

with a and b as constants. Theoretical basis for the emperical relationship was given by Amar and Kamal[3] and Lavrenko and Chekhovishi[6].

Amar and Kamal[3] found that the values of slopes were independent of acid concentration in H_2SO_4 , HNO_3 and HCl whilst in H_3PO_4 the value was found to vary with the acid concentration. Their deduced values of slopes were 1.18 in H_2SO_4 , 1.26 in HNO_3 1.16 in HCl, 1.2 in 0.1 N and 1.0 N solutions of H_3PO_4 and 1.34 in 5 N H_3PO_4 solution.

Lavrenko and Chekhovishi[6] studied the kinetics of anodic oxidation of titanium in saturated oxalic acid solution at various current densities ranging from 5 to 60 mA/cm^2 and at different temperatures (25-60°C). They found that the ratio of the change in potential difference to change in transition time is in accord with the equation.

$$\log (dE/dt) = 1.69 + 0.783 \log I \qquad \ldots\ (2)$$

TABLE 1

PARAMETERS OF THE RELATIONSHIP IN EQUATION 2.

Electrolyte	Slope	Intercept
0.1 M KOH + 0.1 M NaF	1.1	2.58
0.1 M ammonium citrate	1.0	2.48
0.05 M sodium oxalate	1.1	2.46

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