Effect of Temperature on the Kinetics of Anodic Oxidation of Titanium in 40% Sulphuric Acid.

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THE kinetics of the anodic oxidation of titanium have been studied in 40% sulphuric acid at a constant current density of 8 mA/cm² and at various temperatures ranging from 0°C–70°C. From the plots of formation voltage vs time it is found that the unitary field strength (F) and breakdown voltage are decreased linearly with increase in temperature. Applying the Cabrera-Mott type theory parameters 'a' (Half barrier width) and 'W' (Height of the energy barrier) deduced are found to be 1.02 Å and 0.93 eV respectively.

The kinetics of formation of anodic films on titanium in various electrolytes have been reviewed by Young[1] and Dyer and Leach[2], Johansen, et al[3]. and Laser et al[4] who made valuable contributions. Dyer and Leach[2] discussed the phenomenon of breakdown and efficiency of anodic oxide growth on titanium. Others[5,6] studied the anodic oxidation of titanium in concentrated H_2SO_4 using galvanostatic and potentiostatic techniques and the effect of temperature on the kinetics of anodic oxidation of zirconium in 40% H_2SO_4[7] and further the effect of halide ions on the kinetics of formation of anodic films on titanium in 0.1 M Propionic acid and incorporation of sulphate ions[8,9] has been reported.

In the present work an attempt is made to study the effect of temperature on the unitary field strength (F) and breakdown voltage.

EXPERIMENTAL

Chemically polished titanium samples were used and the procedure followed was described earlier[8,9]. Closed cells of 200 ml capacity were used. The platinum cathode used had 20 cm² superficial area. Specimens were suspended vertically from the heavily anodized tag, the minimum amount of which was immersed in the electrolyte. The electrolyte used was 40% H_2SO_4 and all the experiments were carried out at a constant current density of 8 mA/Cm².

A stabilised power supply built by GARGYA RESEARCH INSTRUMENTS, NEW DELHI was used for constant current.

RESULTS AND DISCUSSION

Anodization was carried out in 40% H_2SO_4 at various temperatures ranging from 0°-70°C. The plots of formation voltage vs time were found to be linear even upto the breakdown voltage. When the breakdown voltage was plotted against the temperature it too gave a linear relationship.

The value $\frac{1}{i}\frac{dV}{dt}$ was called the unitary rate[3], where i is the ionic current density and measuras the field of formation. This unitary field (F) was calculated for each temperature from the plots of formation voltage vs time. It is assumed that there is 100% current efficiency[1] during the anodization.

The unitary field of formation and breakdown voltage were found to decrease with the increase in temperature. Details are shown in Table-I.

TABLE I

Anodic films formed in 40% H_2SO_4 at various temperatures.

Temperature K	Unitary field V/cm × 10⁴	Breakdown Voltage. V
273	6.295	60
288	5.362	55
301	4.256	49
313	3.756	42
325	2.804	37
343	2.378	30

Guntherschultze and coworkers[10] were the first, to emperically establish under steady state and high field conditions that the ionic current density (i) depends to a first approximation on the field (F) in an exponential way, viz.,

$$i = A \exp [B F] \quad \ldots \quad (1)$$

Where A and B are temperature dependent constants for a particular metal.

Applying the Cabrera-Mott[11] type theory, assuming the rate determining step is at the oxide/electrolyte interface the equation is

$$i = n\nu q \exp [-(W-qaF)/kT] \quad \ldots \quad (2)$$

Where n, the number of cations per cm^2 of metal surface able to undergo anodic transfer into the film = 4.597×10^{15}; ν, the vibrational frequency of a moving ion = 10^{13}/Sec; k, the Boltzman constant = 8.617 eV; W, the height of the energy barrier at the metal/oxide interface; a, the half barrier width and q = 4e. The value of q was taken as 4e by considering the growth of the oxide on titanium occurs at the oxide/electrolyte interface by a mechanism of cation migration through a stationary oxygen sub-lattice[12].

Taking logarithms on both sides of the equation (2) and rearranging it we get

$$T = (W-qaF) \Big/ 2.303k \log \left(\frac{n\nu q}{i}\right) \quad \ldots \quad (3)$$

Substituting the values of n, ν, q, k and i the above equation becomes

$$T = -1600aF + 400W \quad \ldots \quad (4)$$

Using this equation, unitary field (F) is plotted against Temperature which gave a linear relationship. From the slope the value of 'a' is evaluated and is found to be 1.02Å. 'W' is estimated by substituting the value of 'a' and unitary field at a given Temperature in the equation (4) and is found to be 0.93 eV.

The values of 'a' and 'W' are comparable to that of values obtanied with zirconium[7,13].

It was reported[14] from the I. R. reflection spectrometric analysis that the amount of SO_4^{2-} penetration in the anodized film formed on tantalum in H_2SO_4 decreased linearly with temperature.

In view of this the decrease in unitary field and breakdown voltage with the increase in temperature observed in the present work may be attributed to decrease of incorporation of sulphate ions into the films with the increase in temperature

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