ELLIPSOMETRIC STUDY OF ANODIC OXIDE FILM FORMATION ON TITANIUM IN 5 N KOH

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Passivating anodic oxide films on titanium have been studied by many workers in weakly alkaline solutions [1-8]. It has been shown in a number of studies by electron diffraction that these films consist of titanium dioxide having the structure of anatase [1, 9, 10] or rutile [10]. Formation of anodic oxide films on titanium has not been studied as widely in concentrated alkali solutions as in weakly alkaline or acidic solutions, since their behavior is complicated by lower stability of titanium dioxide in these solutions. In the present work we studied the formation of anodic oxide films on titanium in 5 N KOH at 20°C by a combination of electrochemical and ellipsometric techniques.

The measurements were made with an RR-2000 Rudolph Research automatic ellipsometer.* The operating principle of this ellipsometer has been described in [11]. The quantities directly obtained in the measurements are the azimuth α, the ellipticity ε, and the relative intensity change, I_r, of the reflected light. The anodic current was recorded simultaneously. The relations

$$\Delta = 90° - 2\alpha; \quad \psi = 45° - \varepsilon$$

were used to recalculate quantities α and ε to the customary parameters of the polarized light, Δ (the phase shift) and ψ (the amplitude ratio of the electric vector components parallel (E_p) and perpendicular (E_s) to the plane of incidence of the light).

The measurements were made at a wavelength of 640 nm. The angle of incidence of light upon the sample was 68.5°. The measuring procedure and the design of the ellipsometric and electrochemical cell were reported in [12, 13]. The electrode was made from filament-grown titanium. Prior to the experiments it was carefully polished to obtain an optically reflecting surface. The potentials were measured relative to a mercury–mercuric oxide reference electrode in 5 N KOH, and recalculated to the potentials relative to the normal hydrogen electrode. Formation of the initial anodic film was conducted at E = 0.8 V at the air-oxidized titanium surface, and continued until a constant value of current was attained. Then the potential was switched to E = 1.3 V, and oxide formation at this potential was continued at the anodically oxidized electrode surface. The optical constants and film thickness were calculated in accordance with the fundamental ellipsometric equation [14],

$$e^{i\Delta}\tan\psi = |E_p/E_s|$$

using an ES-1022 computer and program EL5UR† set up while allowing for the reflection coefficients.

The complex refractive index, $\hat{N}_T = n_T - k_T i$ of the bare titanium surface was 2.32-2.37i as calculated from the experimental data. The data for the refractive index, n_T, and absorption coefficient, k_T, of titanium are somewhat different from literature data, which exhibit large scatter. However, the above values of n_T and k_T are within the limits of variation of the optical constants determined by various workers [16-20]. The calculated value of the complex refractive index of the metal was used to determine the characteristics of the oxide layer. The experimental data obtained are rather nicely described by the two-layer film model. The optical constants of the two layers exhibited practically no change over the first 90 min starting from the time

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†Program EL5UR is a modification of program EL3U [15].

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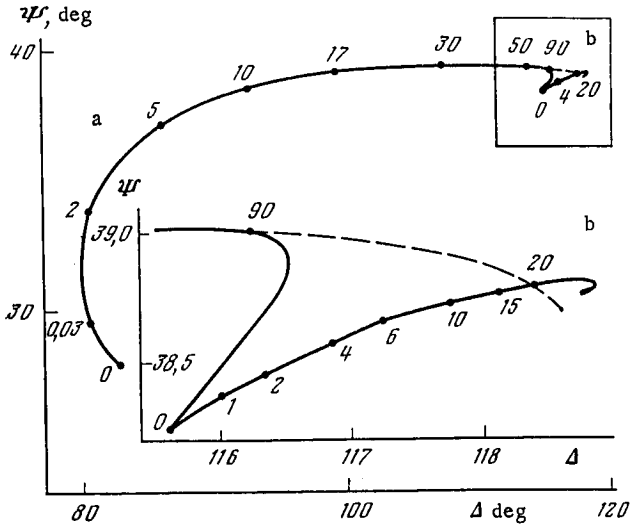

Fig. 1. Plot of Δ against ψ for potentiostatic growth of the oxide at E = 0.8 V (a) and E = 1.3 V (b). Numbers show the time of oxide formation in minutes.

when the anodic potential of E = 0.8 V was applied. The plot of Δ against ψ is smooth in this segment of time (Fig. 1, curve a). Further polarization leads to a change in the smooth Δ vs. ψ plot, which can be attributed to a change in the optical constants of the surface being oxidized. The complex refractive indices of the inner and outer layer of the film were, $\dot{N}_{f_1} = 1.97 - 0.15i$, $\dot{N}_{f_2} = 1.49 - 0.002i$, respectively. One can suggest from the refractive indices of these layers that the oxide layer adjacent to the metal is more compact. The two layers of the film exhibit monotonically increasing thickness which approaches limiting values as a function of time (Fig. 2). The time variation of the anodic current at E = 0.8 V follows a parabolic law, and is characterized by a straight line with three slopes when plotted as i against $t^{-1/2}$ (Fig. 3, curve a). Thickness growth of the two oxide-film layers also follows a parabolic law over certain time intervals (Fig. 4), which is an indication for diffusional limitations in oxide formation. Deviations of oxide growth from the parabolic law during the first moments after application of the potential of E = 0.8 V are explained by transient diffusion conditions. Formation of the inner oxide layer follows the parabolic law somewhat longer than that of the outer oxide, which grows according to this law for approximately 20 min following application of the potential. Deviations of the growth law of the outer layer from the parabolic law are reflected in the curve for the decay of anodic current as a function of time and are characterized by a change in the slope of the i vs. $t^{-1/2}$ straight-line plot (Fig. 3, curve a). Secondary changes in the slope of the i vs. $t^{-1/2}$ straight-line plot can be attributed to changes in the growth law of the inner layer, which also begins to approach its final value starting at a particular moment of time.

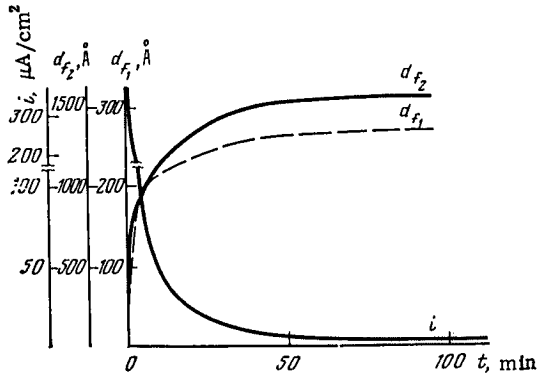

Fig. 2. Anodic current density i, thickness d_{f_1} of the inner layer, and thickness d_{f_2} of the outer layer of the film as functions of time during anodic polarization of titanium at E = 0.8 V.

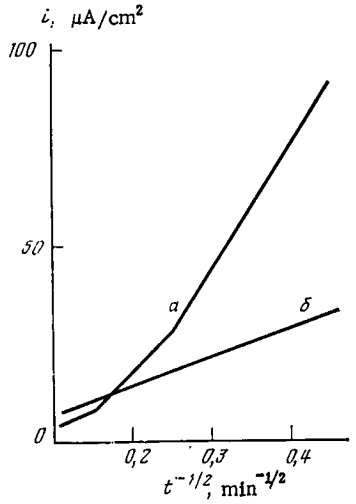

Fig. 3. The anodic current density, i, as a function of $t^{-1/2}$ for E = 0.8 V (a) and E = 1.3 V (b).

The plot of Δ against ψ corresponding to oxide formation at E = 1.3 V is shown in Fig. 1, curve b. On the assumption that the anodic oxide forming at this potential also contains an outer, less compact layer which upon application of the potential varies according to a parabolic law, we calculated the characteristics of all oxide formed. The calculations have shown that even at E = 1.3 V the anodic film includes a more compact inner layer in addition to the outer layer suggested here. A discontinuous increase of potential produces an insignificant initial change in optical constants and growth of the inner layer. Further growth of the inner film layer is monotonic, and after 10 to 15 min the film reaches its limiting size. The total changes in thickness of the inner layer at E = 1.3 V are small, on the order of 20 Å. The optical constants of the inner layer remain practically unchanged during its monotonic growth, and remain at the level of the inner-layer constants of the film produced at E = 0.8 V. The anodic current decreases as a function of time according to a parabolic law, and is characterized by a linear dependence of i on $t^{-1/2}$ (Fig. 3, curve b).

It follows from the above experimental data for anodic titanium oxidation in 5 N KOH that regardless of the initial state of the surface, the anodic oxide film on titanium consists of two layers: an outer, less compact and thick layer, and an inner, thin and more compact layer. The nature of the two oxide layers does not depend on prior treatment of the titanium surface. Considering the x-ray studies of the anodic oxide films on titanium in alkaline solutions of high concentration [10] and the above values for the refractive indices of the oxide-film layers, one can suggest that the inner layer consists of titanium dioxide with a more highly defective structure than bulk oxide. The outer layer seems to be a hydrated titanium dioxide. Regardless of pretreatment of the titanium surface, the same formation behavior of the anodic oxide film is seen: The oxide upon application of the potential first grows to a certain thickness, then one sees certain changes in its optical properties.

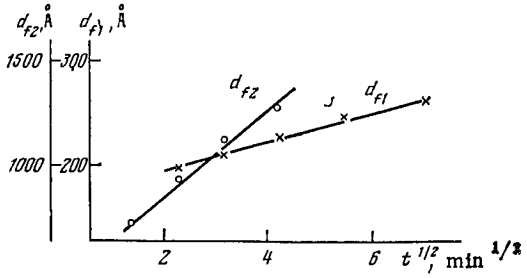

Fig. 4. Thickness variation of the inner (1) and outer (2) film with $t^{1/2}$ at an oxide formation potential of E = 0.8 V.

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