ELLIPSOMETRIC STUDY OF ANODIC FERROUS OXIDE FILMS ON IRON IN ALKALINE SOLUTIONS

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Passive and prepassive anodic oxide films on Fe in neutral and weakly alkaline solutions have been studied by many workers. It was shown in a number of papers [1-3] that the anodic oxide films have a complicated structure. They consist of two layers with different optical constants: a compact barrier film adjacent to the metal, and an outer, strongly hydrated film. It was shown in [4] that thick hydrated outer layers (200-400 Å, with a refractive index of $n = 1.5$ and an absorption coefficient k close to zero) which contain solution ions can be obtained when adding Fe^{2+} ions to the solution. On the other hand, when the concentration of these ions in the solution is lower or zero, the hydrated layer is thinner or completely lacking, and anodic oxidation mainly produces the barrier film [2]. In the present work, anodic films were studied which are formed on iron in 1 and 5N KOH under potentiostatic conditions at potentials where the $Fe(OH)_2$ film exists on the electrode.

Plates of carbonyl iron (99.99%) measuring 1.5×2.0 cm, with a thickness of 1 mm, were used as the electrodes. They were ground optically flat, then polished with diamond dust. The cell was provided with three plane-parallel windows for measurements at different angles of incidence of the light and allowed the electrochemical measurements to be made simultaneously with the ellipsometric ones.

The spectral ellipsometer used, which was designed and built in the L. Ya. Karpov Physicochemical Scientific-Research Institute, employs the operating scheme: polarizer (P)–compensator (K)–sample–analyzer (A), with fixed compensator. Parameters Δ and ψ of the elliptically polarized light were determined from the azimuths of P and A in the position of extinction. The measurements were conducted in a light beam with the wavelength 605 nm. The ellipsometric data were analyzed mathematically with the programs developed by É. V. Kasatkin for the ES-1022 computer [5, 6]. All measurements were made in purified nitrogen atmosphere at a temperature of 20 ± 1°C. The potentials were measured relative to a silver–silver chloride reference electrode in the same KOH solution.

Ellipsometric measurements were made in air at three different angles of incidence of the light (63, 68, and 73°) in order to determine the optical parameters of the electrode surface without oxides. The following results were obtained after corresponding calculations: $N = 3.3-3.14i$ for the metal's complex refractive index, $N = 4.2-0.2i$ for that of the air oxide film, and 57 Å for the thickness of this film.

After its immersion into the solution the electrode was reduced for an hour with a cathodic current, i_c, of 10^{-2} A/cm^2. The ellipsometric parameters Δ and ψ were measured at $i_c < 10^{-3}$ A/cm^2 over the range from −1.18 to −1.1 V. Under these conditions the values of Δ and ψ did not vary with potential, which is evidence for some stable state of the surface.

We saw after measuring the ellipsometric parameters Δ and ψ at three angles of incidence of the light and $E = -1.18$ V and performing the calculation that an unreduced oxide film with $N = 4.25-0.76\,i$ which is about 50 Å thick remains on the electrode after cathodic polarization.

Plots of ellipsometric parameters Δ and ψ obtained in 1N KOH when performing consecutive anodic oxidation of the electrode over a period of 30 min at $E = -0.98$ V, with periodic cathodic reduction for 1 h at $i_c = 10^{-2}$ A/cm^2, are presented in Fig. 1. Points 1, 1', 1", and 1"' correspond to the state of the electrode surface at $E = -1.18$ V after 1 h of reduction. For thin films, the length of the linear sections in the ψ vs. Δ plots is proportional to thickness of the resulting film. One can conclude from Fig. 1, therefore, that only a small part of the oxide produced before is reduced during cathodic polarization, and after each cycle of anodic oxidation and reduction, a thicker film of irreducible oxide remains on the electrode.

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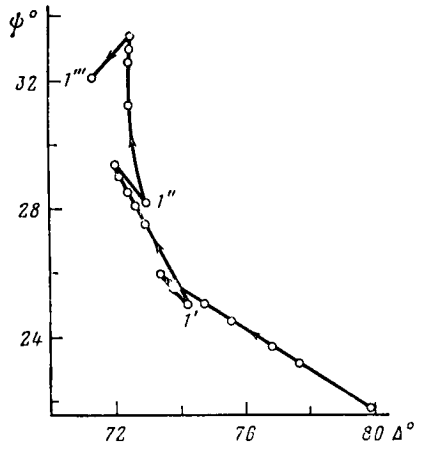

Fig. 1

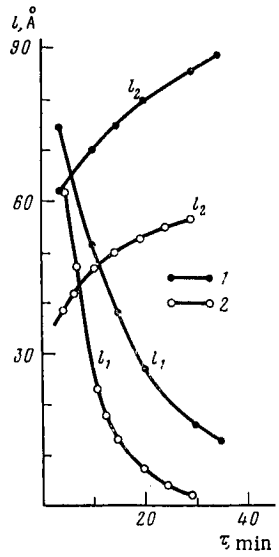

Fig. 2

Fig. 1. Plots of ellipsometric parameters Δ and ψ obtained in 1N KOH during periodic anodic oxidation at E = −0.98 V and subsequent cathodic reduction.

Fig. 2. Time variation of the thicknesses of the hydrated (l_1) and barrier (l_2) film during anodic oxidation: 1) in 5N KOH at E = −0.96 V; 2) in 1N KOH at E = −0.98 V.

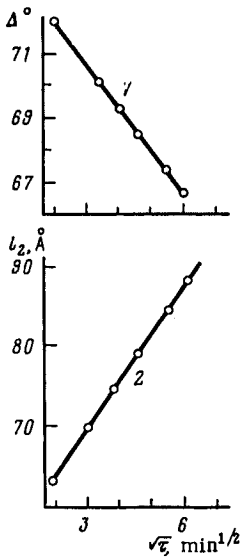

Fig. 3

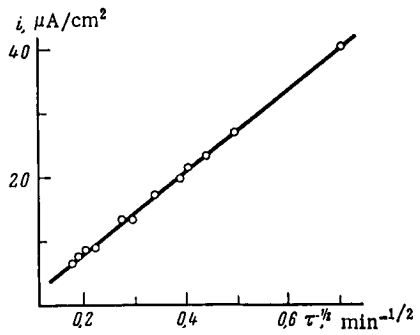

Fig. 4

Fig. 3. Plots of Δ against $\sqrt{\tau}$ and of barrier film thickness l_2 against $\sqrt{\tau}$ for E = −0.96 V in 5 N KOH.

Fig. 4. Anodic current i as a function of $\tau^{-1/2}$ at E = −0.96 V in 5N KOH.

The formation of an oxide of more complicated structure could be inferred from the result of this experiment, as well as from the observation that the parameters of the elliptically polarized light corresponding to the bare metal surface (Δ = 105.20°, ψ = 23.01°) do not fit the straight-line part of the Δ vs. ψ plot (this should be the case with homogeneous films).

A calculation was performed with the two-layer film model, which had given good agreement with the experimental data. The optical parameters for the outer film in contact with the solution were $N_1 = 1.34-0.13\,i$ in 1N KOH and $N_1 = 1.27-0.08\,i$ in 5N KOH; those of the barrier film in contact with the metal were $N_2 = 4.22-0.53\,i$ in 1N KOH and $N_2 = 3.94-0.60\,i$ in 5N KOH. The variation of calculated film thickness with oxidation time is reported in the form of curves in Fig. 2. One can see there that the thickness of the barrier film (l_2) increases; that of the outer film (l_1) decreases with time. It is quite possible that the difference between the N-values for films produced in 1 and 5N KOH is an indication for the effect of solution ions on composition and structure of the surface compounds.

The above ellipsometric and electrochemical results can be used to suggest the following growth mechanism for the anodic films on iron. The more compact anodic film in contact with the metal is produced by deposition of a layer of $Fe(OH)_2$ on the electrode. Its growth rate is limited by the speed with which the Fe^{2+} ions produced during anodic polarization move toward the boundary with the outer film under the effect of potential and concentration gradients [7]. This leads to the parabolic growth law observed experimentally. Figure 3 shows a plot of ellipsometric parameter Δ, which varies in proportion to film thickness, against the square root of time (curve 1), and also a plot of calculated barrier film thickness (l_2) against $\sqrt{\tau}$ (curve 2). The linear plot of film thickness against $\sqrt{\tau}$ illustrates the parabolic growth law. A further expression of this law is the linear relation between the anodic current and $\tau^{-1/2}$ (Fig. 4).

The formation of the outer, more open and probably strongly hydrated film is likely to occur as follows. The oxide existing on the electrode dissolves in KOH yielding $HFeO_2^-$. The same ions are produced during the anodic polarization of iron together with $Fe(OH)_2$. Supersaturation with respect to $HFeO_2^-$ ions is reached in the solution layer next to the electrode, and as a result of hydrolysis these ions are deposited onto the electrode as $Fe(OH)_2$. In this process they entrap solution ions and form the outer, hydrated film. Subsequently the outer film undergoes destruction by losing water and giving off OH^- ions to the diffusing Fe^{2+} ions, and thus is transformed into a more compact layer. The experiments of [2] and [4] mentioned above can serve as indirect evidence for secondary formation of the outer film from solution ions.

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