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INVESTIGATION OF DYNAMICS OF ANODIC OXIDE FILM GROWTH BY LUMINESCENCE METHOD

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Introduction

During the DC electrolysis of aqueous solutions of electrolytes a thin oxide film is formed at the anode[1]. At the same time, the emission of light of very low intensity takes place[2]. The intensity of the light emission depends, first of all, on the nature of the metal used as anode, but also on the kind and concentration of the electrolyte, as well as on the applied voltage, current density etc[3]. The luminescence is most pronounced in the case of valve metals (Al, Ta, etc.) used as anode. In our preliminary report at the 8th SPIG[4] we proposed that the light emission process is mainly related to the formation of the oxide film at the interface electrolyte-electrode. The present experiments completely confirm this conclusion. Moreover, we were able to give quantitative relation between oxide film thickness and luminescence intensity and to obtain, for the first time, the shape of optical emission spectra at different applied voltages.

Experimental

The electrolytic cell was a quarz vessel filled with a boric acid - borax solution (0.1 mol/dm^3 H_3BO_3 + 0.05 mol/dm^3 $Na_2B_4O_7 \cdot 10\,H_2O$). The electrodes were: a platinum wire (cathode) and an alluminium foil (anode), the purity of Al being better than 99,99 per cent.

Maintaining the current through the cell constant, we measured the temporal change of voltage and light intensity (at a chosen wavelength). From these two sets of data we obtained optical emission spectra at different time moments, i.e. at different voltages.

The power source for electrolysis was a laboratory-made device (80 milliamps, 400 volts DC), which can maintain the pre-set current within ±0.1%, automatically changing the voltage, if necessary.

The voltage was measured by an AVO electrometer (RN 170) connected with a standard resistance, the signal being recorded by an X-t plotter.

For the measurement of light fluxes we used an optical monochromator (Zeiss SPM-2), a photon couting system with an EMI 9558 photomultiplier (S-20 photocathode) and an ORTEC multiscaller (6240B) for data acquisition. A standard tungsten strip lamp (OSRAM Wi-17G) was used for determination of spectral sensitivity.

The optical arrangement was such that only the Al-foil was seen by the monochromator.

Voltage-time dependence

During the electrolysis under these conditions a non-porous oxide film is grown at the Al-anode surface[5]. The system alluminium-axide-electrolyte acts as an n-type seminconductor, which is in this case reversely polarized. The film thickness is growing with time, the resistivity as well as the voltage needed for the maintainance of constant current also increase.

Figure 1. gives the cell voltage as a function of time. This dependence is a linear function until 150-200 volts, but only for pure Al-samples as used in this experiment. (For other Al-samples with purities lower than 99,99%, the slope of these curves is rather different).

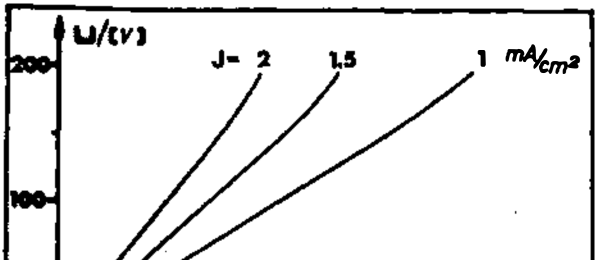

Fig. 1. The dependence of cell voltage on time; the current density is a parameter.

This can be understood under following conditions: (a) the growth of the oxide film, in these circumstances, has a constant time rate; (b) the mechanism of growth and the structure of oxide film do not change until they reach 150 (or 200) volts. (Each volt corresponds to approximately 1,4 nm of the oxide film thickness).

The voltage-time dependence can be represented by:

$$U = U_o + k_u t \quad (1)$$

It is found that the slope of the voltage-time curves (k_u) is a linear function of the current density $k_u = 0{,}45 \cdot j$. The U_o value corresponds to the allumininum-oxide which is present before the electrolysis is started.

Light-emission-time dependence

For each wavelength and current density chosen, the emission of light was measured as a function of time, i.e. as a function of voltage (see Fig. 1). In each measurement a new sample of Al-foil anode was used. The measurements were repeated many times, the standard deviation being within 5-10 per cent.

The emission of light at a given wavelength was nearly an exponential function of time (or voltage), until 150-200 volts (Fig. 2). This dependence can be represented by the equation:

$$I_s = I_o \left(e^{kt} - 1\right) \quad (2)$$

where both parameters I_o and k depend on wavelength and current density. The deviation from this a equation started earlier for shorter wavelengths.

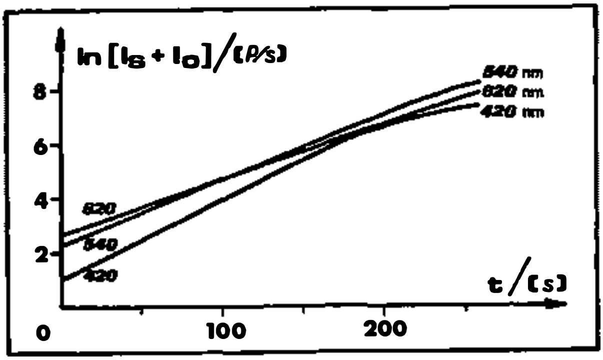

Fig. 2. Logarithm of light intensity as a function of time at different chosen wavelengths, $j=1{,}5$ mA/cm^2.

We have found that the initial light intensity (I_o), at a given wavelength has the following dependence on current density:

$$\ln I_o = C_2 - \frac{C_3}{j} \qquad (3)$$

where the constants C_2 and C_3 (having the dimensions of current density) are both positive. The dependence of I_o on wavelength, at a constant current density, is a rather complicated function of λ.

On the other hand, the parameter k has linear dependence of both j and λ, with a negative slope in the case of $k=f(\lambda)$, $j=\text{const}$.

The real physical meaning of all these relations has not been understood until now. But it is clear that the luminiscence method (based on Eq. 2) is more sensitive (in investigation of dynamics of anodic oxide film growth) than the method of simple voltage measurement (Eq. 1). Moreover, the luminescence method can give us new information concerning the processes taking place at the interface electrolyte-electrode, which are not well known.

Emitted spectra

Starting from the data illustrated by Figures 1 and 2 we were able to construct the emission spectra at different voltages (Fig.3).

It is seen that all spectra are continuous with some broad maxima. With rise in voltage, the blue part of spectra increases, and the red part diminishes, but the positions of maxima remain practically unchanged. No other experiments of this type have been reported until now, but in some similar investigations[6,7] the continual spectra with broad maxima are also shown. At this moment we are not able to give an explanation of the spectra obtained. but it seems that they are connected with band structure of the semiconductor at the interface electrolyte-electrode, the latter being obviously influenced by the purity and structure of the Al-anode as well as by the electrolyte used.

Acknowledgment

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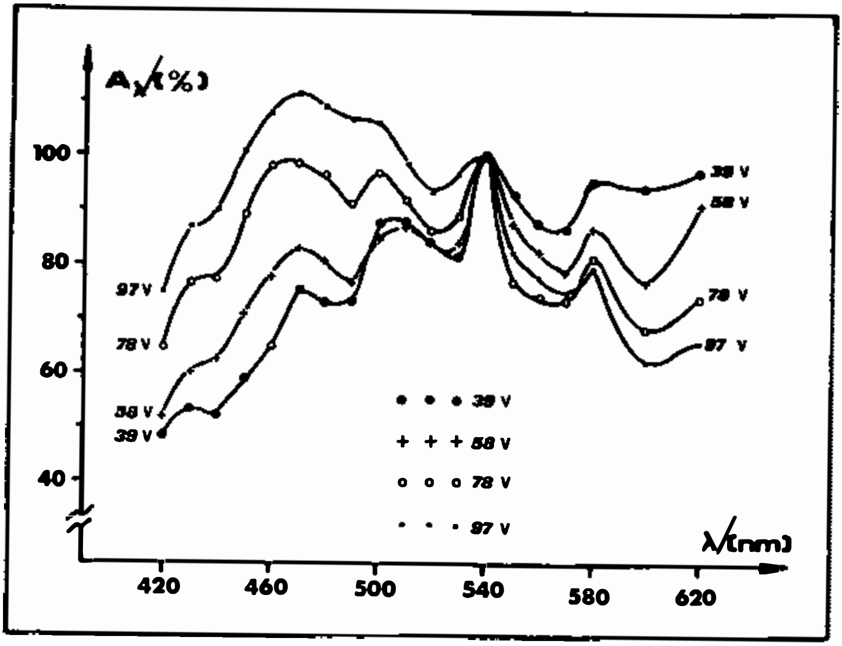

Fig. 3. Optical spectra emitted from Al-anode surface at different DC voltages. The spectra are corrected for spectral sensitivity and normalized at 540 nm.

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