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Effect of cold rolling on the anodic electroluminescence accompanying the electrolytic oxidation of cadmium *

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The anodic luminescence accompanying the electrolytic oxidation of cold-rolled cadmium has been investigated. It has been found that the parameters of the observed luminescence strongly depend on the degree of plastic deformation executed by cold-rolling.

1. Introduction

The phenomenon of the electroluminescence accompanying the electrolytic oxidation of some metals was the subject of very intensive studies, spurred by both the science and technology [1]–[3]. The technological importance of aluminium and the oxide layer formed on its surface caused that the electroluminescence in both the "wet" $Al-Al_2O_3$–electrolyte system and the "dry" $Al-Al_2O_3$–metallic (or semiconducting) counterelectrode system was studied much more exhaustively than the electroluminescence accompanying the electrolytic oxidation of other valve metals (Ta, W, Zr, Zn, Mg, Bi, Hg, In, Sb and Ga), [1]–[4]. There are also few papers in the literature devoted to the studies of the anodic electroluminescence accompanying the electrolytic oxidation of cadmium [5]–[8].

Despite of its great importance from both the purely scientific and technological points of view, the problem of the effect of physical state of the surface of valve metals on their electrolytical oxidation and the electroluminescence accompanying this process remains practically unexplored until now. As far as we know, there are only few papers related to the matter in question. SMITH [9] observed a decrease in the intensity of electroluminescence accompanying the electrolytic oxidation of aluminium caused by the electrochemical etching of its surface prior to the oxidation. In our laboratory, it has been shown that the preliminary thermal oxidation of cadmium markedly increases the intensity of its anodic electroluminescence [6], [7]. In our further paper [8], the preliminary results of the studies of the effect of cold-rolling of cadmium on the intensity of electroluminescence accompanying

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the electrolytic oxidation were reported. These observations indicate the possibility of application of this phenomenon for studies of the energetically excited surface layer of valve metals. The purpose of the present study is to present the results of more systematic studies of the effect of plastic deformation on the electroluminescence accompanying the early stage of the process of anodic oxidation of cadmium.

2. Experimental conditions

The experiments were performed on cadmium plates cut from the industrial cadmium sheets of the purity of 99.95 wt.%, containing trace admixtures of Zn, Pb, Fe and Tl. Before the deformation and electrolytic oxidation, the plates were submitted to 3 min chemical cleaning in solution of the following composition: CrO_3-22 wt.%, $H_2SO_4-2.5$ wt.%, $CH_3COOH-1.5$ wt.% and H_2O-74 wt.%. Next, the plates were rinsed first in running and next in distilled water. Finally, the plates were immersed in 10% water solution of KOH for 10 s, and again rinsed in the water.

The electrolytic oxidation of cadmium plates was carried out in water solution containing 0.1 M of KOH and 0.1 M of K_2CO_3 per litre. During the process of electrolytic oxidation the cadmium plates were used as anodes, a platinum plate being used as the cathode. The oxidation process was carried out at constant voltage of 35 V.

The intensity of light emitted from the cadmium anodes during the oxidation process was measured using an FEU-38 photomultiplier, the sensitivity of which covers the range of wavelengths from 300 to 800 nm. The time dependence of the photomultiplier current, proportional to the integral intensity of light emitted from cadmium anodes, was registered either by means of an oscilloscope or a BAK 5T pen recorder.

The plastic deformation of investigated cadmium plates was executed by rolling at room temperature. The deformation degree was estimated as the relative reduction of the thickness due to the cold-working procedure.

More detailed description and block diagram of the measuring system was given in [6].

3. Results and discussion

The time dependence of the intensity of electroluminescence accompanying the early stage of electrolytic oxidation of cadmium, observed on the oscilloscope screen, is represented in Fig. 1. As it may be seen, the cadmium plate starts to emit the light about 1 s after having switched the electrolytic cell on. At the constant voltage (35 V), the intensity of electroluminescence increases very rapidly up to some maximum value, and then decreases with decreasing rate and after few seconds becomes constant.

As it may be seen from Figure 2, both the maximum value of the electroluminescence intensity I_0 and the area under the curve depicting the time dependence of the

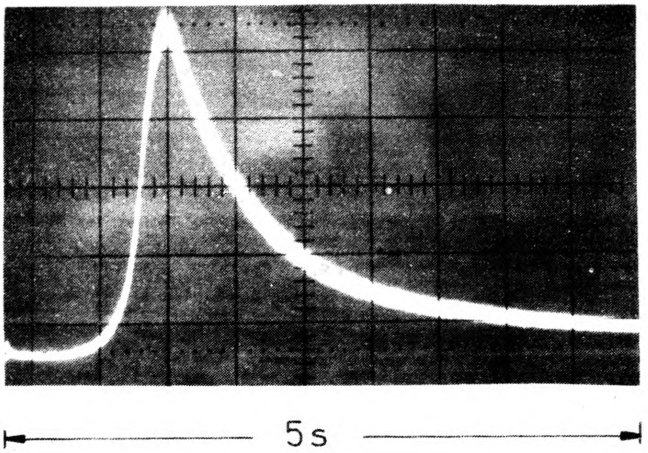


Fig. 1. Oscilloscope trace of the changes in the intensity of electroluminescence accompanying the early stage of anodic oxidation of undeformed cadmium plate at a constant voltage of 35 V

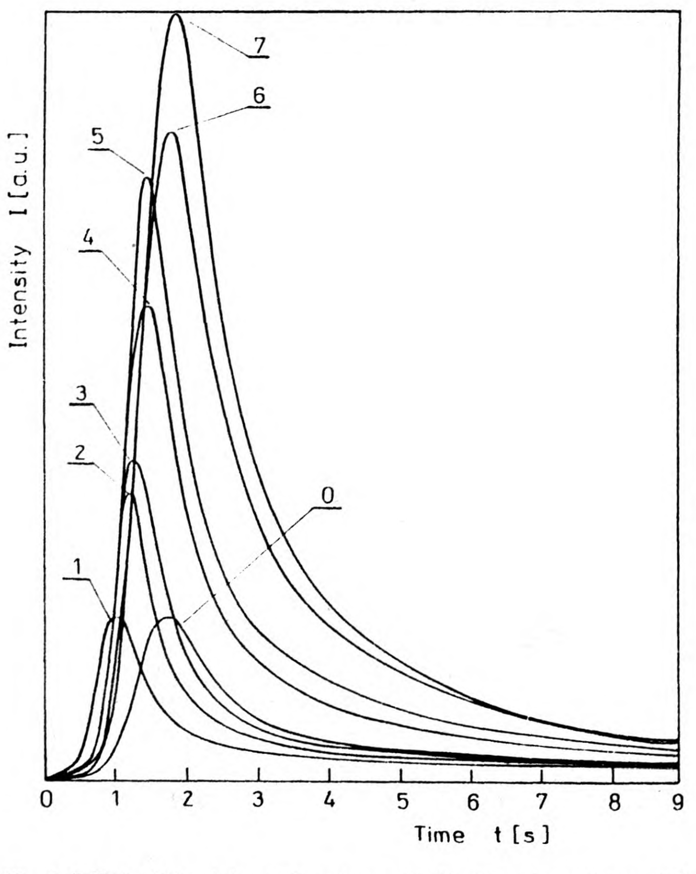


Fig. 2. Effect of the deformation degree on the time dependence of the intensity of electroluminescence accompanying the early stage of anodic oxidation of cadmium at a constant voltage of 35 V

intensity of electroluminescence (the so-called "sum of light") strongly depend on the degree of deformation of investigated samples. This behaviour may be ascribed to the changes in the electric field strength in the oxide layer formed on the surface of cadmium caused by the increased defectiveness of the cold-rolled mother material.

The dependence of the maximum intensity I_0 of the observed luminescence on the deformation degree D is represented in Fig. 3. As it follows from this figure, to a first approximation, the maximum intensity I_0 of anodic electroluminescence accompanying the early stage of anodic oxidation of cadmium is directly proportional to the deformation degree

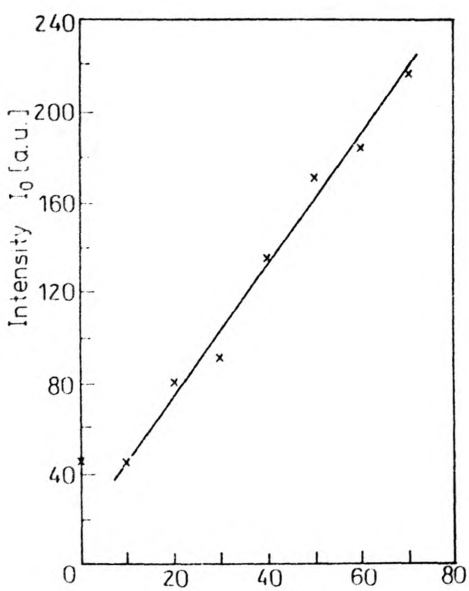
$$I_0 \sim D. \tag{1}$$

The effect of the deformation degree D on the sum of light

$$S(t) = \int_0^t I(t)dt \tag{2}$$

emitted in the early stage of anodic oxidation of cadmium is represented in Fig. 4. The linearity of semilogarithmic plot of this dependence suggests that the sum of light $S(t)$ emitted in the early stage of anodic electroluminescence is an exponential function of the deformation degree D

$$S(t) \sim e^D. \tag{3}$$



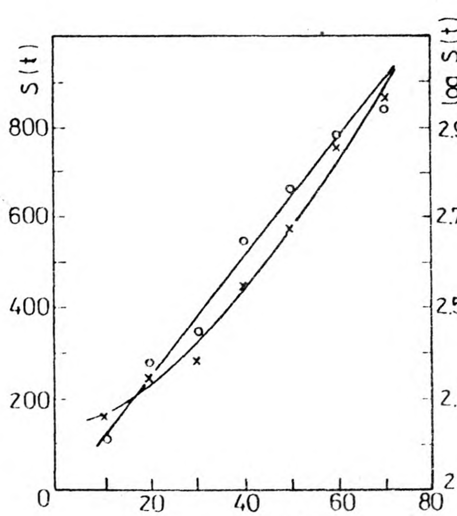


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Fig. 3. Dependence of the maximum intensity of electroluminescence of electrolytically oxidized cadmium plates on the degree of their deformation

Fig. 4. Linear and semilogarithmic plot of the dependence of the "light sum", $S = \int_0^t I(t)dt$, emitted in the anodic electroluminescence peak on the degree of deformation of cadmium plates

The results obtained suggest that the structure and electrochemical properties of the surface layer of cold-rolled cadmium are markedly different than those for undeformed metal, the difference being the larger the higher is the deformation degree.

The observed luminescence of anodically oxidized metal may be interpreted as the electroluminescence of the oxide layer growing on its surface. The intensity of this electroluminescence depends on the concentration of crystal lattice defects in luminescent material which, in turn, is genetically related to the defect structure of the mother substrate metal which changes with the changing degree of plastic deformation. The regularities established in the present study seem to confirm the possibility of application of the anodic electroluminescence to studies of the defect structure of the energetically excited layer of valve metals. Further studies are in progress.

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