THE INFLUENCE OF ELECTROLYTE ON GALVANOLUMINESCENCE OF BARRIER OXIDE FILM ON ALUMINIUM

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Abstract. The processes of formation and galvanoluminescence (*gl*) of anodic oxide film of ultra-high purity Al in ammonium tartarate as electrolyte have been investigated. Many important differences have been found in comparison with the case of inorganic electrolytes. First, under the same conditions *gl* intensity in ammonium tartarate is 2-5 times greater than in boric acid-borax solution. Second, *gl* intensity is approximately a linear function of the film thickness d, including the case of annealed samples to which in inorganic electrolytes corresponds an exponential growth of N_λ *vs* d. Third, *gl* spectrum corrected for interference effect has, in the range 400-750 nm, only one broad maximum instead of at least 5 maxima found in inorganic electrolyte. These differences should be attributed to the different nature of luminescence in the two cases investigated.

Introduction

During the DC anodization of valve metals (Al, Ta, etc.) a weak luminescence (galvanoluminescence, *gl*) at the interface metal-oxide-electrolyte takes place[1]. According to a recent classification[2] one should distinguish at least three types of DC galvanoluminescence: (i) *gl* of "pure" (activator free) metal in inorganic electrolytes (f.i. boric acid aqueous solution), which is produced by oxide breakdown at the surface defects ("flows")[3]; (ii) *gl* of "pure" (activator free) metal in some organic electrolytes (f.i. aliphatic acid aqueous solutions), which is produced bv excitation of luminescent centres (carboxylate ions incorporated in the oxide film) in collisions with electrons[4]; (iii) *gl* of doped (f.i. with Mn, Eu, Tl, Dy, etc.) valve metals, which is produced by excitation of these impurities in oxide film, both in organic and inorganic electrolytes[5].

In a paper reported at 6th Symposium[6] we investigated *gl* of the first type. Now, we report some new results on *gl* of the second type (pure Al in organic electrolyte) and compare the results obtained.

Experimental

The experimental method used has been described in our previous papers[6,7]. It enables us to perform spectroscopically and time resolved measurements of *gl* , even for very low spectral intensities.

In investigations we used as anode ultra-high purity Al foils (99,9995%)[8], previously annealed at 350°C for 6 hours, and then - in same of the experiments - electropolished by the method given in[9]. The cathode was a Pt wire, and the electrolyte was an aqueous solution of ammonium tartarate (0.1 mol/dm^3), or an aqueous solution of boric acid-borax (0.1 mol/dm^3 H_3BO_3+0.05 mol/dm^3 $Na_2B_4O_7\cdot 10H_2O$). All the measurements are performed with a current density $j = 5$ mA/cm^2 and at room temperature (20°C).

Results and discussion

Fig. 1 shows spectral intensity N_λ *vs* forming voltage U, for an inorganic (boric acid-borax, A) and an organic (ammonium tartarate, B) aqueous electrolyte. In both cases Al-anodes were previously annealed at 350°C for 6 hours, but not electropolished. It is seen that in inorganic electrolyte N_λ is about 2-5 times smaller than in ammonium tartarate solution. In the first case the N_λ *vs* U dependence is nearly an exponential one, but in the second case I_λ is a nearly linear function of U. In both cases the oxide film is of the "barrier type"[2] and the film thickness d is connected with the forming voltage U by the relation: $d(A^o)=13,5\ U(V)$.

For electropolished samples in tartarate solution one obtains for N_λ *vs.* U more complicated curres (Fig. 2), which some maxima and minima. This can be explained by interference between monochromatic light passing directly through the film and the corresponding light reflected from the polished Al-surface[10]. For

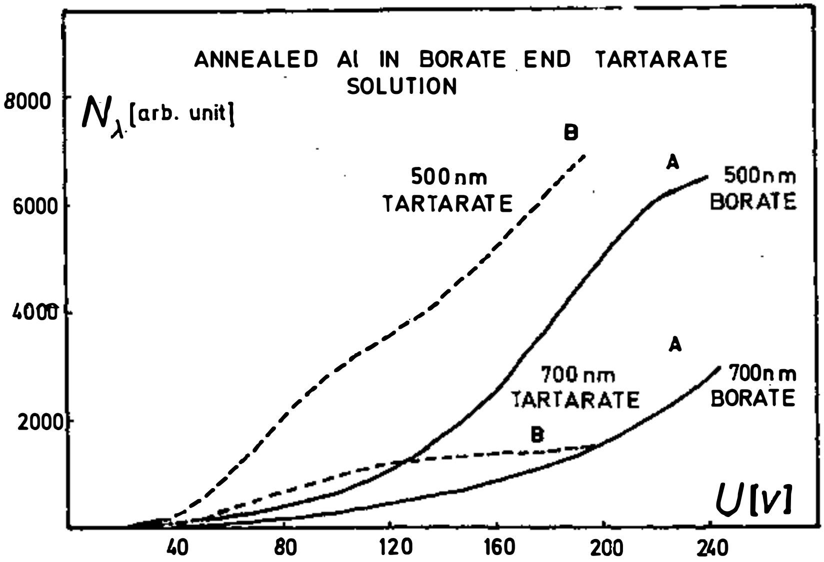

Fig. 1. Spectral intensity of *gl* N_λ *vs* forming voltage U for annealed pure Al in boric acid-borax solution (A) and in ammonium tartarate solution (B), N_λ is corrected for spectral sensitivity of the measuring system.

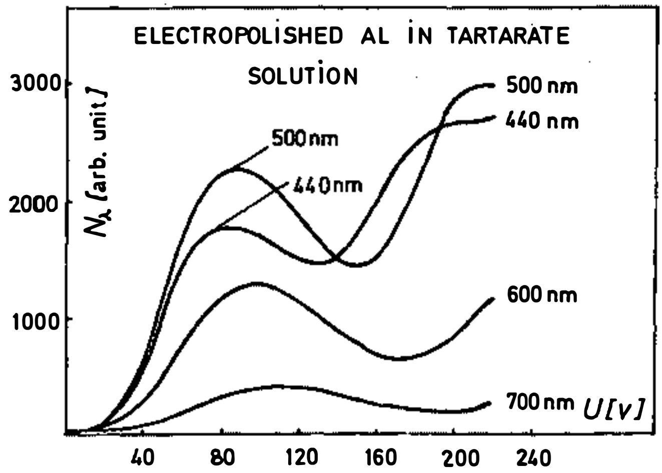

Fig. 2. N_λ *vs* U for annealed and electropolished pure Al in ammonium tartarate solution. The parameter is wave-lenght in nm. N_λ is corrected for spectral sensitivity of the measuring system.

electropolished samples in boric acid-borax solution *gl* intensity, if existing at all, is very low and can not be measured in our experiment.

A comparison of *gl* spectra in inorganic (A) and organic (B) electrolytes is given in Fig. 3. The parameter is forming voltage U or film thikness, d. In the case A, as refered in[6], some well pronounced maxima (at least five) are found. In the case B there is only one broad maximum (at about 480 nm) and the differences between the curve of this set are mostly produced by interference effect. This is demonstrated by dashed curve in the same figure, which shows the real emission spectrum in tartaric solution corrected for interference effect. The spectrum in ammonium tartarate electrolyte, which is published for the first time, is practically the same as the spectrum in oxalic acid in[2], which means that the nature of *gl* is the same for all aliphatic carboxylic acids or their salts.

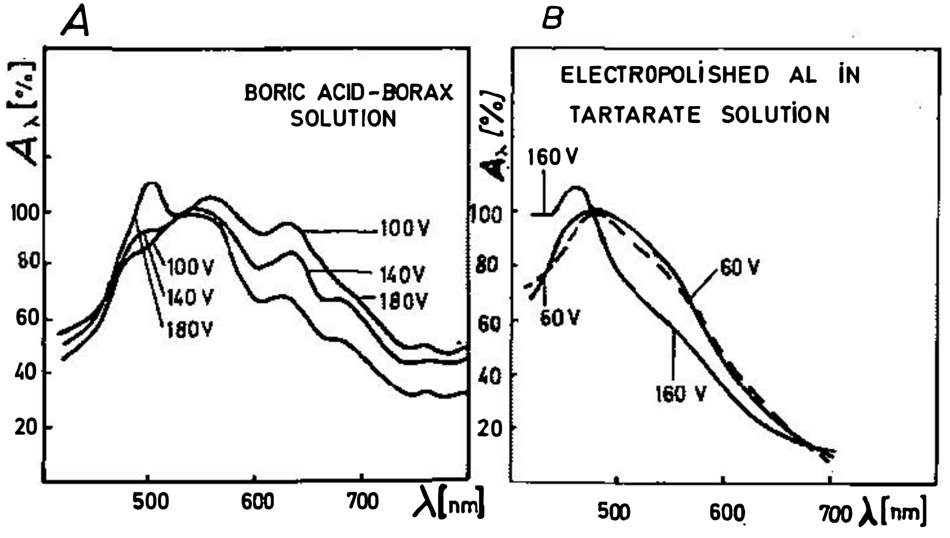

Fig. 3. Galvanoluminescence spectra. A - pure annealed non-electropolished Al, boric acid-borax electrolyte. B - pure annealed, electropolished Al, ammonium tartarate electrolyte. Dashed line corresponds to spectrum B corrected for interference effect. All spectra are corrected for spectral sensitivity of the measuring system.

It should be expected that interference of light has also some influence on the measured spectra in inorganic solutions (Fig. 3, A) but not very pronounced, because of low reflectivity of nonpolished annealed aluminium. This can be one of the possible explanations of the differences between spectra of different film thikness shown in Fig. 3, A.

Conclusions

The results obtained confirm the classification of DC *gl* on pure Al given by Tajima[2]. The important differences between inorganic and organic electrolytes can be understood if one accepts different mechanisms of light production in these two cases: breakdown of oxide film at surface deffects in the first case, and impact oxcitation by electrons of the luminescent centres (carboxylate ions) incorporated in the oxide film in the second case. For complete understanding of the processes involved it is necessary to take into account the phenomenon of light interferene, as it is shown in this work.

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