The Increase in Thermal Stability of Anodic Alumina Films on Aluminum

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Thermal stability of the "aluminum – anodic alumina film (AAF)" system for the oxide films formed in the surfactant-containing electrolytes is discussed.

Anodized aluminum is widely used in microelectronics to produce switching plates, multiterminal VLSI packages, multichip modules, various sensors, etc. [1]. One of the factors limiting the wide use of aluminum substrates coated with the Al_2O_3 films is low thermal stability of the "Al – AAF" system due to differences in the linear thermal expansion coefficients of aluminum ($\alpha_{Al} = 23 \cdot 10^{-6}$ K^{-1}) and alumina ($\alpha_{ox} = 5 \cdot 10^{-6}$ K^{-1}).

A number of technical solutions allowing improving thermal stability of the "Al – AAF" system such as a thermal annealing to 477 K, anodizing in different electrolytes followed by pore filling with pyrolytic Al_2O_3, etc. is known. However, these methods lead to an increase in the process duration and are not always effective.

A high voltage anodizing of aluminum porous was found on the basis of the theoretical analysis and electron-microscopic studies to be one of the possible ways for reducing the level of thermal stresses in the aluminum – anodic alumina system. The two-stage anodization was used. First, a low-voltage anodization of aluminum substrate was carried out, then the anodizing electrolyte was changed and the aluminum substrate was anodized at high anodizing voltages. The choice of the electrolyte for the second anodizing stage is very important at that.

The 1.5 mm thick aluminum substrates made of commercially available alloy AMg-2 were used. The anodization was performed in three types of electrolytes, namely: 2% oxalic acid, 1% citric acid, and 4% phosphoric acid with the addition of triethanolamine. The study of the thermal stability of the "Al – AAF" system was made by measuring the bending deflection under heating.

The stress calculation was carried out according to the formula [2]:

$$s = \frac{(a_{Al} - a_{ox}) \cdot \Delta T}{h_0 (1 - n) \left(\frac{1}{E_0 h_0} + \frac{1}{E_2 h_2} \right)}$$

where a_{ox} and a_{Al} are the linear thermal expansion coefficients of aluminum and alumina; n is the Poisson's ratio of the substrate; DT is the increment of temperature; E_0 is the Young's modulus of the alumina; E_2 is the Young's modulus of aluminum; h_0 and h_2 are the thicknesses of the film and substrate correspondingly.

As was revealed, the sequential anodizing of aluminum first in the oxalic acid electrolyte and further in the electrolyte of phosphoric acid with the addition of triethanolamine at 200 V allows the stress at the "Al – AAF" interface resulting from the high temperature treatments to be reduced significantly. This can be explained by the presence of a plastic deformation zone at the Al – AAF interface, where the stress relaxation takes place.

[1] V. Sokol, V. Shulgov, Electrochemical Aluminium Oxide Technology for Production of Electronics, *Proceedings of International Conference on Oxide materials for electronic engineering – fabrication, properties and application*, OMEE-2012, Lviv, Ukraine, 2012, pp. 55-56.

[2] D.H. Bradhurst, J.S.L. Leach, The mechanical properties of thin anodic films on aluminum, *J. Electrochem. Soc.* **113** (1966) 1245-1249.