

BREAKDOWN PHENOMENA DURING PORE-FILLING OF ANODIC ALUMINA FILMS

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Received March 17, 1983

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Summary

Breakdown phenomena during pore-filling of anodic alumina films were studied. Two types of porous films were produced galvanostatically in aqueous solutions of oxalic acid and sulfuric acid, respectively. Pore-filling was carried out using aqueous borate electrolyte, aqueous solution of ammonium bicarbonate and dimethyl formamide solution of ammonium salicylate. The breakdown characteristics of the porous and non porous films formed using different electrolytes were compared.

Two types of anodic oxide films on aluminium are formed depending on the electrolyte properties:

1) Barrier (non-porous) anodic films are obtained in non-dissolving electrolytes.

2) Porous oxide films are formed in dissolving electrolytes.

Both of them have a significant industrial importance. The barrier anodic films are used in the electrolytic capacitor production. The porous films find wide applications for corrosion and abrasion protection, or as electroisolating and decorative coatings. It is well known that porous films exhibit a double layer structure as shown on Fig. 1. Fast by the metal there is a thin barrier sublayer which determines the corrosion and the electrical resistance of the film as a whole. Above this sublayer the thicker section of the film grows with the uniformly distributed pores oriented perpendicularly to the metal surface. This film section defines mainly its abrasion resistance and coloring ability. From these circumstances is obvious that a better corrosion resistance could be achieved by increasing the barrier sublayer thickness. How it could be done in practice? As was shown by Wilson [1], and Tominaga and al. [2] the pores of the film could be filled through a second anodization in a non-dissolving electrolyte. This process of pore-filling or "re-anodization" terminates at a

* Lecture delivered at the Technical University Budapest March 8, 1983.

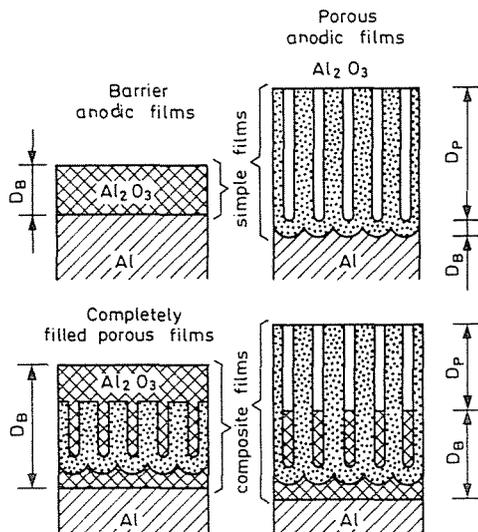


Fig. 1. Schematic picture of different types of anodic films on aluminium: barrier type alumina film obtained in a non-dissolving electrolyte, and porous alumina films formed in a dissolving electrolyte. The "composite" films during the "re-anodization" of porous films can be obtained, too

"breakdown" voltage (U_B) which limits the maximum thickness of the barrier part of the film. This fact predetermines a significant scientific and practical importance of breakdown phenomena during the pore-filling. Their investigation was the purpose of the present study.

Experimental

The experiments were carried out with aluminium electrodes of 99.999% purity and working area of 5 cm^2 . Before anodization they were degreased, electropolished and brightened by the known methods. Porous films were formed galvanostatically in aqueous solutions either of $(\text{COOH})_2$ at 20°C or of H_2SO_4 at -10°C . By this way, two types of porous films with different concentration and pore-dimension were obtained. Films with various pore depth were formed by varying the duration of the anodizing. The thickness was controlled by a non-destructive method with Dermatron D-9E, UPA Techn., USA. Three non-dissolving electrolytes were used at 20°C for pore-filling process:

- 1) Aqueous borate electrolyte (ABE) with $\text{pH} = 6, 4$.
- 2) Ammonium hydrocarbonate aqueous solution — NH_4HCO_3 .
- 3) Dimethylformamide solution of ammonium salicylate — AS/DMF.

Before use the electrolytes had been "adapted" by known methods.

Results

Two kinds of behaviour of U_B could be observed during the pore filling process. In the first case, where the film thickness is small and the pores are comparatively shallow, a change in the kinetic curve slope appears, shown in Fig. 2, curve 1. The bend corresponds to the moment of completely filling of the total porous film. After this moment the rate of increase of the formation voltage (U_f) with time (t) falls down and becomes equal to that of the direct formation of barrier film in the same electrolyte — ABE. From Fig. 2 it is seen, that the breakdown voltage is identical in both cases of wholly filled porous film and of directly formed barrier film. This value is characteristic only for the non-dissolving electrolyte used.

When the porous film is sufficiently thick for breakdown to occur in the pores, the breakdown voltage is higher compared to that of aqueous borate electrolyte used. This can be seen from Fig. 2, curve 2.

Films formed in H_2SO_4 and in $(COOH)_2$ were used for investigation of the influence of porous film thickness on U_B . The pore-filling was carried out at equal temperature and current density in the aqueous borate electrolyte. From Fig. 3 and Fig. 4 it is clearly seen that U_B increases significantly with the increase of the porous film thickness. A comparison revealed that the values of U_B are almost equal in both kinds of porous films.

Most typical breakdowns characteristic for the system METAL/OXIDE/ELECTROLYTE are well known dependences of the breakdown voltage on

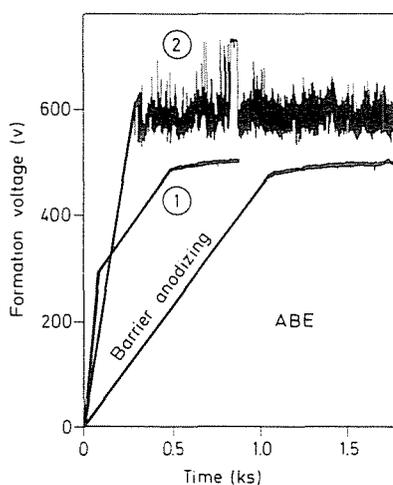


Fig. 2. Dependence of the formation voltage on the pore-filling of anodic alumina films in ABE (pH = 6); curve 1—films with shallow pores; curve 2—films with deep pores and the curve of direct barrier anodization in the same electrolyte

the logarithm of electrolyte resistivity ($\log \rho_{EL}$). For determining of $U_B(\rho_{EL})$ dependence, porous films with the same thickness formed in $(COOH)_2$ at other equal conditions were filled in aqueous solution of NH_4HCO_3 and in a non-aqueous solution — AS/DMF. These two electrolytes were chosen as typical representatives of non-dissolving electrolytes with the capability of resistivity variation in a wide range. The results are given in Fig. 5 and Fig. 6. It is seen from Fig. 5 that breakdown voltage may not only increase but also decrease concerning U_B characteristic for the barrier anodization. In the case of a non-aqueous electrolyte, however, only increased U_B values were obtained, compared to those for direct barrier anodization.

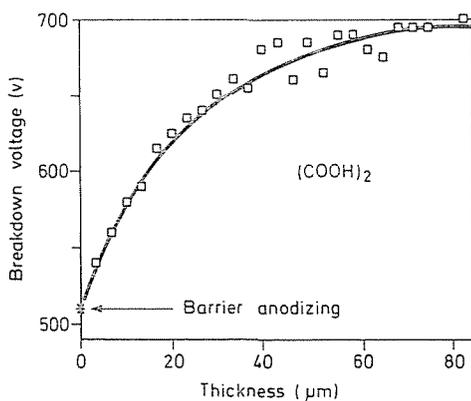


Fig. 3. The breakdown voltage during the pore-filling in ABE with 10^{-3} A/cm² current density as a function of the thickness of porous films, produced in $(COOH)_2$ with $2 \cdot 10^{-2}$ A/cm² current density at 20 °C

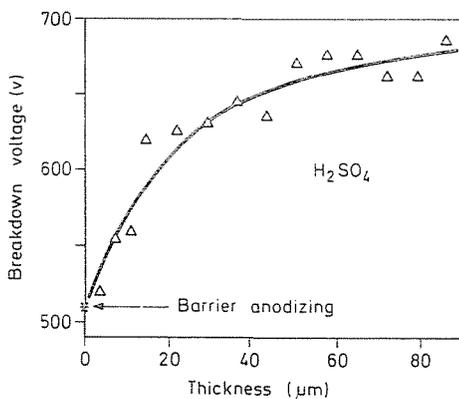


Fig. 4. The breakdown voltage during the pore-filling in ABE with 10^{-3} A/cm² current density as a function of the thickness of porous films, produced in H_2SO_4 with current density $2 \cdot 10^{-2}$ A/cm², at -10°C

The influence of current density on U_B during pore-filling process has been studied, too. For this purpose, porous films with equal thickness formed in $(COOH)_2$ were filled in aqueous borate electrolyte at various current densities. From Fig. 7 it is seen that U_B is slightly dependent on the current density.

This phenomenon of the breakdown events are not thoroughly explainable. The existing theories [3, 4] easily explain:

1) The slight decrease of breakdown voltage with the current density during pore-filling process.

2) Equal breakdown voltage for both completely filled porous and barrier films.

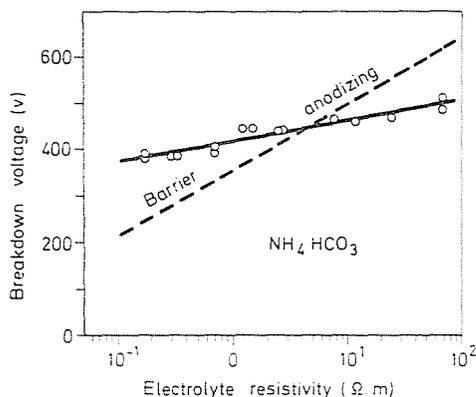


Fig. 5. The dependence of U_B on $\log \rho_{EL}$ in NH_4HCO_3 at current density $10^{-3} A/cm^2$ during the pore-filling of porous films which were produced in $(COOH)_2$ at $2 \cdot 10^{-2} A/cm^2$ and $20^\circ C$

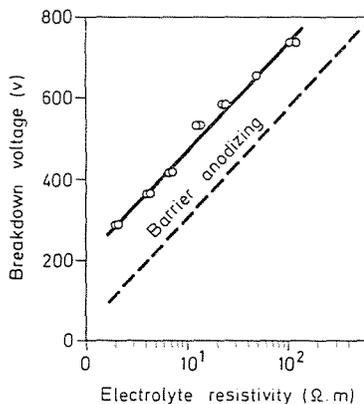


Fig. 6. The dependence of U_B on $\log \rho_{EL}$ in dimethylformamide solution of ammonium salicylate (AS/DMF) at current density $10^{-3} A/cm^2$ during the pore-filling of porous films which were obtained at the same conditions as the films of Fig. 5

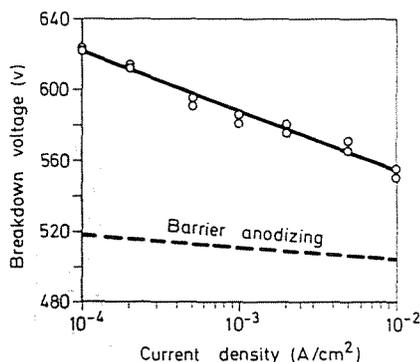


Fig. 7. The breakdown voltage of filling porous films as a function of current density in ABE. The porous films were the same as the films of Fig. 5 and Fig. 6

3) The linear increase of the breakdown voltage with the logarithm of electrolyte resistivity.

There is no direct explanation for the observed dependence of U_B on the pore depth, on the porous film thickness respectively, when breakdown occurs at the bottom of the pores. For a proper explanation of this phenomenon it is necessary to assume some additional suppositions.

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