

## THERMOGRAVIMETRIC STUDIES ON ALUMINIUM FOILS FOR ELECTROLYTIC CAPACITORS

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Thermogravimetry was applied in studies of aluminium foils for electrolytic capacitors. Scanning electron microscopy, X-ray diffraction and surface area determination were also used in the interpretation of the results.

Both the specific surface area and the capacity of the foils showed a linear relationship to the height of the oxidation step measured by TG, which was found suitable for following the processes of anodic oxidation and thermal treatment of the foils as well.

Electrolytic capacitors consist of cathode and anode foils, an aluminium oxide insulating layer and a paper soaked by the electrolyte. In order to achieve higher specific capacity, the surface areas of the foils are increased by means of etching [1].

Erdey and coworkers [2, 3] developed a derivative thermogravimetric method combined with X-ray diffraction measurements for phase analysis of the insulating layer in the presence of the aluminium base metal. Dorsey [3] determined the amount of water evolved during the thermal treatment of anodically oxidized foils in a thermal conductivity cell, and described the character of the water bonding by means of IR reflectance spectroscopy.

In the present paper mainly the oxidation step in the TG curve of capacitor foils is discussed. Additional information was obtained with scanning electron microscopy (SEM), X-ray diffraction and surface area determination.

### Experimental

#### *The samples included*

- (a) Commercial anode foils (of 45 to 115  $\mu\text{m}$  thickness and 99.99 per cent purity);
- (b) Commercial cathode foils (of 30 to 50  $\mu\text{m}$  thickness and 98 to 99.99 per cent purity);
- (c) Etched and thermally or anodically oxidized anode foils.

Manufacturers of the foils: Becromal SpA, Milano, Italy; Société Anonyme de Traitement des Métaux et Alliages, Goncelin, France (samples denoted by Satma);

Aluminium-Walzwerke Singen GmbH, Singen, FRG; and Mechanikai Művek, Budapest, Hungary (sample denoted by MA).

Thermal treatment of etched foils was carried out in a furnace connected to a Chinoin LP 839 digital temperature programmer [4]; the flow rate of the air was 10 l/h. Parameters of industrial technology were applied in anodic oxidation.

TG and DTG curves were recorded on a Du Pont 951 TGA (thermobalance) in flowing air with a 10 deg/min heating rate. Pieces of identical area (3.2 cm<sup>2</sup>) were cut out of the foils and rolled up on a wire of 3 mm diameter. The rolled foil was then placed into the sample holder of the thermobalance.

The determination of surface areas was based on gravimetric adsorption measurements on a Sartorius Thermo-Gravimat balance. Samples were first degassed in high vacuum. The amount of adsorbed argon was then measured at the boiling point of oxygen under 5–6 different pressures (in the 0.05–0.30 relative pressure range). The reference sample holder contained a smooth foil of the same size in order to avoid buoyancy differences. Specific surface areas were calculated with the BET method.

SEM investigations were carried out on a JEOL JSM 50 A apparatus. In order to make them conducting, a thin layer of gold was evaporated onto the surface of the samples. The angle of incidence of the primary beam, accelerated by a 20 kV voltage, was 45°; secondary electron images were taken.

Crystal structure was investigated with an X-ray diffractometer (model HZG 4/4 c, Zeiss, Jena). A tube with a copper anode, a nickel filter and a proportional counter were used. Both the oxidized foils and the isolated dielectric layers (obtained by dissolution in iodine/methanol) were measured. In the former case several sheets of the foil were placed into the sample holder, one on top of the other; in the latter the powder technique was applied.

## Results and discussion

Figure 1 shows the TG and DTG curves of four different etched capacitor foils. The unit of specific surface area values written above each DTG curve is dm<sup>2</sup>/dm<sup>2</sup>, i.e. the real surface area (determined by the BET method) divided by the geometric area (determined by the sizes).

The mass changes below 100° can be attributed to the water adsorbed by the foils; then the amorphous aluminium hydroxide and the gibbsite (curve 1) lost water. The temperature and the degree of oxidation different, depending on the characteristics of the base foil and the parameter of etching.

The height of the oxidation step was found to be a function of the specific surface area of the foil and the characteristics of the oxide/hydroxide layer on the surface. Figure 2 represents the relationship between the height of the oxidation step (from the TG curve) and the specific surface area. (Areas below 50 m<sup>2</sup>/m<sup>2</sup> could be determined with poor accuracy.) Low-voltage anode foils (prepared for anodic oxidation below 100 V) showed a linear mass change vs. surface area relation, with a 0.06 mg/dm<sup>2</sup>

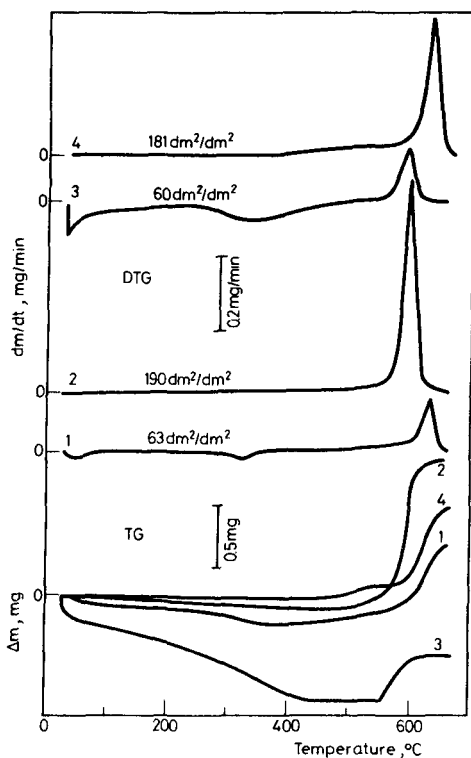


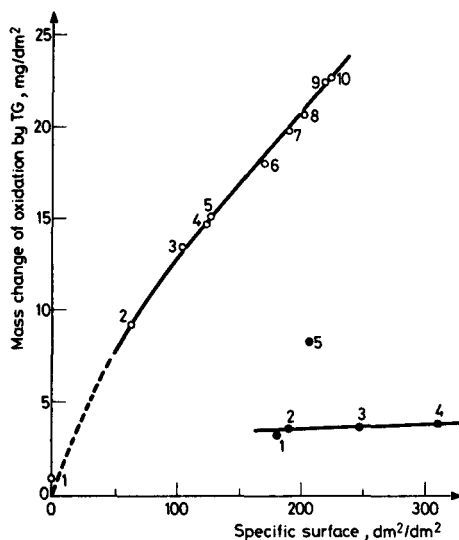
Fig. 1 TG and DTG curves of aluminium foils after anodic etching. 1 – Becromal Delta-944; 2 – Singen 2025; 3 – Becromal Alpha-901; 4 – Singen 2005

slope. The oxidability of high-voltage anode foils was less and seemed to be almost independent of the surface area.

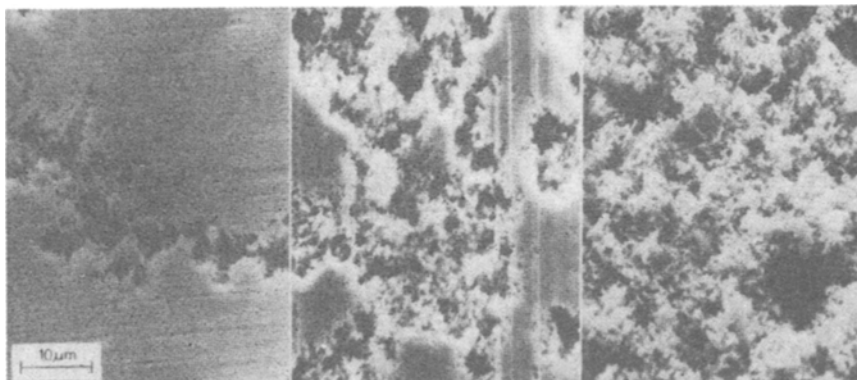
The differences between high and low-voltage foils can be explained by the different compositions and morphologies of the surface layers, due to the different manufacturing technologies. The same explanation can be given to the fact that the point of foil 5 (from another manufacturer) does not fit the line of the Becromal high-voltage series.

The surface layer of good quality low-voltage etched aluminium foils contains a small amount of water (1–3 mg/dm<sup>2</sup>), usually as amorphous aluminium hydroxide (curve 2 of Fig. 1), sometimes as gibbsite (curve 1 of Fig. 1). Far more water and, consequently, amorphous aluminium hydroxide is present in the surface layer of Becromal high-voltage foils (curve 3 of Fig. 1). Aluminium hydroxide, covering the surface, hinders the oxidation of Al metal; on the other hand, it contributes to the BET surface owing to its own structure.

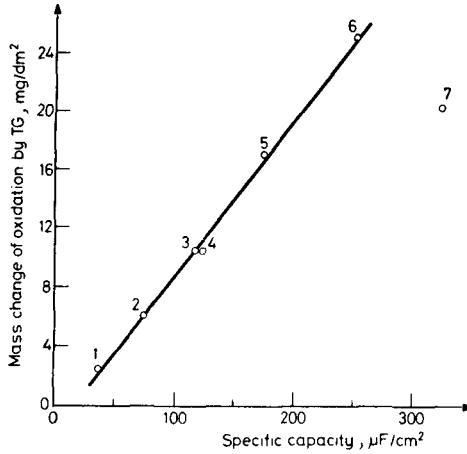
SEM images of three foils (included in Fig. 2) are presented in Fig. 3 (with the same magnification). The etched structure characteristic of the Becromal high-voltage



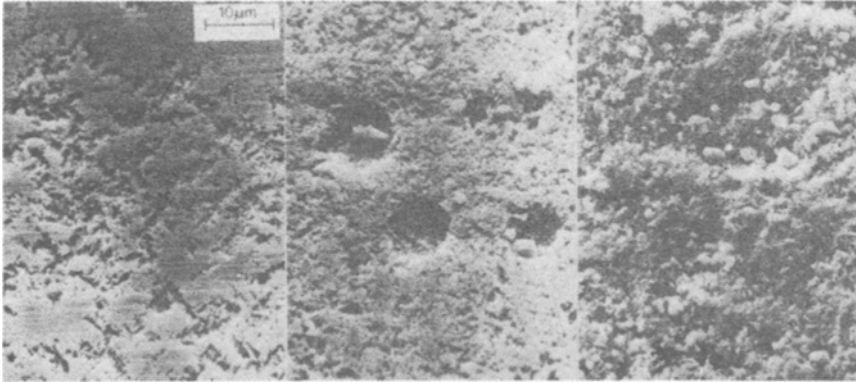
**Fig. 2** Relationship between the thermal oxidability and surface area of anodically etched aluminium foils. O – Low-voltage anode foils: 1 – Singen 2050; 2 – Becromal Delta-944; 3 – Satma R-647-65; 4 – Becromal Delta-813; 5 – Singen 2024; 6 – Becromal Delta-833; 7 – Singen 2025; 8 – Singen 2026; 9 – Singen 2028; 10 – Satma M-044-1. ● – High-voltage anode foils: 1 – Becromal Alpha-901; 2 – Becromal Alpha-932; 3 – Becromal Alpha-934; 4 – Becromal Alpha-840; 5 – MA-721



**Fig. 3** Scanning electron micrographs of some low-voltage anode foils included in Fig. 2: Singen 2050 (left), Satma R-647-65 (middle) and Singen 2028 (right)



**Fig. 4** Thermal oxidability of anodically etched cathode foils as a function of capacity measured at OV. 1 – Singen 2002; 2 – Becromal Gamma-503; 3 – Singen 2005; 4 – Becromal Kappa-303; 5 – Singen 2008 ('79); 6 – Singen 2008 ('76); 7 – Satma C-557-1



**Fig. 5** Scanning electron micrographs of some cathode foils included in Fig. 4: Singen 2002 (left), Singen 2005 (middle) and Satma C-557-1 (right)

series can be seen on the left-hand side of Fig. 8; it is different from that of the low-voltage types.

As the specific capacity, the most important parameter from the aspect of application is proportional to the specific surface area, a close relationship between the capacity and the height of the oxidation step in the TG curve could also be expected. Figure 4 shows the oxidation mass change as a function of the specific capacity measured at OV for several cathode foils. SEM images of three of them (with characteristic surface structure) are presented in Fig. 5.

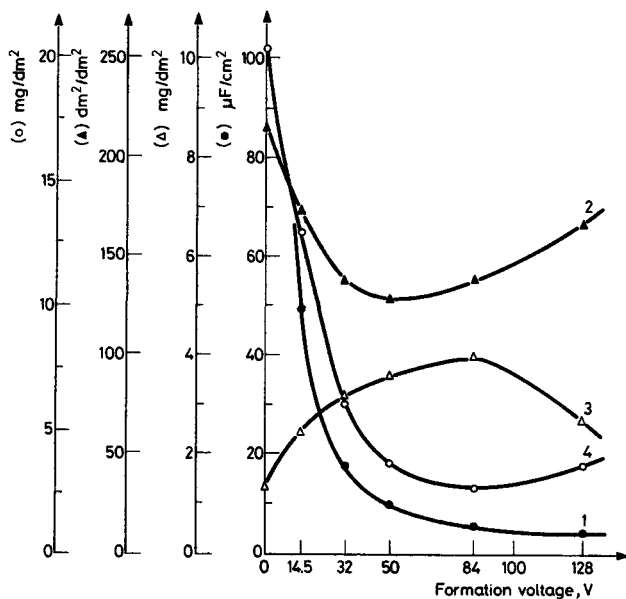


Fig. 6 Capacity (●, curve 1), surface area (▲, curve 2), water content (△, curve 3), and thermal oxidability (○, curve 4) of anodically oxidized foils as functions of formation voltage

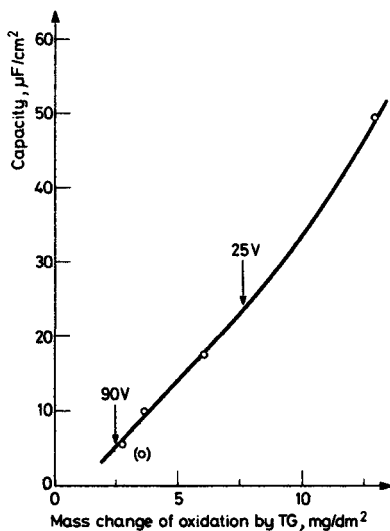


Fig. 7 Relationship between the capacity and thermal oxidability of foils oxidized at different voltages

The straight line in Fig. 4 is valid for most points. However, some Singen and Satma cathode foil types which appeared recently on the market do not fit this line (e.g. point 7 of Fig. 4). In these cases, the capacity is higher than would be expected on the basis of the oxidability, while the water content is the same. These facts indicate the special surface treatment of the new foils.

In the manufacturing technology of electrolytic capacitors, the etched aluminium foils are oxidized at a voltage depending on the intended use (this step is called formation). Oxide layers formed with the industrial technology at 14.5 V, 32 V, 50 V, 84 V and 128 V were studied.

Figure 6 demonstrates the capacity, surface area, water content and oxidability of these samples (the last two obtained from TG curves) as a function of the formation voltage.

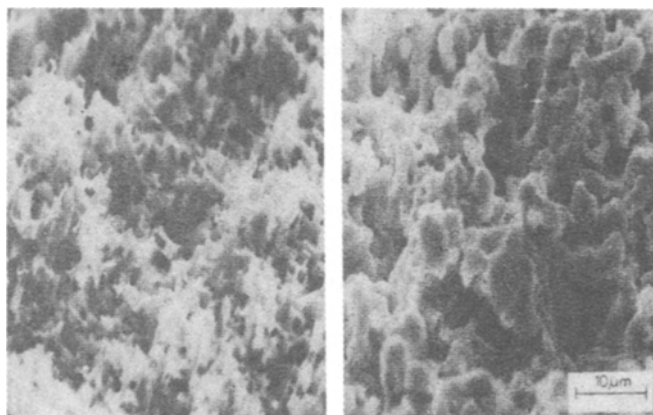
The fact that an increase in the formation voltage caused a decrease in the capacity can be explained by the increase in the thickness of the dielectric layer (directly proportional to the formation voltage), and also by the decrease in the specific surface area. The  $\text{Al} \rightarrow \text{Al}_2\text{O}_3$  transformation results in a layer 50 per cent thicker than the original, bringing about a less indented surface. The surface area values directly show the decrease in indentedness up to 50 V formation voltage. The increase in the surface area above this voltage indicates a porous oxide layer. This is confirmed by the increasing part of the thermal oxidability curve. The lower water content of the sample formed at 128 V points to a dielectric layer with different characteristics.

A comparison of the curves in Fig. 6 reveals that the thermal oxidability values bear the closest relation to those of specific capacity vs. oxidation mass change diagram the points of samples formed at different voltages in the range 25–90 V fit a straight line with a slope of  $0.35 \mu\text{F}/\text{mg}$  (Fig. 7).

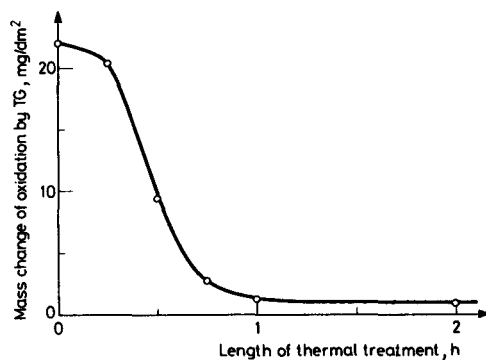
X-ray diffraction subsequent to dissolution of the base metal detected  $\gamma$ -alumina in the barrier layers formed at 50, 84 and 128 V.

Of course, changes in the conditions of formation influence the shape of the curves shown in Fig. 6, characterizing the oxide layer. In the case of some formation technologies the thermal oxidation step occurs only in the TG curves of foils oxidized below 50 V. Good-quality anode foils formed at 100 to 600 V were not oxidable thermally. Scanning electron micrographs of a product oxidized at 600 V are presented in Fig. 8. There, the crystalline phase of the dielectric layer was also  $\gamma$ -alumina, which could be detected by X-ray diffraction even in the presence of the base metal. Several technologies prescribe a thermal treatment of the etched anode foil before formation. Figures 9 and 10 show the decrease in the height of the thermal oxidation step as a function of the length and temperature of the thermal treatment prior to formation. The original mass gain (without thermal treatment) was  $21.9 \text{ mg}/\text{dm}^2$ . The TG TG curve obviously suitable for control of the effect of thermal treatment included in the technology.

Similarly as in the examples above, the appearance and growth of the oxidation step of the TG curve can characterize the progress of etching in the course of capacitor foil manufacture.



**Fig. 8** Scanning electron micrographs of Becromal Alpha-901 high-voltage anode foil after etching (left) and after oxidation at 600 V (right)



**Fig. 9** Thermal oxidability of etched anode foils after thermal treatment of different durations at 550°



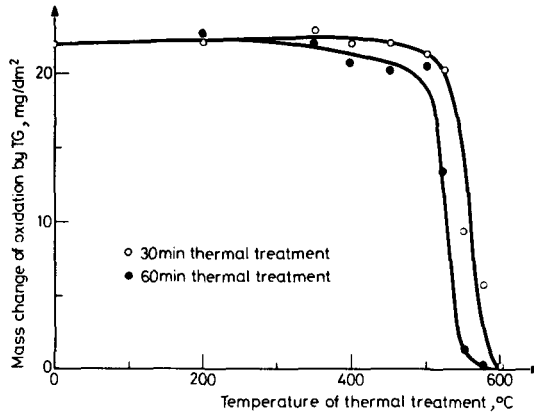


Fig. 10 Thermal oxidability of etched anode foils after 30 and 60 minute thermal treatment at different temperatures

## Conclusions

Thermogravimetry can be applied in the direct characterization of aluminium capacitor foils. The surface area of etched foils can be estimated from the oxidation step in the TG curve (thermal oxidability), provided the manufacturing technology is similar. In the case of a known specific surface area, the decrease in thermal oxidability provides information about the thickness and porosity or compactness of the surface layer. The etching, thermal treatment and formation of capacitor foils can be followed and controlled on the basis of the height of the oxidation step (measured by TG), which is closely related to the specific capacity of the foil as well.

## References

- 1 M. S. Hunter, *Electrochem. Technol.*, 1 (1963) 151.
- 2 L. Erdey, S. Gál and T. Kormány, *Anal. Chem.*, 200 (1964) 218.
- 3 S. Gál, T. Kormány, M. Mezey and L. Erdey, *Anal. Chem.*, 239 (1968) 106.
- 4 G. A. Dorsey, *J. Electrochem. Soc.*, 113 (1966) 169 and 284; 115 (1968) 1057.
- 5 S. Gál, J. Muráti and J. Sztatisz, *J. Thermal Anal.*, 21 (1981) 163.

**Zusammenfassung** — Die Thermogravimetrie wurde zur Untersuchung von Aluminiumfolien für Elektrolytkondensatoren angewandt. Zur Interpretation der Ergebnisse wurden auch durch Raster Elektronenmikroskopie, Röntgendiffraktometrie und Oberflächenmessungen erhaltene Daten herangezogen. Sowohl die spezifische Oberfläche als auch die Kapazität der Folien verhalten sich proportional zur Höhe der thermogravimetrisch gemessenen Oxydationsstufe, die sich zur Verfolgung des Prozesses der anodischen Oxydation und der thermischen Behandlung der Folien als geeignet erwiesen hat.

**Резюме** — Термогравиметрия была использована для изучения алюминиевой фольги электролитических конденсаторов. Наряду с этим, была использована сканирующая электронная микроскопия, рентгеновская дифракция и определение площади поверхности. Значения удельной площади поверхности и емкостная способность фольги находились в линейной зависимости от степени окисления, измеренной методом ТГ. Было установлено, что метод ТГ является приемлемым также для последующих процессов анодного окисления фольги и ее термической обработки.