DSC OF ETCHED ALUMINUM FOILS FOR USE IN ELECTROLYTIC CAPACITORS

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Abstract

A DSC method for evaluating the surface area of etched Al foils for use in high performance electrolytic capacitors is presented. A linear relationship between the etching degree (effective surface area) and the thermal resistance of the sample is obtained by means of DSC, based on the transient phenomenon. This method using the transient state in DSC measurement is not only novel, but also rapid and simple in evaluating the surface area of an etched aluminum foil. The method is effective even when the Al foil has a naturally oxidized surface.

Keywords: DSC, electrolytic capacitors, etched Al foils, thermal resistance, transient state

Introduction

Applications for electrolytic capacitors are expanding in step with the increasing diversification of electronic equipments. Particularly, aluminum electrolytic capacitors using aluminum foils as the electrodes play an important role in consumer electronics. In an aluminum electrolytic capacitor, capacitance is proportional to the surface area of the aluminum foil. To maximize this area, the surface of the aluminum is scored with thousands of microscopic pits using an electrochemical etching process. The evaluation of surface area is therefore important in developing a process for producing more compact capacitors having higher capacitance.

The surface area A of an aluminum foil in an electrolytic capacitor is obtained electrically according to the following equation:

$$C = \varepsilon A/t$$

where, C is the capacitance, t is the distance between the electrodes, and ε is dielectric constant. More precisely, A represents the 'effective surface area'. This can be expressed by a ratio n with respect to the effective surface area A_0 of a non-etched aluminum foil, i.e., $n=A/A_0$. This ratio n is referred herein as 'etching degree'. For example, the effective surface area of an etched aluminum foil having an etching degree of 40 is 40 times as large as that of a non-etched aluminum. In this method, however, it becomes extremely difficult to accurately determine the distance t between the electrodes with increasing effective surface area, because, as is shown in the schematic cross section of Fig. 1(a), t changes with the depth of etching.
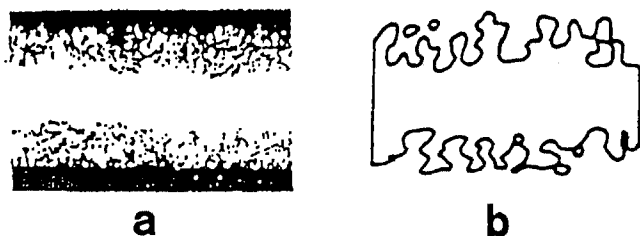
Fig. 1 Schematic cross section of etched aluminum foil; a) a cross-section micrograph,
b) schematically drawn structure of etched pits

The heavily etched surface of aluminum can be regarded as a 'porous material'. Porosity is closely related with thermal resistance [1]. An attempt is made to rapidly and simply evaluate the effective surface area of etched aluminum foils by using DSC.

Experimental

Determination of specific heat capacity of Al foils

Table 1 shows the samples used in the first DSC runs. The samples are obtained by etching a 99.99% pure aluminum (Al) foil. Figure 1 shows the schematic cross section of an etched Al foil, where (a) shows the cross-section micrograph and (b) shows a schematically drawn structure of the etched pits. A group of samples differing in etching degree can be obtained by selecting samples Nos 1, 2 and 3. Another group of samples differing in surface oxide thickness can be obtained by selecting samples Nos 4, 5 and 6.

The samples were each punched out so that they may fit an Al sample pan 5.2 mm in diameter. About 20 mg each of the samples were weighed out by using a Mettler H20T semi-micro balance. The number of punched out foils are, 6 (20.00 mg) for No. 1; 8.5 (20.60 mg) for No. 2; 12 (20.00 mg) for No. 3; 12 (20.10 mg) for No. 4; 11.4 (19.80 mg) for No. 5; and 10 (19.40 mg) for No. 6. A

Table 1 Aluminum samples (Nos 1–6)

Sample No.	Foil thickness/ μm	Etching degree/ n	Oxide thickness/ Å
1	90	1 (Non-etched)	0–50 (Naturally oxidized)
2	90	40	0–50
3	90	100	0–50
4	90	100	100
5	90	100	350
6	90	100	900

19.53 mg weight sapphire disk was used as the reference material. DSC runs were performed on a heat-flux DSC 200 operated by SSC 5040 TA station manufactured by Seiko Instruments Inc., over a temperature range of from 40 to 400°C at a heating rate of 15°C min^{-1} in two scanning areas (40 to 240 and 200 to 400°C). Data are therefore obtained for a temperature range of from 50 to 390°C. The data thus obtained were analyzed and specific heat capacity was calculated using DSCSUB and DSCCP programs supplied in SSC5200 Ver.4.30 Thermal Analysis software package.

Because surface oxidation of aluminum samples was suspected to occur during heating, samples Nos 1, 2 and 3 were scanned under the same conditions except for flowing gaseous N_2 at a flow rate of 60 ml min^{-1}.

Transient states observed by DSC on heating the samples from 350°C

Seven samples N-1 to N-7 shown in Table 2 were newly used in the measurement. About 20 mg weight samples were held at 350°C, and were each heated at a heating rate of 2, 5 and 10°C min^{-1}. Samples were climped in the sample pan, but without using an Al lid.

Table 2 Aluminum samples (N-1~N-7)

Sample No.	Foil thickness/ μm	Etching degree/ n	Oxide thickness/ Å
N-1	90	1	0–50
		(Non-etched)	(Naturally oxidized)
N-2	90	40	0–50
N-3	90	80	0–50
N-4	90	100	0–50
N-5	90	100	100
N-6	90	100	350
N-7	90	100	900

Results and discussion

Specific heat capacity of samples Nos 1 to 6

Figure 2 shows the specific heat capacity for samples Nos 1, 2 and 3 obtained in air for a temperature range of from 50 to 390°C. Significant discrepancies which increase with elevating temperature are observed particularly for samples Nos 2 and 3.

The specific heat capacity C_p of the samples is expressed by percentage deviation (relative error) from a literature value [2] in Fig. 3. The literature value is given only for the purpose of providing a standard, and not for discussing the accuracy of the measurement. For other standards, reference may be made to other literatures [3].
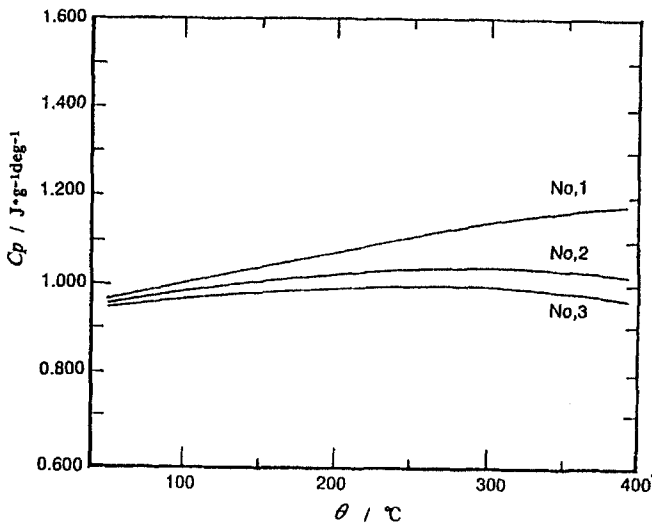
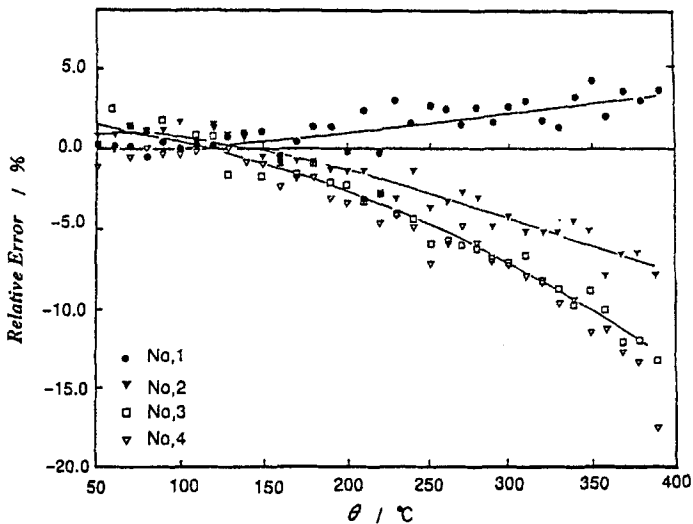Fig. 2 Specific heat capacity for aluminum samples Nos 1 to 4 (50~390°C; in air)

Fig. 3 Specific heat capacity for aluminum samples Nos 1 to 4 (50~390°C; in air) expressed by percentage deviation from literature value

From Fig. 3, it can be seen that C_p values for samples Nos 2 and 3 with reference to a standard value decrease with increasing temperature, and that the deviation is greater with increasing etching degree. This is assumably due to thermal lag caused by the thermal resistance between the sample and the sample pan as well as that within the sample, because the etching degree is closely related with porosity
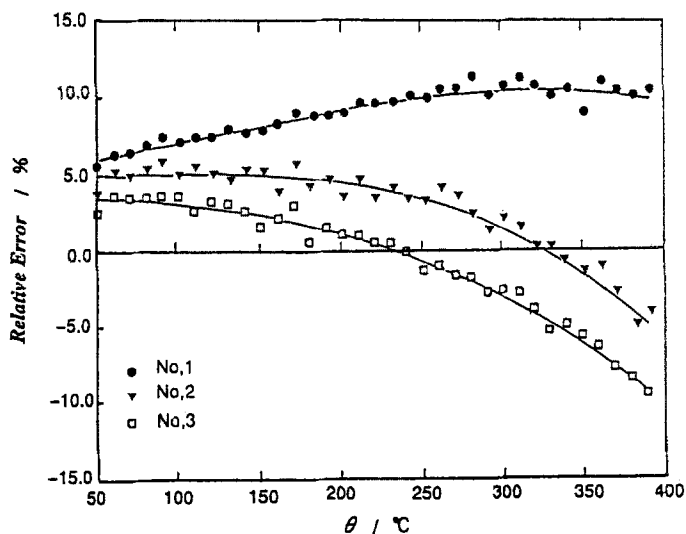
Fig. 4 Specific heat capacity for aluminum samples Nos 1 to 3 (50~390°C; in gaseous N_2)

(this can be understood from the sample description above showing a decrease in density with increasing etching degree).

Referring to Fig. 3, results for sample No. 4 are also plotted in the figure to see how C_p is influenced by the presence of an additional surface oxide. It can be seen that the plots for sample No. 4 fall close to those of sample No. 3. Furthermore, the plots for samples No. 5 and No. 6 fall close to those of No. 4 [4]. Thus, those for No. 5 and No. 6 are omitted from the graph. Moreover, if the results should be influenced by the increase in volume of Al oxide due to the increase in surface area (i.e., if the samples should be considered as composites of Al and Al oxide), the relation between the results for sample No. 3 and No. 2, in which the surface Al oxide of sample No. 3 has a volume 2.5 times as large as that of sample No. 2, must
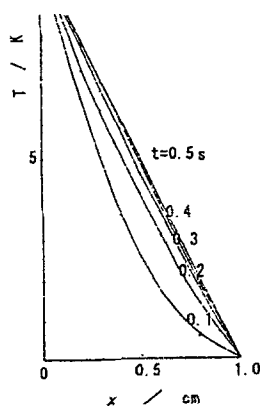

Fig. 5 One-dimensional temperature distribution in aluminum sample calculated by Crank-Nicolson method (Al No. 1, D=2.60 g cm^{-3}; C_p=954 J (kg K)$^{-1}$; C_d=240.5 W (m K^{-1}))

be similar to that between sample Nos 3 and 4 (No. 4 contains Al_2O_3 at a volume more than 2 times as large as that of No. 3). However, the results show that the surface Al oxide does not have a clear influence. Assumably, the DSC results more clearly reflect the effect of the etching degree, i.e., the surface roughness.

Figure 4 shows C_p values for Al samples Nos 1, 2 and 3 expressed by relative error, obtained under the same conditions as those shown in Fig. 3 except for flowing gaseous N_2 at a flow rate of 60 ml min^{-1}, because the surface oxidation was suspected to occur on the heavily etched samples. However, the same tendency as that observed in Fig. 3 is obtained, and, moreover, the values are shifted to the positive error side. This is assumably due to the influence of cold flow of gaseous N_2.
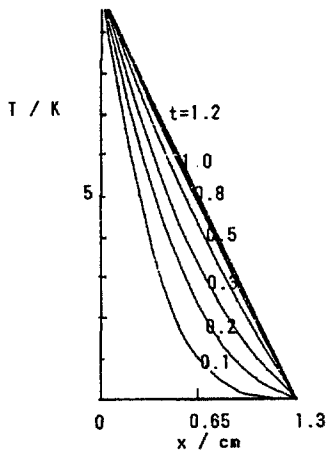

Fig. 6 One-dimensional temperature distribution in aluminum sample calculated by Crank-Nicolson method (Al No. 2, D=1.95 g cm^{-3}; C_p=954.5 J (kg K)$^{-1}$; C_d=138.7 W (m K^{-1}))
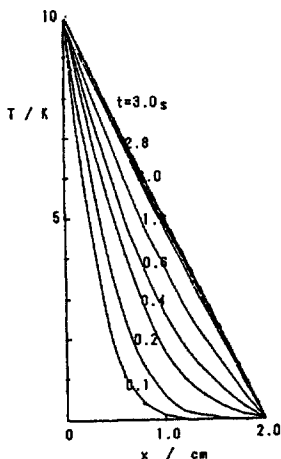

Fig. 7 One-dimensional temperature distribution in aluminum sample calculated by Crank-Nicolson method (Al No. 3, D=1.00 g cm^{-3}; C_p=954.5 J (kg K)$^{-1}$; C_d=65.98 W (m K^{-1}))

Thermal lag due to low thermal conductivity and change of sample height

By principle, steady heat of flow in the sample is requisite in performing DSC runs for the calculation of C_p. However, thermal conductivity decreases and sample height increases with increasing porosity. Thus, effective thermal conductivity C_d of the samples was calculated by treating the sample as a composite of solid with pores containing gas dispersed therein according to the following equation [5]:

$$C_d = C_s(1 - p^{2/3}) + C_g p^{1/3}$$

where, C_s is thermal conductivity of solid, C_g is thermal conductivity of gas in pores, and p is the porosity of the sample. Then, the time necessary for attaining a steady heat of flow was calculated for three model samples similar to samples Nos 1, 2 and 3 according to the well-known Crank-Nicolson method or modified Euler method [6]. That is, the change in temperature within a one-dimensional sample is shown graphically in Figs 5 to 7. The details for the samples used for the calculation are given in the figure captions. These figures show that samples Nos 2 and 3 take 2.4 times and 6 times longer than No. 1 to acquire a steady flow of heat inside the sample.

Analysis of DSC curves on starting heating from 350°C

By analogy to an RC electric circuit consisting of a serial connected resistance R and capacitance C in a transient state, DSC curves obtained on starting heating is shown schematically in Fig. 8. The ordinate is heat flow, and is $(T_s-T_h)/R$ at time $t=0$, where T_s is the temperature of the sample, T_h is the temperature of the heat sink, and R is the thermal resistance between the sample and the heat sink. That is, at the instant of starting heating at 350°C, the temperature difference (T_s-T_h) must be the same for all samples so long as the same heating rate is selected. Because thermal resistance R and capacitance C are serial connected, the heat flow $q(t)$ from that instance changes in accordance with
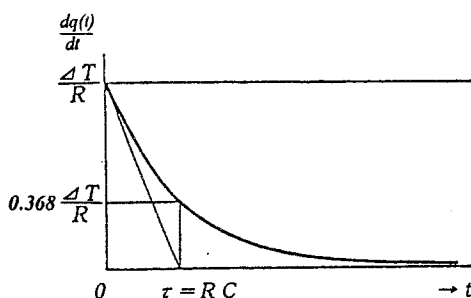
$$q(t) = [(T_s - T_h)/R] \exp(-t/RC)$$

where t is time.
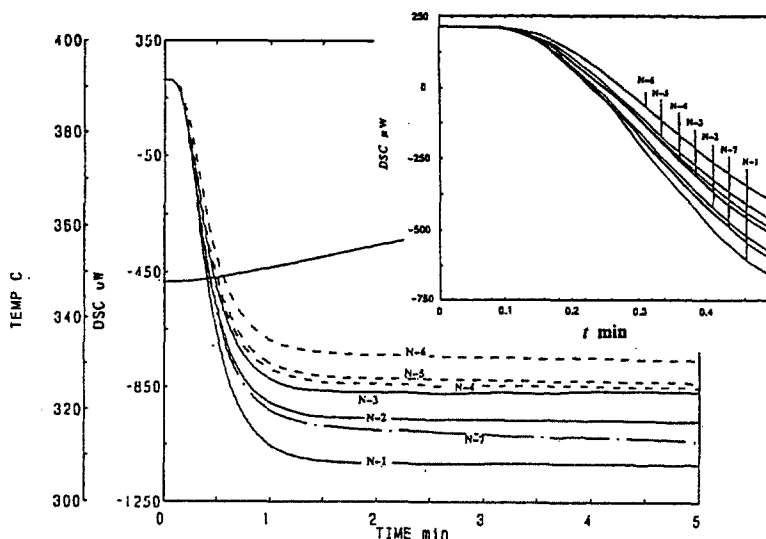

Fig. 8 Change in heat flow on starting heating

Fig. 9 DSC curves obtained on starting heating from 350°C (transient state; heating rate 5°C min⁻¹), enlarged curves are shown in embedded window
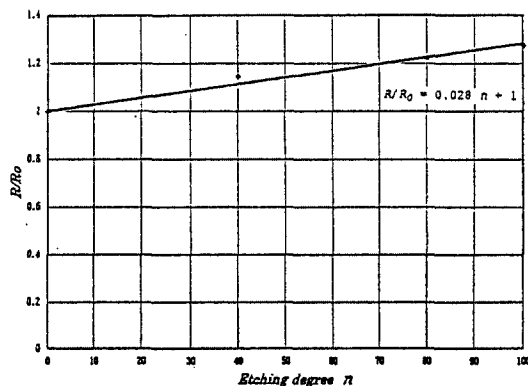

Fig. 10 Relation between etching degree and thermal resistance R/R_o (by DSC)

Because $(T_s–T_h)$ is the same for all the samples on starting heating at the same heating rate, the drop height of the DSC curve from the baseline as is shown in Fig. 9 is directly related with R which differs depending on the sample. Thermal resistance R in this case is the total for the serial connected thermal resistances. Thermal resistance inherent in the instrument R_i is obtained from the melting curve of a standard sample zinc (Zn) as

$$R_i = 8.70 \times 10^{-4} \text{ min °C mJ}^{-1}$$

Because R_i is serial connected withe the rest of the resistances mainly those inherent in the sample, R_i is simply substracted from the R obtained from the DSC curves by assuming that (T_s-T_h) is equal to the heating rate (i.e., an initial (T_s-T_h) is taken as 10 deg in this case). Thus, R for samples Nos 1 to 7 are obtained as 6.27, 7.18, 7.67, 7.99, 8.16, 8.90 and 6.63 ($\times 10^{-2}$ min $°C$ mJ^{-1}). This signifies the R_i is less than 1/100 of the R for any sample, and that in approximation, the value is negligible. The results are plotted in Fig. 10 by taking the etching degree in the abscissa, and by taking the ratio of each of the samples R to the resistance of the non-etched sample No. 1 (R_0). A linear relationship is obtained between R/R_0 and etching degree n expressed by:

$$R/R_0 = 0.0028n + 1$$

The relationship is obtained between R/R_0 and the surface oxide thickness is to be discussed elsewhere.

Conclusion

The use of high performance aluminum (Al) electrolytic capacitors is increasing steadily with the diversification of consumer electronics. Because capacitance is proportional to the surface area of the Al foil, it is important to evaluate the surface area by methods other than electric ones. By using samples differing in surface area (etching degree) but with naturally oxidized surface (assumably less than 50 Å in thickness), a linear relationship is obtained between the etching degree and the thermal resistance of the sample. It is also found that the effect of surface natural aluminum oxide can be neglected in this case using DSC as a rapid and simple method for evaluating the surface area of an etched aluminum foil.

Similar results can be obtained by using DDSC. This is to be presented elswhere.

It is also to be stressed herein that the present results suggest the applicability of DSC as a simple and rapid method in evaluating rough surfaces.

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