

# Thermoluminescence of $Al_2O_3$ layers formed by anodic oxidation in oxalic acid

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Thermoluminescence (TL) of  $Al_2O_3$  layers obtained by electrolytic oxidation of aluminium in aqueous solution of oxalic acid has been investigated. It has been found that the  $Al_2O_3$  layers show both the natural (without excitation) as well as the UV-excited thermoluminescence. By applying the method proposed by Alencev-Fok and Antonov-Romanovskii it has been shown that in the case of the layers formed at d.c. voltage the TL-curve consists of 5 and 3 elementary glow-peaks depending on whether thermoluminescence is natural or stimulated. For the layers formed at a.c. voltage 2 or 6 elementary glow-peaks were observed, respectively. For all the observed elementary glow-peaks the activation energy of the electron traps has been calculated.

## 1. Introduction

Although the thermoluminescence of  $Al_2O_3$  has been already studied by several authors [1-6], the number and nature of electron traps present in the oxide still remains to be the subject of controversy.

RIEKE and DANIELS [1] observed three maxima on the thermoluminescence (TL) curve of the chemically synthesized  $Al_2O_3$ . They associated the two low-temperature maxima of 376 and 437 K with the presence of crystallization water in the sample and the high temperature maximum at 593 K with the presence of crystal lattice defects on the sample surface. Similar results were obtained by SAŁAJCZYK and SUJAK [3, 4] who investigated the anodically deposited  $Al_2O_3$  layers.

MICHNO and co-workers [5] investigated the effect of external electric field in the TL-curve of  $Al_2O_3$  obtained by electrolytic oxidation in aqueous solution of oxalic acid. They have stated on TL-curve five maxima at temperatures of 368, 413, 463, 513 and 593 K with activation energy of electron traps equal to 0.71, 0.89, 1.11, 1.24 and 1.31 eV, respectively.

The TL-curves of  $Al_2O_3$  are much complicated, making it difficult to interpret the observed phenomena. Consequently, the exact determi-

nation of the parameters of electron traps responsible for the observed thermoluminescence is not possible. There is in the literature one paper [6] concerning the analysis of the experimental TL-curves of anodically deposited  $\text{Al}_2\text{O}_3$  layers by the procedure based on the method proposed by ALENCEV-FOK [7] and ANTONOV-ROMANOVSKII [8] method. The method proposed in [6] is especially useful in the case of the overlapping of individual glow-peaks, e.g., in the case of thermoluminescence of  $\text{Al}_2\text{O}_3$ .

The purpose of the paper is to present the analysis of the experimental TL-curves of the anodically formed  $\text{Al}_2\text{O}_3$  into elementary glow-peaks and to compare the corresponding values of the electron traps depth determined by means of the ANTONOV-ROMANOVSKII [8] method with those obtained by applying the method proposed by CURIE and CURIE [9].

## 2. Experimental methods

Thin  $\text{Al}_2\text{O}_3$  layers were deposited electrolytically on the Al anodes (0.06 mm thick foil of the 99.50% purity) in 1% water solution of oxalic acid. As a cathode a platinum plate was used. Electrolysis was carried out during 2 hours at direct current (d.c.) or alternating current (a.c.) voltage of 60 V. Temperature of electrolyte during the anodization process was not higher than 308 K.

After anodizing the Al-anodes were rinsed first in running water, then in distilled water and subsequently dried at the room temperature in closed box containing atmospheric air dried with the use of  $\text{P}_2\text{O}_5$ . The 0.06 mm thick disc-shaped samples with diameter of about 1.5 cm were cut from the anodized plates. The samples were heated at a constant heating rate of 0.9 k/s in the temperature range from 300 K to 700 K. The sample temperature was controlled with the aid of iron-constantan thermocouple with the accuracy within  $\pm 5$  K.

The intensity of thermoluminescence was recorded by an FEU-19 M photomultiplier connected with a G1B1 recorder. Both the integral and colour TL-curves were recorded. In the case of integral TL-measurements a 2 mm thick water filter was placed between the sample and the multiplier in order to protect the multiplier against the thermal radiation. The colour TL-curves were measured in both the UV and visible ranges of spectrum. They were obtained by placing appropriate absorption filters between the sample and photomultiplier. The filters used transmit the broad UV or visible bands lying within the spectral sensitivity of photomultiplier. The spectral characteristic of the fil-

ters are shown in Fig. 1, together with the spectral sensitivity of the photomultiplier (curve a).

Both the natural and UV-excited thermoluminescences were investigated. The natural TL was measured directly after the oxide had been formed and dried. For the measurements of the UV-excited thermoluminescence

the samples were previously tempered in atmospheric air at temperature of about 870 K and after cooling submitted to 20 min UV-irradiation from the quartz

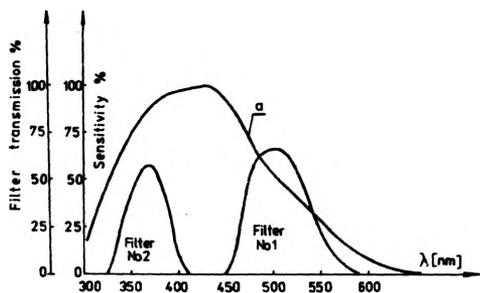


Fig. 1. Spectral distribution of the transmittance of filters and the spectral sensitivity of the photomultiplier (curve a)

lamp with a HBO-50 burner. Thereupon, the heat treatment-excitation-TL measurement cycle was repeated in order to check whether the TL-curve is affected by the duration of thermal treatment.

### 3. Results of measurements

#### 3.1. Integral TL-curves

Figure 2 shows the curves of the integral natural thermoluminescence for  $Al_2O_3$  samples formed at d.c. (curve a) and a.c. (curve b) voltages. Both the curves are normalized to the height of the highest maximum. The absolute value of the TL-intensity for the samples formed at a.c. voltage is about 10 times greater than that for samples formed at d.c. voltage. Independently of the oxide formation process, both the TL-curves show a high temperature maximum at about 603 K. For the oxide formed at a d.c. voltage there is also a broad low-temperature glow-peak, its intensity being distinctly smaller than that of the high temperature glow-peak.

The normalized curves of the integral UV-excited thermoluminescence for samples formed at d.c. (curve a) and a.c. (curve b) voltage are shown in Fig. 3. They have shape of the broad bands with a great intensity in their low temperature region. The shape of the TL-curve for samples formed at d.c. voltage is more regular than that for the sam-

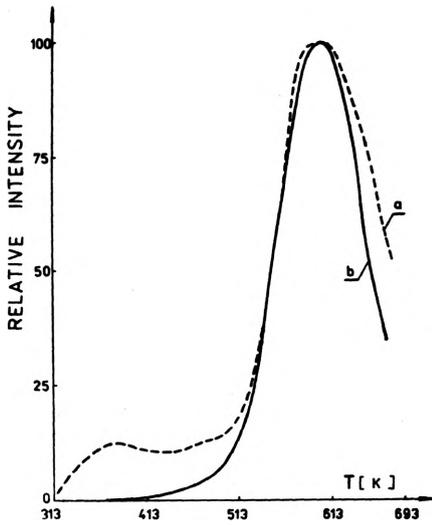


Fig. 2. Natural integral thermoluminescence of aluminium oxide formed at d.c. (curve a) and a.c. (curve b) voltage

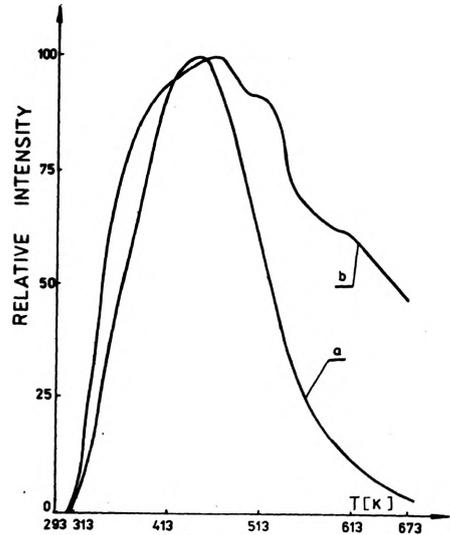


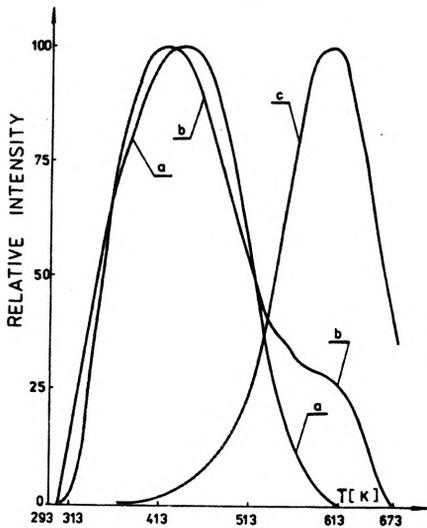
Fig. 3. UV-excited integral thermoluminescence of aluminium oxide formed at d.c. (curve a) and a.c. (curve b) voltage

ples formed at a.c. voltage. The position of maximum on the TL-curve for samples formed at d.c. voltage (443 K) does not depend on the duration of the heat treatment, whereas for samples formed at a.c. voltage the position of the main maximum of the TL-intensity, occurring in the vicinity of 460 K, depends slightly on the duration of the heat treatment. In contrast to the natural thermoluminescence, the absolute intensity of the UV-excited TL for samples formed at d.c. voltage is greater than that for samples formed at a.c. voltage.

### 3.2. Colour TL-curves

From observation we have performed it follows that the observed thermoluminescence occurs in both the UV and visible interval of spectrum. Therefore, apart from the integral TL-curves, the colour glow-curves were measured for both the natural and UV-excited thermoluminescence with the use of filters whose transmittance is shown in Fig. 1.

The colour glow-curves of both the natural and UV-excited thermoluminescence, measured with the use of filter 1 (see Fig. 1) for samples formed at d.o. and a.c. voltages are shown in Fig. 4. Except for the very weak luminescence observed in the low-temperature thermoluminescence of samples formed at d.c. voltage, the colour glow-curves of



the natural thermoluminescence for samples formed at a.c. and d.c. voltages (curve c) are very similar. They show also a distinct similarity to the integral TL curves presented in Fig. 2. The same concerns also both the integral and colour glow-curves of the UV-excited thermoluminescence for samples formed at

Fig. 4. UV-excited colour thermoluminescence of aluminium oxide formed at d.c. (curve a) and a.c. (curve b) voltages and the natural colour thermoluminescence (curve c)

d.c. voltage (see Fig. 3). However, the colour glow-curves of the UV-excited thermoluminescence for samples formed at a.c. voltage differ from the corresponding integral TL-curves, the main maximum of the colour curve being shifted towards lower temperatures with respect to the integral TL-curve (curves b in Figs. 3 and 4). The colour curve shows also fewer lateral maxima as compared with the integral TL-curve. There is also seen a relative diminution of the TL-intensity within the whole high temperature region with respect to the integral glow-curves.

Relations between the intensities of natural and UV-excited colour luminescence are analogous to those for integral TL.

The shape of the colour TL-curves measured with the use of filter 2 (also in the UV-region) is similar to that observed in the visible interval of spectrum, the absolute value of the measured intensity of the former being few times smaller than that of the latter. This is because the transmittance of filter 2 is smaller than that of filter 1, and possibly because of the smaller intensity of UV-radiation in the measured thermoluminescence, as compared with that for the visible component.

#### 4. Analysis of the TL-curves

Although the thermoluminescence method is commonly applied in determining the parameters of the electron traps in crystals, the results obtained with the use of the hitherto existing methods for evaluating the TL-curves in many cases are not unambiguous. In general, some simplifications are necessary to analyse the complex glow-curves. It is commonly accepted to perform the analysis under assumption of an oversimplified crystal model with one trap level lying under the bottom of the conductivity band [10-15]. The observed glow-curves of  $\text{Al}_2\text{O}_3$  are, however, very complex, and therefore these methods do not permit the unambiguous determination of the parameters of traps existing in  $\text{Al}_2\text{O}_3$ . The method we have applied is based on the combination of the methods proposed by FOK [7] and ANTONOV-ROMANOVSKII [8]. A detailed description of this method and its application to analysis of the TL-curves of anodically formed  $\text{Al}_2\text{O}_3$  layers is given in [6].

The combined Alencev-Fok and Antonov-Romanovskii method was employed to analysis of the colour UV-excited TL-curves, whereas the natural TL-curves were analysed by the Antonov-Romanovskii method, since in the latter case one appropriate deformation of the glow-curve

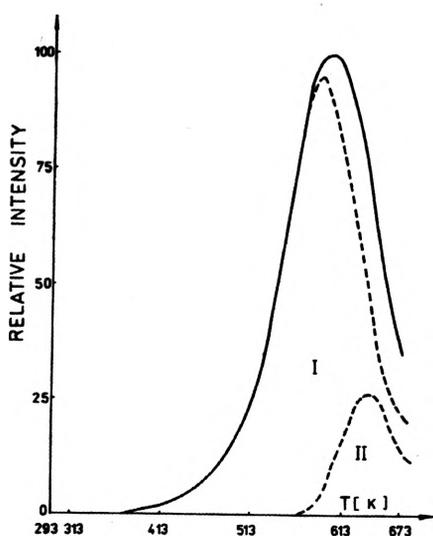


Fig. 5. Analysis of the natural colour TL-curve of aluminium oxide formed at a.c. voltage

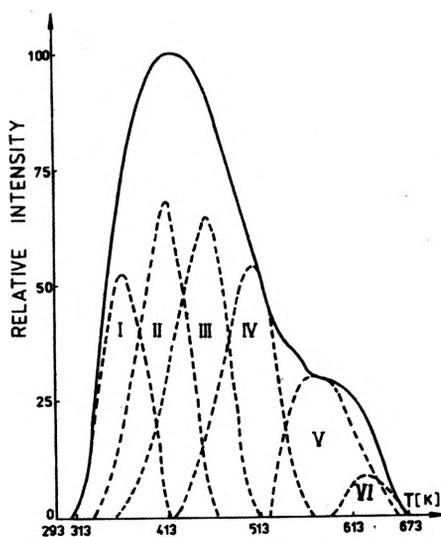


Fig. 6. Analysis of the UV-excited colour TL-curve of aluminium oxide formed at a.c. voltage

could not be performed. Due to very weak intensity of the natural thermoluminescence of the samples formed at d.c. voltage, only the integral TL-curves were analysed. The results of the analysis are shown in Figs. 5-8. Figures 5 and 6 show the results of analysis of the experimental natural and UV-excited colour thermoluminescence of the samples formed at a.c. voltage. The natural glow-curve (Fig. 5) consists of 2 elementary glow-peaks, that for the UV-excited thermoluminescence being composed of 6 peaks (Fig. 6). Figures 7 and 8 represent the results of analysis of the experimental glow-curves of the natural and UV-excited thermoluminescence of samples formed at d.c. voltage. As it is seen, the natural TL-curve (Fig. 7) consists of 5 elementary peaks, whereas that of the UV-excited thermoluminescence consists of 3 peaks (Fig. 8).

For all the glow-peaks occurring in the analysed TL-curves the frequency factors and activation energies of the corresponding electron traps were evaluated. The obtained results were collected in the Table. The method used together with the accuracy of determination of the position of TL-peaks permits to determine the value of the activation energy of electron traps with accuracy of about 5%. In all the cases the measurements were repeated on several samples, the results obtained being reproducible.

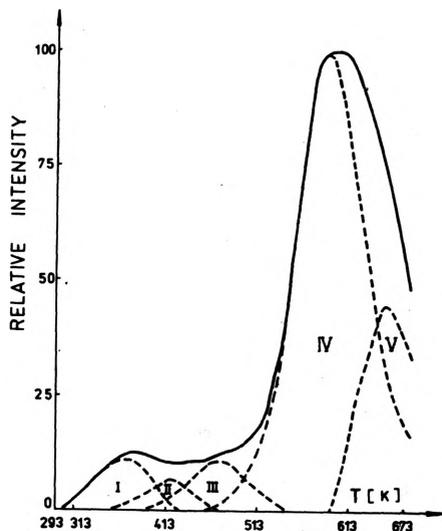


Fig. 7. Analysis of the natural integral TL-curve of aluminium oxide formed at d.c. voltage

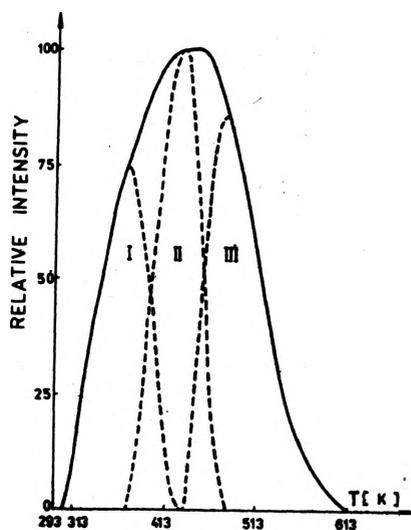


Fig. 8. Analysis of the UV-excited colour TL-curve of aluminium oxide formed at d.c. voltage

Table. TL parameters of  $Al_2O_3$  anodic layers

Sample preparation and excitation	Peak number	Kinetics	Peak temperature [K]	Activation energy [eV]	Factor $s$ [ $s^{-1}$ ]	Factor $n = \tau s^m$ [ $s^{-1}$ ]	Activation energy calculated according to the Curis method [eV]
Natural TL of $Al_2O_3$ formed at a.c. voltage (Fig. 5)	I	bimol.	590	1.10	-	$5 \cdot 10^7$	1.08
	II	bimol.	640	1.43	-	$5 \cdot 10^9$	1.41
UV-excited TL of $Al_2O_3$ formed at a.c. voltage (Fig. 6)	I	monomol.	367	0.39	$1 \cdot 10^4$	-	0.41
	II	"	414	0.54	$1 \cdot 10^5$	-	0.54
	III	"	455	0.57	$7 \cdot 10^4$	-	0.59
	IV	"	507	0.73	$5 \cdot 10^5$	-	0.75
	V	bimol.	574	1.07	-	$7 \cdot 10^7$	1.07
	VI	"	629	1.40	-	$5 \cdot 10^9$	1.40
Natural TL of $Al_2O_3$ formed at d.c. voltage (Fig. 7)	I	monomol.	370	0.40	$1 \cdot 10^4$	-	0.41
	II	"	421	0.63	$1 \cdot 10^6$	-	0.63
	III	bimol.	471	0.77	-	$5 \cdot 10^6$	0.78
	IV	"	592	1.10	-	$7 \cdot 10^7$	1.10
	V	"	653	1.44	-	$5 \cdot 10^9$	1.45
UV-excited TL of $Al_2O_3$ formed at d.c. voltage (Fig. 8)	I	monomol.	371	0.40	$1 \cdot 10^4$	-	0.41
	II	"	432	0.64	$1 \cdot 10^6$	-	0.65
	III	bimol.	478	0.78	-	$5 \cdot 10^6$	0.79

## 5. Conclusions

From the results we have obtained the following conclusions may be formulated:

i) A natural thermoluminescence occurs in samples formed at both the d.c. and a.c. voltages and is not affected by UV-irradiation. The number of elementary glow-peaks occurring in the TL-curves of samples formed at d.c. and a.c. voltages is different (see Figs. 5 and 7). Parameters of the electron traps responsible for the observed TL-peaks are given in Table. As it is seen, the group of electron traps of the activation energy of 1.10 eV and 1.44 eV occurs in both the samples formed at d.c. and a.c. voltages, whereas the group of electron traps with activation energies of 0.77 eV, 0.63 eV and 0.40 eV occurs only in the samples formed at d.c. voltage. The natural TL-curves obtained in the present work are similar to those reported by SAŁAJCZYK [2, 4] who, however, did not analyse the TL-curves he had obtained.

ii) There is also the thermoluminescence observed after UV-irradiation of samples submitted previously to the heat treatment. Analysis of the obtained TL-curves (Figs. 6 and 8) and the results of evaluation of electron traps parameters (Table) show that in the samples formed at a.c. voltage there occur the traps of the activation energy of 1.40, 1.10, 0.73, 0.57, 0.54, and 0.39 eV, whereas in the samples formed at d.c. voltage there is only the group of low-temperature traps with activation energies of 0.78, 0.64 and 0.40 eV. The curves of the UV-excited thermoluminescence obtained in the present study differ from those reported by SAŁAJCZYK [3, 4] and MICHÓ [5].

iii) When comparing the natural and UV-excited thermoluminescence it seems to be of interest to note that the preheating process for samples formed at a.c. voltage causes the appearance of the low-temperature traps (see Figs. 5 and 6), whereas preheating of the samples formed at d.c. voltage causes the disappearance of the high-temperature traps (Figs. 7 and 8).

iv) In connection with the results reported by RAO and DAS [16] who investigated the UV-excited thermoluminescence of  $\alpha-Al_2O_3$  powder it is noteworthy that their values of the frequency factor are distinctly larger than those obtained by us for anodically formed  $Al_2O_3$ . Nevertheless, the latter seem to be reliable, being confirmed by the fact that the activation energy of electron traps evaluated by the method proposed by CURIE and CURIE [9] with the use of our values of the frequency factor was in good agreement with the results obtained by means of the Antonov-Romanovskii method (see columns 5 and 8 in the Table).

v) The visible and UV-components observed in both the natural and UV-excited thermoluminescence show clearly that two kinds of luminescence centres are present in the investigated oxide. The centres can be formed owing to the admixtures of other metals present in the oxidized aluminium. They are subsequently built into crystal lattice of the oxide formed on aluminium. In our case the aluminium contains admixture of Fe, Si, Cu, Zn and Ti. The determination of the nature of these contents requires further studies.

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ТЕРМОЛЮМИНЕСЦЕНЦИЯ ПЛЕНОК  $Al_2O_3$ , АНОДНО ОБРАЗОВАННЫХ НА АЛЮМИНИИ  
В ВОДНОМ РАСТВОРЕ ЩАВЕЛЕВОЙ КИСЛОТЫ

В работе представлены результаты опытных исследований термолюминесценции (ТЛ) окиси алюминия ( $Al_2O_3$ ), полученной путем электролитического окисления алюминия в водном растворе щавелевой кислоты. Установлено, что электролитически образованный  $Al_2O_3$  обнаруживает естественную термолюминесценцию (без возбуждения UV), а также возбужденную ТЛ после предварительного прогрева окиси и облучения его излучением UV. Применяя метод, который предложили Аленцев-Фок и Антонов-Романовский, было доказано, что экспериментальная неэлементарная кривая ТЛ окиси, образованной постоянным напряжением, состоит из 5 элементарных пиков термовысвечивания в случае естественной ТЛ и 3 элементарных пиков в случае возбужденной ТЛ. Неэлементарная же кривая ТЛ окиси, образованной переменным напряжением, состоит из 2 элементарных пиков термовысвечивания для естественной ТЛ и 6 элементарных пиков для возбужденной ТЛ. Определена энергия активации электронных ловушек всех выступающих элементарных пиков термовысвечивания по методу Антонова-Романовского и проведено сравнение с энергией активации, рассчитанной с помощью метода Кюри.