EFFECT OF HEAT TREATMENT OF ANODIC OXIDE FILMS ON ALUMINIUM ON THEIR PHOTOLUMINESCENT PROPERTIES

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Heating of anodic oxide films on aluminium produced irreversible changes in their photoluminescent properties. In the case of oxalic acid films, for instance, PL intensity increased exponentially with increasing heating temperature up to 600°C. Above this temperature, PL intensity decreased rapidly with increasing heating temperature and disappeared at 800°C. Similar tendencies were also found with other carboxylic and hydroxy-carboxylic acid films. On the other hand, inorganic acid films gave no photoluminescence even after heat treatment. It was found that our hypothesis that the luminescent centres of anodic oxide films on aluminium might be incorporated carboxylate ions as presented in a previous paper, proved to be appropriate to explain these observations.

1 INTRODUCTION

In the previous paper, we have presented the hypothesis that the luminescent centres of anodic oxide films on aluminium might be the carboxylate ions incorporated during film formation. As established by numerous investigations, anodic oxide films on aluminium are usually amorphous and contain an appreciable amount of water not in a free form but in the form of either hydroxide or hydrated oxide (AlOOH) in addition to carboxylate ions. Thermal treatment of anodic oxide films on aluminium causes considerable changes in their structure by crystallization (γ, α), dehydration of bound water, and by decomposition of carboxylate ions. Consequently, it can be expected that heat treatment of anodic oxide films on aluminium may cause many irreversible changes in their photoluminescent properties, and such expectations proved to be true.

In this paper, the correlation between the structural changes of anodic oxide films on aluminium taking place during heating, and the resulting changes of their photoluminescent properties are discussed.

2 EXPERIMENTAL

2.1 Anodic Oxidation

Aluminium specimens of 99.999% (Superraffinal, Alusuisse), 99.99%, and 99.8% purity, 0.05 cm thick, 2.5 cm wide, 4 cm long were degreased with acetone and then rinsed with distilled water. Anodic oxide films were formed with conditions shown in Table I.

2.2 Heat-treatment

Samples were mounted on a boat in a quartz tube, with an attached thermopile, heated in air by a Bunsen burner, and quenched in air. Above 660°C, i.e., the melting point of aluminium, oxide films stripped from the substrate were used.

Measurements of PL intensity, emission spectra, and infrared spectra were carried out using the same procedures as reported in the previous paper.

| Electrolyte         | Anodizing condition                | Time  |
|---------------------|-----------------------------------|-------|
| ammonium borate     | 20°C, 0.1M, 20mA/cm²              | 10min.|
| succinic acid       | 15°C, 0.1M, 20mA/cm²              | 15min.|
| tartaric acid       | 15°C, 0.1M, 20mA/cm²              | 15min.|
| citric acid         | 15°C, 0.1M, 20mA/cm²              | 15min.|
| malic acid          | 15°C, 0.1M, 20mA/cm²              | 15min.|
| maleic acid         | 15°C, 0.1M, 20mA/cm²              | 15min.|
| malonic acid        | 15°C, 0.1M, 20mA/cm²              | 15min.|
| formic acid         | 15°C, 0.1M, 20mA/cm²              | 15min.|
| oxalic acid         | 15°C, 0.1M, 20mA/cm²              | 15min.|
| H₂SO₄               | 15°C, 0.1M, 20mA/cm²              | 15min.|
| H₃PO₄               | 15°C, 0.1M, 20mA/cm²              | 15min.|
| CrO₃                | 15°C, 0.1M, 20mA/cm²              | 15min.|
| HSO₃NH₂             | 15°C, 0.1M, 20mA/cm²              | 15min.|

TABLE I

Anodizing conditions.
3 RESULTS AND DISCUSSION

The heat treatment of the oxide films causes irreversible changes in their photoluminescent properties. Figure 1 shows the correlation between the PL intensity of oxalic acid films and the heating time. When the films are heated to temperatures below 600°C, PL intensity increases rapidly with heating time and reaches, within 5 min, the saturation value determined by the heating temperature and further heating at the same temperature gives no changes. When the films are heated to the temperatures over 600°C, PL intensity increases rapidly to a certain value and then decreases gradually with heating time.

Figure 2 shows the correlation between the PL intensity of the oxalic acid films and heating temperature.

The correlation between the PL intensity and the heating time: 1. 300°C, 2. 600°C, 3. 650°C.

| Electrolyte     | T<sub>max</sub> (°C) | I<sub>max</sub>/I₀ |
|-----------------|----------------------|-------------------|
| inorganic acids |                      |                   |
| formic acid     | 450                  | 4.6               |
| oxalic acid     | 600                  | 2.9               |
| tartaric acid   | 600                  | 1.9               |
| citric acid     | 550                  | 1.7               |
| malonic acid    | 600                  | 2.1               |
| maleic acid     | 570                  | 2.0               |
| malic acid      | 550                  | 1.7               |
| succinic acid   | 600                  | 1.8               |

The peak temperature of PL intensity and the ratio of the PL intensity at this temperature to that of the as-anodized film are listed in Table II for each oxide film. Contrary to the remarkable effect of heating of organic acid films on their photoluminescent properties, inorganic acid films gave no photoluminescence even after heat treatment. The peak temperature of PL intensity is different for each film and lies in the range of 450°C (formic acid film) to 600°C (oxalic acid film).

In the case of formic acid films, the value of I<sub>max</sub>/I₀ is larger than those of the other films. This is closely connected with the colour change of the films by the temperature rise. Formic acid films exhibit a deep brown colour. As reported in the previous paper, the colour of the films had a tendency to disturb the transmittance of excitation beam through the films, causing the decay of the PL intensity. During heating, decoloration occurred at about 300°C and the colour of the film turned from deep brown to light yellowish-brown. This may increase the transmittance of the excitation beam through the film and results in the larger value of I<sub>max</sub>/I₀. Accordingly, in the case of the formic acid film, it is considered that the heating of the film has an effect to remove the factor which acts unfavourably upon the PL intensity in addition to the other effects on its PL intensity which will be referred to...
PHOTOLUMINESCENT ANODIC OXIDE FILMS

FIGURE 3  The emission spectra of oxalic acid films: 1. as-anodized, 2. heat-treated at 600°C.

below. In the case of other organic acid films, such a change of the colour of the films caused by their heating was not found. Heating the formic acid films up to over 500°C, the colour changed again from light yellowish-brown to deep brown and the photoluminescence decreased markedly.

Figures 3 and 4 show the emission spectra of oxalic and formic acid films heat-treated at various temperatures. Almost no difference were found between the spectra of the original film and that of the film heat-treated at the peak temperature of PL intensity for both cases. However, heating the films above this temperature produces pronounced changes in their photoluminescence spectra. The emission spectra of the films after such a treatment are dominant in the long wavelength region. Among organic acid films, this tendency is the most remarkable with formic acid films.

At the present stage, we have two observations on the photoluminescence of anodic oxide films on aluminium, which are suggestive of the nature of the luminescent centres: (a) Photoluminescence is seen only with anodic oxide films formed in the solution of organic acids; and (b) Photoluminescence of organic acid films show similar responses, i.e., passing through a maximum intensity and decreasing rapidly, when they were heat-treated.

In the previous paper,1 we have assumed that the luminescent centres of anodic oxide films were the carboxylate ions incorporated during the film formation, and supposed that they exist interstitially in amorphous and three dimensional network structures interacting with O–H group from bound water or with the substrate alumina. As established by numerous investigations, heating of anodic oxide films on aluminium produces considerable changes in their structure involving γ- or α-Al2O3 crystallization, lattice rearrangement due to dehydration of bound water similarly as in hydrated oxide, decomposition and subsequent removal of the carboxylate ions.

Figure 5 shows the infrared transmittance spectra of oxalic acid films heat-treated at various temperatures. The double absorption peaks at 1580 cm⁻¹ and 1460 cm⁻¹ are those arising from the resonance between the two possible C–O bonds in the oxalate ion structure, these intensities decreasing slightly with increasing heating temperature up to 600°C. When the oxalic acid films are heated above this temperature, this absorption decreased rapidly and disappeared at 800°C. It may be obvious that the

FIGURE 4  The emission spectra of formic acid films: 1. as-anodized, 2. heat-treated at 450°C, 3. heat-treated at 550°C.

FIGURE 5  The infrared transmittance spectra of oxalic acid films:  as-anodized,  heat-treated at 400°C,  heat-treated at 600°C.
The thermal decomposition of oxalate ions is significant only at temperatures above 600°C. Thermally decomposed oxalate ions would either be removed from the film or be subjected to carbonization which gives the films deep brown shades.

These results suggest that the lattice rearrangement process due to dehydration of bound water by heating may be one of the important factors controlling the photoluminescence of anodic oxide films on aluminium. Such changes may either be reflected in the configuration of the nearest surroundings of the luminescent centres which are presumed to be the carboxylate ions, or may remove the interaction between the luminescent centres and O—H group from bound water. Thus both may give favourable effects on the luminescent centres. These effects may be more pronounced at higher temperatures, being dominant below the peak temperature of PL intensity, since the thermal decomposition of carboxylate ions may not be appreciable in this range. Heating the oxide films above their peak temperatures of PL intensity, the decomposition and subsequent removal of carboxylate ions may become dominant, and such changes cause either irreversible disappearance of the photoluminescence or deep brown colouring of the films. As is clear from our experimental observations referred to above, the remarkable changes of the photoluminescence of anodic oxide films on aluminium are observed by heating them to temperatures below 800°C. On the other hand, γ- or α-Al₂O₃ crystallization has been known to occur at about 800°C for the former and 1170°C for the latter. Consequently, it may be concluded that these changes have no effects on the photoluminescence of the films.

We have suggested that the interaction between O—H group from the bound water and luminescent centres causes deactivation of the excited luminescent centres. Hence, to find the nature of this interaction may be of importance in complete understanding of the luminescent process. It seems that the modes of the interaction between O—H group of a glass surface and the adsorbed molecules which have C=O group may be instructive on this problem. According to Cusumano and Low, the possible modes of such interactions occur through the charge-transfer process. Similar interaction may be expected in our cases.

On the basis of these results and discussion, it may be concluded that the heating of anodic oxide films on aluminium produce two counteracting effects on their photoluminescence: (a) the favourable effect which is due to the removal of the factors deactivating the excited luminescent centres; and (b) the reverse effect which is due to thermal decomposition of the luminescent centres. It may also be concluded that our hypothesis on the luminescent centres of anodic oxide films on aluminium, namely, the carboxylate theory, seems appropriate to explain all the observations referred to in the previous and present papers.

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