Journal of Luminescence 182 (2017) 233–239

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Full Length Article

Structural and fluorescence characterization of anodic alumina/carbon composites formed in tartaric acid solution

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ARTICLE INFO

Article history:
Received 11 July 2016
Received in revised form
5 October 2016
Accepted 19 October 2016
Available online 20 October 2016

Keywords:
Anodic alumina/carbon composite
Tartaric acid
Time-resolved fluorescence spectroscopy

ABSTRACT

Structure and fluorescence properties of anodic alumina/carbon composites formed by one-step electrochemical oxidation of aluminum in aqueous solution of tartaric acid were studied depending on treatment temperature. According to results of Fourier-transformed infrared spectroscopy, during heat treatment at 200–700 °C the composite structure and composition did not change significantly. Only physically adsorbed water and surface OH groups were removed. At 800 °C more pronounced changes were observed, both carbon and CO_2 were partially deleted from the system, implying the reorganization of oxygen sub-lattice in alumina. By means of steady state spectroscopy it was shown that as-anodized and heat treated at 200–700 °C tartaric acid anodic alumina possesses a wide blue fluoresence in the wavelength range 400–750 nm with maximum at around 460 nm. The time-resolved measurements revealed that fluorescence decay is nonexponetial and can be described with at least two decay times of about 0.3 and 1.8 ns. It was concluded that the emission band at around 460 nm can be caused by bulk and adsorbed OH groups, and band at around 550 nm was due to the presence of amorphous carbon.

1. Introduction

Now alumina/carbon composites are considered to be promising materials to purify waste water due to their high sorption capacity and efficiency together as well as low cost [1,2]. Also these materials can be used as the catalysts or the catalyst supports [3,4]. Various approaches such as solution combustion technique [5], template [6], carbon precursor [7], and simple wet chemical [8] methods are used to prepare alumina/carbon composites. However, in our previous investigations we showed that alumina containing amorphous carbon can be obtained by electrochemical oxidation of aluminum in aqueous solutions of organic acids [9]. Optical properties of thin carbon-bearing anodic alumina films formed in aqueous solution of tartaric acid at current density 60 A m^{-2} were studied. It was shown that band gap value depends on the structure of carbon-bearing components [9]. It was also reported on the formation of alumina/graphene composite films with an unprecedentedly low optical gap (1.53 eV) and an exciting chemical inertness via aluminum anodizing in a tartaric acid solution at extremely high current densities that exceed burning initiation [10]. Structural, optical, and physical chemical properties of anodic alumina strongly depend on the synthesis conditions [11–13]. As it is known, with linearly increasing anodizing current density the concentration of electrolyte components in porous anodic alumina logarithmically increases [14]. So, in the present work we aimed to study the peculiarities of chemical composition and fluorescence properties of the anodic alumina/carbon formed in tartaric acid solution at high current densities and to establish the changes in the system during heat treatment, especially with regard to the role of adsorbed carbon-bearing components and hydroxyl groups.

2. Materials and methods

2.1. Anodizing

The high-purity aluminum foil (99.99 wt.%, 100 μm thick, 15 × 15 mm, AlfaAesar) was used as a starting material. The aluminum specimens were pretreated in a hot solution of 1.5 M NaOH for 15 s, neutralized in 1.5 M HNO_3 for 2 min, then carefully rinsed in distilled water and air-dried. Anodic alumina was formed by double-sided anodizing of aluminum specimens in the 0.4 M aqueous solution of tartaric acid at the constant current density

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http://dx.doi.org/10.1016/j.jlumin.2016.10.026
0022-2313/

700 A m^{-2} and in the 0.3 M aqueous solution of oxalic acid up to the moment when the aluminum was completely oxidized. At the steady state of oxide growth the voltage was of about 205 and 60 V for tartaric and oxalic acid, respectively. The anodizing process was carried out in two-electrode glass cell, in which platinum grid was used as a counter electrode. The solution was stirred by a magnetic stirrer, and the temperature was maintained at a constant value (18.0 ± 0.1) °C by cryostat Lauda (WK 230). The anodizing process was controlled by a direct current power supply GW Instek (GPR–30H100). If indicated, the samples were annealed in temperature range 200–800 °C in air in programmable muffle DM 50 (Zhermack) for 2 h.

2.2. Characterization

Surface morphology of the carbon bearing anodic alumina films was analyzed by scanning electron microscopy (SEM) on a LEO 1402 (Leo Electron microscope). Image analysis was performed by ImageJ software. The carbon content was determined using carbon/sulfur analyzer CS-2000 (Eltra).

The chemical composition of the films was characterized by Fourier transform infrared (FTIR) spectroscopy using a Vertex 70 (Bruker) FTIR spectrometer. The transmission spectra were collected at room temperature in the 500–4000 cm^{-1} wavelength region with a resolution 4 cm^{-1} and 256 averaging scans. A large number of scans was accumulated in order to bring the signal-to-noise ratio to a good level.

Fluorescence spectra were measured with a time-correlated single photon counting spectrometer Edinburgh-F900 (Edinburg instruments). A picosecond pulsed diode laser EPL-375 emitting picosecond (76 ps) duration pulses was used for the excitation at 375 nm with an average power 0.15 mW mm^{-2}. The pulse repetition rate was 5 MHz and the time resolution of the setup was about 100 ps taking into account temporal deconvolution procedure. All fluorescence spectra were corrected for the instrument sensitivity.

For the time-resolved fluorescence measurements a femtosecond Yb:KGW oscillator (Light Conversion Ltd.) was employed. The oscillator produced 80 fs 1030 nm light pulses at 76 MHz repetition rate, which were frequency tripled to 343 nm (HIRO harmonics generator, Light Conversion Ltd.), attenuated, and focused into ~100 μm spot on the sample, resulting in about 1 mW mm^{-2} average excitation power. The maximum time resolution of the whole system was about 5 ps were taken with a Hamamatsu streak camera under the excitation wavelength of 343 nm.

Electron spin resonance (ESR) signals from the as-anodized and heat-treated anodic alumina films were recorded by the standard method [15] on a SE/X 2543 (Radio PAN) radiospectrometer operating in the X-band (f=9.31 GHz) with modulation of a constant polarizing magnetic field B with the frequency 100 kHz and the amplitude 0.1 mT. The spectra were registered at room temperature, in the air in darkness. The sensitivity of the spectrometer was about $3 \cdot 10^{12}$ spin mT^{-1}. A ruby crystal glued to the inner wall of the H_{102} cavity (the glue that did not give an ESR signal was applied) was used to monitor the cavity gain, to tune the phase modulation of the magnetic field, and to calibrate the magnetic component of the microwave electromagnetic radiation.

3. Results and discussion

3.1. Surface characterization

Anodic alumina films formed in 0.4 M aqueous solution of tartaric acid at 700 A m^{-2} are black (Fig. 1, inset). Even though in our experiments the two times higher current density applied than the one in [12,16,17] aluminum anodizing in organic acid solutions, burning phenomenon did not occur. According to SEM studies, the anodic alumina films possessed typical well-ordered porous structure with pore diameter 98–100 nm and pore interval 440–445 nm (see Fig. 1). It should be also noted that our results agree with the data previously obtained for the tartaric acid anodic alumina formed under different anodizing conditions [9,12].

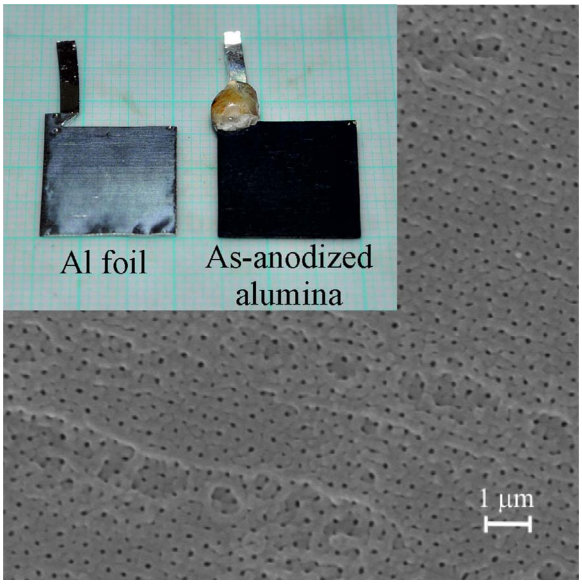

Fig. 1. SEM imaging of the surface of anodic alumina films formed in 0.4 M aqueous solution of tartaric acid. The inset is surface appearance of the aluminum specimen and as-anodized sample.

3.2. Structural characterization

Chemical analysis was carried out to determine the carbon content; in the as-anodized film it was at about 3.2 wt%. These data are comparable with the ones obtained before [18] for oxalic acid anodic alumina. The carbon content was determined to be 2.5 wt%. As it was also shown, the carbon-containing components affected the structural and physical chemical properties of the anodic alumina and possessed high thermal stability up to 1075 °C. Therefore, it should be taken into account while analyzing of FTIR and fluorescence spectra of the heat-treated tartaric acid anodic alumina films.

FTIR transmission spectra for as-anodized and heat-treated at 200–800 °C carbon-bearing anodic alumina films are shown in Fig. 2. In the FTIR spectrum of as-anodized film the following regions can be found:

(i) an unresolved broad band at 1200–500 cm^{-1} that is attributed to stretching vibration of the Al–O–Al bonds. This band is characteristic of amorphous alumina;

(ii) an unresolved broad band at 1750–1250 cm^{-1}, due to C–O stretching vibration in carboxylate and carbonate ions. Certain band assignment to COO^{-} or CO_3^{2-} ions is impossible as bond vibrations of these groups are very close;

(iii) a medium-strong band centered at *ca.* 2137 cm^{-1}, due to C–O stretching vibration in adsorbed CO molecule. The band position is only *ca.* 6 cm^{-1} lower than the frequency of the gas (2143 cm^{-1}), indicating an extremely weak interaction with alumina [19];

(iv) a strong band at *ca.* 2340 cm^{-1}, due to C=O stretching modes in CO_2 molecule. The CO_2 peak position is *ca.* 7 cm^{-1} lower than the gas frequency ($\nu_3(CO_2)$=2347 cm^{-1}), suggesting the presence of weakly held linear end-on Al^{VI}–CO_2 complexes