



Luminescence of Eu ion in alumina prepared by plasma electrolytic oxidation



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ABSTRACT

Eu ion luminescence in aluminium oxide nanocrystals and layers prepared by plasma electrolytic oxidation (PEO) are investigated in this study. The Eu ion in PEO coatings has intense luminescence allowing such material to be used for preparation of various phosphor materials. In this study, Eu ion doped coatings were prepared with two methods: anodization and pulsed bipolar plasma electrolytic oxidation. Also, for comparative studies, alumina nanocrystals with the same amount of Eu ions were prepared using Sol Gel and molten salts methods.

Obtained Eu-doped coatings were studied using luminescence methods. Typical Eu ion luminescence bands were observed, however intensity and spectral distribution differs drastically depending on preparation method and parameters used, therefore the Eu ion luminescence could be used as coating quality luminescent probe. Additionally, the possibility to incorporate the Eu ions in trivalent or divalent state exhibiting bright red and blue luminescence accordingly was demonstrated by using different oxidation parameters. Moreover, comparison measurements between powder samples and coatings were made.

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1. Introduction

To improve chemical and mechanical properties of aluminium surfaces wide variety of coatings are used. In most cases, these coatings are made of Al₂O₃ (alumina) (doped and undoped). Some surface oxidation methods like anodizing (AN) are widely used for almost a century, but intense research of plasma electrolytic oxidation (PEO) method and its applications started only about 60 years ago, when production of lightweight and durable materials became important in manufacturing space satellites. During the last decades, PEO gained even more interest due to possible applications in many fields (e.g.) and promising research results. The main advantages of PEO method are simple metal surface processing, short coating formation time and possibility to obtain modified coatings by using different electrolytes. Coatings formed with PEO process demonstrate enhanced hardness, better wear resistance, reduced coefficient of friction, good thermal properties as well as

good corrosion resistance [1], however all these properties cannot be obtained for the same coating and in single PEO process.

Nowadays, aluminium oxidation processes are widely studied, although one can notice that researches are done using different aluminium alloys, different discharge parameters, different electrolytes etc. Not only the material and preparation procedure differs, but also the coating investigation methods are different, making result comparison very difficult.

Mostly SEM, XRD and microhardness measurements were carried out to investigate the coating quality, however these methods are time consuming and not sufficient, therefore other approaches would be useful. Many metal oxides are luminescent materials and since the luminescence is very sensitive to the material quality it could be used for oxide coating characterization. The spectroscopic studies of light emission from plasma during PEO process already offered promising results [2–5] but we were not able to find any luminescence property studies of PEO coatings, although such measurements could give additional information about PEO process and coating quality.

Recently it was found that incorporation of different rare earth (RE) ions enhance corrosion resistivity and hardness of magnesium alloy coatings [6–10]. The RE ion dopants are also famous for their luminescence properties and the luminescence of PEO

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coatings modified by RE ions is worth of investigation. The present study is dedicated to the investigation of luminescence properties of pure and Eu doped alumina coatings formed on aluminium by anodizing as well as by PEO process. It is well known that aluminium oxide compounds have very good luminescence properties, therefore alumina doping with RE not only enhances mechanical and chemical properties of PEO coatings but also can be used as luminescent quality probe and thus opens new application opportunities.

The Eu ion luminescence is widely studied and Eu ions show very intense luminescence in different host materials, therefore Eu ion was chosen as luminescence centre in samples investigated in the present study. The Eu ion can be incorporated in different matrices as Eu³⁺ or/and Eu²⁺. The most intense luminescence bands of Eu³⁺ ion in alumina are from ⁵D₀ to ⁷F₁ magnetic electron dipole transition and ⁵D₀ to ⁷F₂ electric electron dipole transition. The luminescence intensity ratio of magnetic and electric bands is known as symmetry factor – the larger the ratio the larger symmetry of local crystal field. These luminescence bands appear in the “red” side of spectrum (~ 590 and 610 nm) and are relatively narrow. The luminescence band associated with Eu²⁺ appears in the “blue” range of spectrum and is wide. Therefore the luminescence spectra can provide information about Eu ion charge state in material. The local crystal field in surrounding of Eu³⁺ ion determines its luminescence band position, therefore Eu ions could be used as luminescent probe for host structure and defect studies [11,12]. For example, in case of zirconia Eu luminescence can be used as method for crystal structure determination [13]. This could be useful because PEO coatings can consist of amorphous and crystallic α, γ and β alumina phases [14]. In future, such luminescence study probably could be applied for PEO coating quality control, but since we could not find the luminescence study conducted on PEO coatings up to now, only the preparation of Eu doped PEO coatings on aluminium and their luminescence properties investigation was carried out.

2. Experimental

2.1. Sample preparation

For anodization and PEO experiments two types of Al sheets were used: pure Al 99.999% (NewMet) and 1 wt% Eu doped Al (American Elements) CAS#7429-90-5. Both sheets were polished with SiC sandpapers followed with diamond pastes (50, 10, 2 and ~0.5–1 μm). Surface roughness before oxidation was Ra ≈ 0.3 μm. After polishing, sheets were covered with plastic film and cut with water jet cutter with kerfs size of 0.5 mm to form a set of samples all having the same surface area – 15 cm². After jet cutting, plastic film was removed and samples were washed with acetone followed by ethanol and dried.

2.2. Anodization

The anodic porous alumina layer was formed by a one-step 15 min anodization procedure under a constant cell voltage of 20 V in a 0.3 M oxalic acid (Sigma Aldrich) at the 20 °C temperature. A Pt foil with a surface area of 20 cm² was used as counter electrode and the distance between electrodes was 2 cm. Electrolyte solution was stirred in 250 mL cell. Obtained samples were washed with deionised water and dried in air. Homogenous white coatings were obtained on Al surface.

2.3. Plasma electric oxidation

For plasma electric oxidation processes, custom 5 kW bipolar current impulse generator ELGOO PEO v3 (Applied Electronics labs)

was used. The pulse amplitudes, duration and repetition rate were adjusted during the oxidation process from external PC running unique software LPEO v2.8 (Applied Electronics labs). The same Pt electrode was used as counter electrode and distance between electrodes was 2.5 cm. 1 L water cooled glass jacketed beaker was used for all PEO experiments. The simple electrolyte containing 2.24 g/L KOH was used to reduce number of possible extrinsic defect sources, however similar luminescence properties were also obtained by using other electrolytes. Electrolyte solution was continuously stirred during PEO process.

2.4. Sol-gel and molten salt methods

To compare luminescence spectral distribution two alumina samples doped with the same amount of Eu were prepared in two ways: Sol-gel and molten salt methods [15–18].

For samples prepared by molten salt method aluminium nitrate nonahydrate and europium nitrate hexahydrate were mixed in necessary proportions and ground in agate mortar for about 30 min. The NaNO₃ and NaCl with a molar ratio (0.85:0.15) were used as components for molten salt. The powders of all components together were ground in agate mortar for about 30 min. The obtained mixture of powders was heated to 400 °C for 2 h, followed by rapid cooling to room temperature. Obtained white solid was washed with deionised water and filtered through 0.3 nm cellulose nitrate membrane filters, then dried at 100 °C for 24 h.

In case of samples prepared by sol-gel method glycine was used as fuel and nitric acid as oxidant. Aluminium nitrate nonahydrate and europium nitrate hexahydrate were dissolved in deionised water. The molar concentration of all metal ions in the solution was adjusted to 0.2 M. The molar ratio of metal ions and glycine was 1:2 and molar ratio of glycine/NO₃⁻ was 0.7. The appropriate amounts of metal solutions and glycine were mixed and resulting mixture was evaporated on hot plate while stirring at 80–90 °C and concentrated until a gel consistency was reached. The gel was heated up to 150 °C in an open oven for 2 h until resulting powder became black. Black powder then was heated up to 500 °C in an open oven for 2 h. All chemicals used were reactive grade and supplied by Aldrich. Finally, all powders were calcined at 1000 °C or 1400 °C in air for 2 h. After this process, the calcined powders became white.

The designations of samples, methods of preparation as well as parameters of treatment and oxidation processes are collected in Table 1.

2.5. Morphology and structure measurements

The energy-dispersive X-ray analysis (EDX) of the samples was performed using S4 Pioneer (Bruker AXS) in order to examine the Eu concentrations and to verify the presence of impurities. The crystalline structure of the samples was examined via X-ray diffraction (XRD) using an X-ray diffractometer (D8 Advance, Bruker AXS). The crystallite size was calculated from the broadening of the diffraction peaks using DIFFRAC plus BASIC Evaluation Package (EVA) Release 2007 (Bruker AXS) software.

The surface roughness measurements were performed on Dek-tak 150 (Veeco) using 0.2 mg loading force and needle radius was 12.5 μm.

2.6. Optical measurements

The luminescence measurements were carried out using YAG laser FQSS266 (CryLas GmbH), fourth harmonic, 266 nm (4.66 eV) as excitation source. The luminescence spectra were recorded using the Andor Shamrock B-303i spectrograph equipped with a CCD camera (Andor DU-401A-BV) in one exit port and for luminescence decay kinetics the PMT H8259-02 (Hamamatsu) was connected at

Table 1

Alumina coatings and powder sample names and description.

Sample name	Preparation method	T (°C)	U+ (V)	U- (V)	I+ (mA/cm ²)	I- (mA/cm ²)	T+ (ms)	T- (ms)	Prep. time	Eu (wt%)
14.13b	Sol-gel	1000	–	–	–	–	–	–	2 h	0.98
14.13	Sol-gel	1400	–	–	–	–	–	–	2 h	0.98
14.14	Molten salts	1400	–	–	–	–	–	–	2 h	1.09
11.30	PEO	–	350	100	20	20	1	1	20 min	–
11.68	PEO	–	350	100	20	20	1	1	10 min	0.79
11.72	PEO	–	325	100	60	50	5	1	10 min	0.95
11.75	PEO	–	300	100	180	90	5	1	10 min	1.03
11.92	Anodizing	–	20	0	60	0	–	–	15 min	0.68

other exit port. All luminescence measurements were conducted at room temperature and are not spectrally corrected as only comparative analysis and peak positions are studied.

3. Results and discussion

We succeeded to create the oxide coatings on aluminium with the typical Eu³⁺ ion luminescence bands (Fig. 1). With both oxidation methods (AN and PEO) the Eu incorporation was verified, however the PEO sample 11.75 showed significantly higher luminescence intensity. The higher luminescence intensity of PEO sample 11.75 over anodized 11.92 sample could be related to the fact that anodized coatings are more amorphous. It was impossible to observe XRD peaks related to alumina crystalline phases, even if the sample was anodized for 2 h. Moreover, EDX showed significant presence of oxide in such sample.

In both cases the most intense band is located at 613 nm, which origin from ⁵D₀ to ⁷F₂ electron transition in Eu³⁺. This broad band (605–630 nm) consists from multiple peaks associated with the same electron transition of Eu³⁺ in different crystal fields-surroundings. The studies of these peaks could give additional information about structure and defects in PEO coating.

To study and compare the Eu³⁺ luminescence of PEO coatings, Eu doped alumina powder sample was prepared by Sol Gel method. The first Sol Gel sample 14.13b was annealed at 1000 °C, sufficient for crystal phase formation and the second 14.13 at 1400 °C, at which the α-alumina phase was formed. As expected, the difference of annealing temperature leads to the formation of different structures and different crystalline grain sizes. The sample 14.13b annealed at lower temperature is a mixture of β and γ phase with crystalline grain size 40 nm, whereas sample 14.13 annealed at higher temperature shows α- alumina phase (Fig. 2b) with grain size 230 nm. In addition, XRD spectra for samples annealed at high temperatures shows presence of EuAlO₃ phase. The sample 14.14 was prepared by molten salt method and annealed at 1400 °C. The XRD of sol-gel 14.13 sample and molten salt 14.14 sample showed almost identical spectra (Fig. 2b) and also the crystalline grains sizes

was close 247 nm, thus the phase of alumina is more dependent on annealing conditions and less on sample synthesis method.

The Eu³⁺ luminescence intensity of PEO sample 11.75 was close to powder samples. Similarly to PEO coatings, powder samples showed broad bands which consist from overlapping luminescence peaks (fine structure) of Eu³⁺ ion in different surroundings (Fig. 2a). These different Eu³⁺ surroundings were expected due to possible defects near Eu³⁺ sites. The result is very different from Eu³⁺ luminescence pattern, however to determine these differences and find their cause further experiments and detailed luminescence spectra analysis is needed. First of all, one can be noticed that samples 14.13 and 14.14 annealed at 1400 °C have narrower fine structure bands, which could be related to better crystal structure and larger crystal sizes. Secondly, the luminescence band intensity ratio related to ⁵D₀ to ⁷F₁ and ⁵D₀ to ⁷F₂ electron transitions is higher for these powder samples, which could be an indicative parameter for higher symmetry related to α-alumina, however this symmetry ratio factor could also be strongly affected by defects. Thirdly the

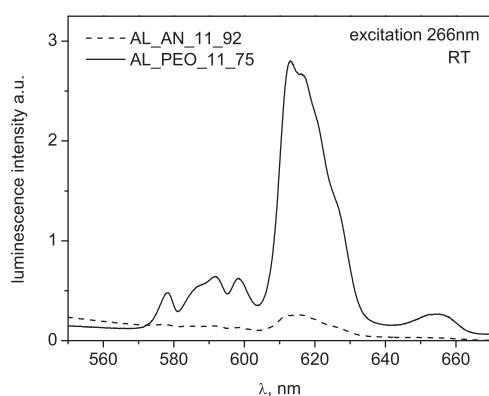


Fig. 1. Eu ion luminescence from anodized and PEO alumina coatings.

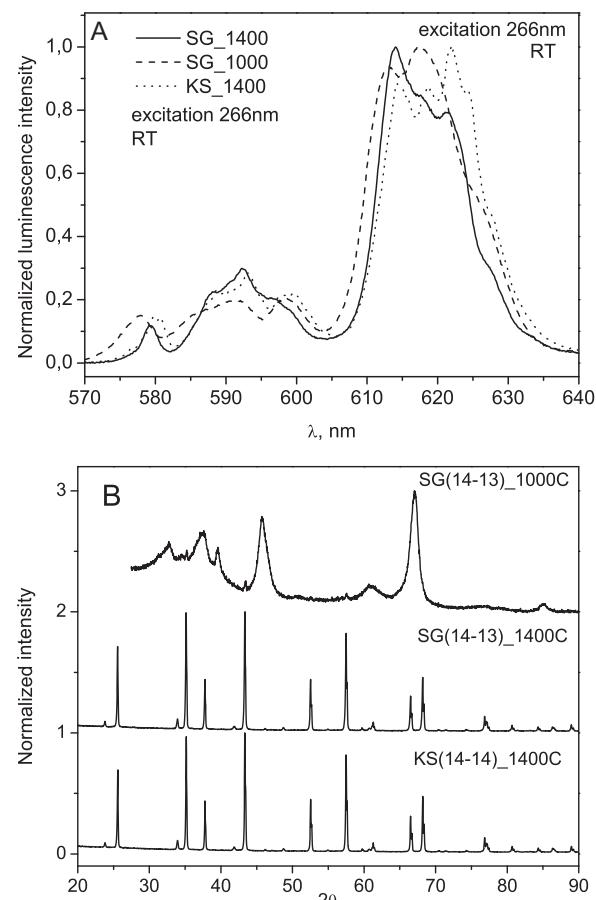


Fig. 2. Eu³⁺ ion luminescence (a) and XRD spectra (b) of sol-gel and molten salt powder samples.

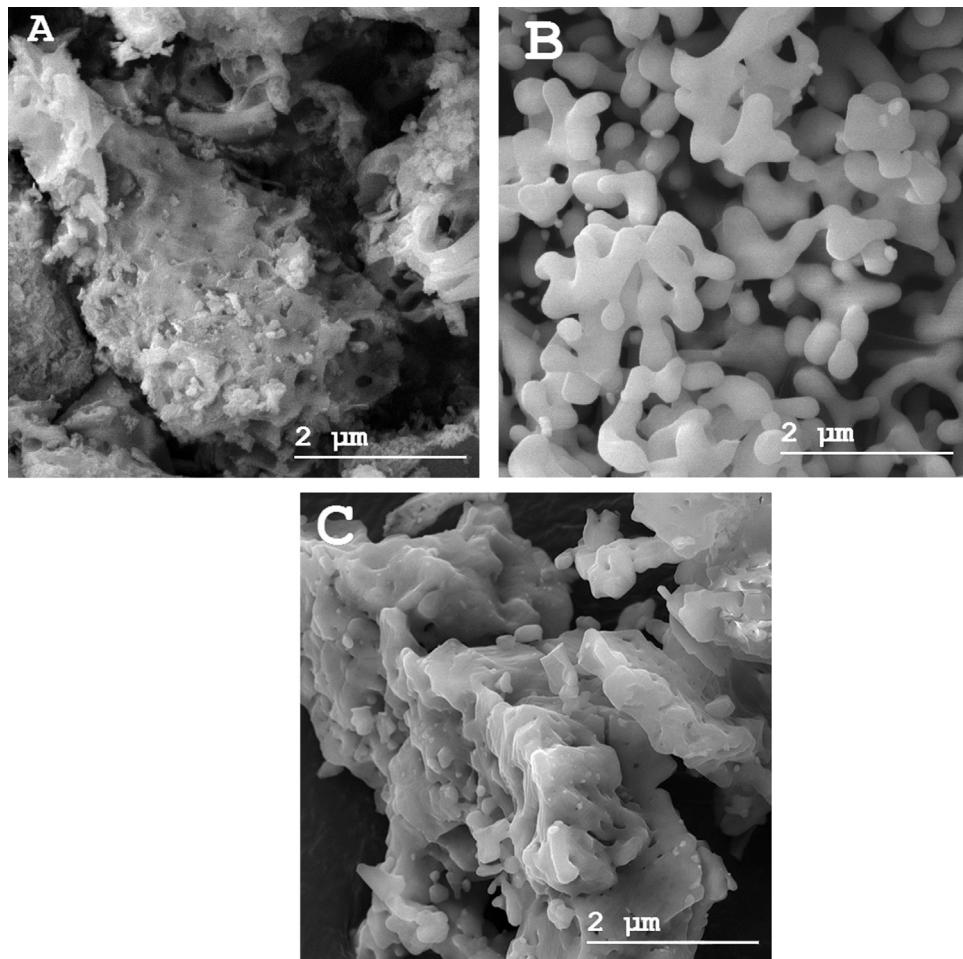


Fig. 3. SEM images of powder samples prepared by Sol Gel method annealed at 1000 °C (a), annealed at 1400 °C (b) and samples prepared by molten salt method and annealed at 1400 °C (c).

luminescence bands of Eu³⁺ are shifted to lower energies compared to sample annealed at lower temperature.

Fine structure-decomposition of the broad band related to ⁵D₀ to ⁷F₂ transition by Gaussians revealed that these fine structure bands are related to the same energies for both samples with α -alumina phase (indicated by arrows in Fig. 2) and differ from sample annealed at lower temperature. Also, the fine structure band intensities in samples prepared by different methods differ, which could be related to different defect distribution in these samples. SEM images prove that the samples annealed at 1400 °C have very different morphology (Fig. 3).

The morphology of the prepared powder samples is different. The sol-gel sample annealed at 1000 °C have fine grains and inhomogeneous agglomeration, whereas the same powder annealed at 1400 °C shows network type morphology, which strongly differs from the sample prepared by molten salt method. These morphology differences could lead to different surface defects, which can explain differences in Eu³⁺ luminescence spectra fine structure.

Similarities can be found in luminescence spectra of powders and PEO coatings, however in PEO coatings a contribution from different luminescence lines is less visible (Fig. 1). This could indicate that the crystallinity of PEO coating is worse than that of powders. The XRD reflection peaks of α -Al₂O₃ for coatings are weak and hard to measure due to their thin size. The estimated grain size for coating sample 11.68 is 44 nm.

We noticed that by changing the PEO parameters it is possible to change the Eu³⁺ luminescence intensity. To understand this

observation we prepared three Eu doped PEO coatings with different Eu³⁺ luminescence intensity (Fig. 4).

Discharge type and also anodic/cathodic current ratio plays significant role in preparation of coatings with intense Eu³⁺ luminescence. If the voltage at the process start exceeds 350 V white

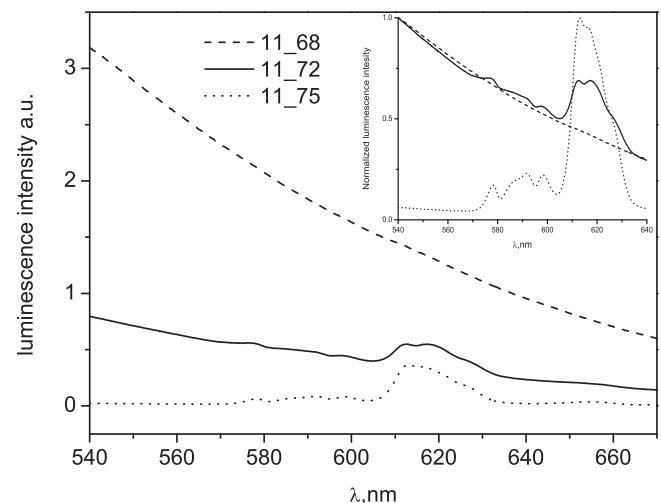


Fig. 4. Luminescence spectral distribution of three PEO coatings with different Eu³⁺ luminescence intensity, the inserted graph shows normalized intensity.

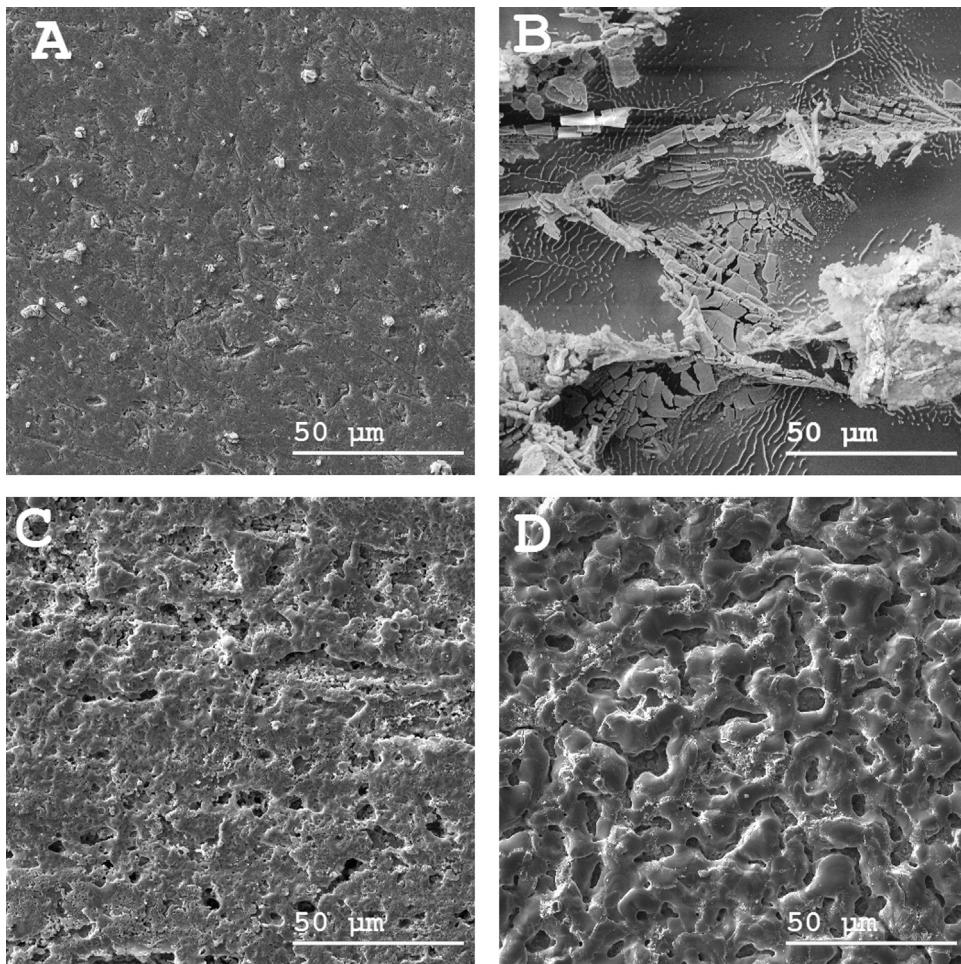


Fig. 5. The SEM images of anodized sample 11_92 (a), and PEO samples 11_75 (b), 11_72 (c) and 11_68 (d).

large discharge sparks appear and Eu³⁺ luminescence intensity in final layer decreases. This Eu³⁺ luminescence decrease could be related to Eu recharging from Eu³⁺ to Eu²⁺ as well as differences of Eu ion diffusion during different discharge types. The current in case of white discharges is significantly smaller and anodic/cathodic current ratio is close to 1:1, whereas in case of layer with well expressed Eu³⁺ luminescence the ratio was close to 1:2. The ratio of anodic and cathodic currents has significant effects on PEO coatings—the surface roughness, morphology, phase composition, microstructure and other properties are affected. [19].

Similarly to powders, in PEO coatings the Eu luminescence properties are strongly dependent on morphology, which also determines the type and distribution of different intrinsic defects. The morphologies seen in SEM images (Fig. 5) of PEO coatings with “blue” luminescence are very similar to ones described by other authors [20,21]. Also the surface roughness of coatings are very different: for sample 11_75 with “red” luminescence $R_a = 5.5 \mu\text{m}$, whereas for sample with “blue” luminescence 11_68 $R_a = 0.4 \mu\text{m}$.

The Eu³⁺ recharging to Eu²⁺ was previously observed by other researchers [22–23]. In addition, it is well known that in various aluminates the Eu incorporates as divalent [24–26]. For example, in case of strontium aluminates if the sample is prepared in reduced atmosphere (oxygen poor), then Eu ions incorporate in divalent state, otherwise in trivalent state [27]. In pure alumina “blue” band is related to intrinsic defects and was studied previously by a number of researchers with conclusion that the intrinsic luminescence bands are dependent on alumina structure [28,29]. Based on this fact, we looked concentrated our attention on the

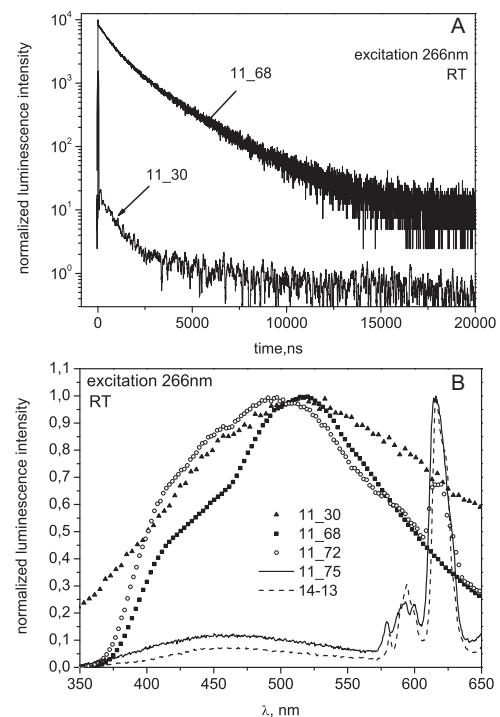


Fig. 6. Luminescence decay kinetics measured at 500 nm (a) and the “blue” and “red” luminescence of PEO coatings and Sol gel powder (b).

“blue” luminescence band present in PEO coatings (Fig. 6b). The “blue” luminescence band intensity of Eu doped sample 11_68 is about 50 times stronger than in sample 11_30 without Eu. This strong luminescence increase could be explained by Eu recharging from Eu down to 2+ state or by the intrinsic defect concentration increase induced by Eu ion incorporation.

The possible Eu²⁺ luminescence band position in alumina overlaps with intrinsic luminescence bands of alumina but the intrinsic luminescence decay times for undoped 11_30 and Eu doped 11_68 differ significantly (Fig. 6a). The luminescence decay of blue luminescence at 500 nm for pure 11_30 sample can be approximated by two exponents with decay times of 23 ns and 1.3 μs, whereas for Eu doped samples luminescence decay have complex origin. In addition, one can notice that luminescence decay time of Eu doped PEO coating is significantly longer which is typical for partially forbidden Eu electron transition.

Due to the large ionic radii differences of Eu and Al, Eu incorporation in low symmetry sites is expected, thus in more crystalline α-alumina coatings the Eu could agglomerate or incorporate in grain boundaries which could lead to charge state changes.

Further studies on processes and formation of PEO layers for “red” or “blue” luminescence in Eu doped PEO coatings are needed

4. Conclusions

The coatings doped with Eu ions were prepared and the Eu ion luminescence of PEO alumina coating was observed.

The luminescence from Eu³⁺ ion of powder samples and PEO coatings were close, which means that PEO could be applied to produce alumina coatings for luminescent applications.

The Eu³⁺ luminescence spectral distribution depends on structure and defects. It is proposed that analysis of Eu³⁺ electron transition from state ⁵D₀ to ⁷F₂ luminescence band analysis could give information on PEO coating structure and impurities.

It is possible to obtain “red” or “blue” luminescence from PEO coatings by varying the PEO parameters. Moreover, the ratio of “blue” and “red” bands can be adjusted.

The “blue” luminescence could be related to Eu²⁺.

The coatings with Eu³⁺ luminescence have significantly higher surface roughness.

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