



**UNIVERSITY
OF LATVIA**

FACULTY OF PHYSICS, MATHEMATICS AND OPTOMETRY

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**OPTICAL PROPERTIES OF PLASMA
ELECTROLYTIC OXIDATION COATINGS ON
ALUMINIUM ALLOY SURFACE**

SUMMARY OF DOCTORAL THESIS

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Subfield of Material Physics

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Annotation

Plasma Electrolytic Oxidation (PEO) is a process for producing thick (tens of microns), hard and chemically stable oxide coatings on metal surfaces. For decades, the process is under investigation by both scientific and industrial communities due to the low operational cost and ease of production. Due to the flexibility of the process, in the last couple of years, novel possibilities of PEO are quickly emerging: biocompatibility, antibacterial, photovoltaic, photocatalysis and other properties of the coatings are intensively studied.

This work explores the different aspects of luminescence properties of PEO coatings which was not studied prior. Both process modification possibilities and practical applications are studied, with the focus on correlation between synthesis parameters and optical properties of the coatings.

Three main topics are covered in this thesis:

- 1) Doping of the coating oxide structure with additives that alter the luminescence output
- 2) Production of coatings with dosimeter properties and evaluation of their performance
- 3) Synthesis of complex oxide structure of doped strontium aluminate thus creating persistent phosphorescent coatings

In combination with inherited PEO properties like outstanding hardness, great adhesion to the surface, chemical stability and quick production, the added luminescence properties can make this coating technology promising for practical applications in various fields of science and technology.

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1. Introduction

From all the coating techniques Plasma Electrolytic Oxidation (PEO) stands out as one producing the best adhering, hardest, most chemically stable and easily reproducible coatings on valve metals. Thanks to the many desirable characteristics and in combination with acceptable cost and ease of production of the PEO, the process gained large interest in both scientific and industrial communities. In addition, large amount of variable parameters allows the process to be modified to meet specific needs of each individual application. Historically, the process is mainly used to improve mechanical and chemical characteristics of Al, Ti, Mg, Zr metals and their alloys by creating a thick (hundreds of microns) protective oxide coating on the surface. However, the ability to create crystalline structures and implement dopant atoms in the lattice makes PEO process suitable for production of “functional” coatings – ones with added benefits of increased luminescence output or the ability to convert one type of energy to another (e.g. X-rays to visible light). Although the process is suitable, there is a notable lack of studies on the PEO coatings with the focus on their luminescent properties, thus thorough search for practical applications of the technology should be performed.

1.1. The aim of work

The aim of this work is to explore the possibilities for PEO coating technology to be used for production of coatings with enhanced luminescent properties.

The following tasks are set:

- 1) explore the different possibilities to dope the coating oxide structure with additives that alter the coating luminescence;
- 2) produce a PEO coating with dosimetric properties for detection and quantification of ionizing radiation;
- 3) explore the ways to create a persistent luminophore coating using PEO.

1.2. The contribution of the author and the scientific novelty of work

The author of this work participated in the PEO setup development: the development of software for automation of PEO process that allows dynamic pre-defined control of all electrical parameters and registration of measured voltage and current. The software is described in more detail in section 3.1.2. Additionally, some modifications of PEO setup were performed to improve crucial parameters of the device (cooling, ventilation, sample holding).

The author developed the software for thermostimulated luminescence (TSL) setup that was used to evaluate the dosimetric properties of the coatings. In

addition, some hardware modifications were performed by the author in this and other luminescence measurement setups.

PEO sample synthesis was performed by the author unless stated otherwise in the corresponding publications. Same goes for the data analysis, luminescence measurements, the electron microscopy and structure measurements. Other contributors in measurements, data analysis and publication of the results in peer reviewed journals are reflected in the author list of respective publications in section 6.3.

The author of this work is a main author of three publications related to the topic of this work, is a co-author of 3 PEO-related publications and co-author in 27 other scientific publications in indexable peer-reviewed journals. Full list of publications can be found in section 7.

The author is a scientific advisor of one defended bachelor's thesis connected with the development of PEO luminescent coatings and one bachelor's thesis about the dosimetry of alumina oxide.

2. Literature review

2.1. Electrolytic passivation processes

With the development of electric circuits and discovery of electrolysis the ability to increase the thickness of naturally occurring oxide layer on various metal surfaces emerged. The science of anodization investigates the possibilities to use the electric potential to controllably increase oxide layer on the metal surface. The electric circuit for electrolysis is therefore implied – the part to be coated is the anode (hence the term “anodic alumina oxide” or AAO in case of coatings on aluminium) with the counter-electrode (often inert metal like platinum, however, other options are possible) as the cathode. Due to the widespread use of the process, the parameters of the process are well-established: anodization usually is performed in slightly acidic or neutral electrolytes (pH 5-7) (Diggle et al.) (Keller et al.) using constant voltage in range of 10-100V.

The PEO is a method to produce ceramic coatings on various metal and alloy surfaces exhibiting outstanding corrosion, thermal, electrical and mechanical properties. Naturally, PEO evolved from conventional anodization by application of substantially higher current and voltage to the part so that the electrical discharge will occur through the anodized oxide layer. The characteristic factor of PEO is the use of high voltage power supply to apply the DC, AC, bipolar or modulated DC electrical power on metal in appropriate electrolyte. The process is of high interest for industrial applications due to the relatively low time of production, wide variety of metals that can be coated (Zn (Grigorjeva et al.), Mg (White et al.), Ti (Aliofkhazraei and Rouhaghdam; Martini et al.), Ta, Hf, Nb, Zr and others), eco-friendly resource use and ease of scalability; therefore, the technology is already applied in various fields - aviation, automotive, medicine and biology, maritime transport and others. Historically, PEO coatings are used for their outstanding mechanical and chemical properties – the benefits of a thick layer of oxide on a metal prone to corrosion and scratching are hard to replicate with other coating methods (paints, anodization). However, the variability of composition, possibility to obtain crystalline structures and relative simplicity of experimental setups motivated scientists to expand the list of possible applications and create functional, optical and other non-conventional coatings.

The successful use of PEO implies precise control of all variable parameters to get desired and reliable results. When compared to anodization where electrodes, electrolyte and voltage should be carefully thought through, PEO includes even more power supply parameters (especially in pulsed bipolar DC mode) and exhibits even greater dependence on quality, composition, and temperature of the electrolyte. Although the amount of variable parameters is overwhelming at first, it offers additional possibilities to control the structure and composition of the

coating and adds the ability to include foreign atoms in the crystalline lattice of the oxide - an extremely useful property for modification of luminescence properties of the layer.

2.2. Luminescence

Luminescence is a spontaneous emission of light by electron radiative transition from higher energy level to lower (Fox). For electron to emit a photon by decrease of its energy, firstly the energy should be increased via the “excitation” process, therefore a broad field of luminescence is usually divided into the subsections by specifying the excitation process – e.g. photoluminescence (PL), x-ray luminescence (XRL), bioluminescence and so on. Light emitting displays, most of the modern lighting options, glow-in-the-dark toys and emergency signs all use some type of luminescence and even more possible applications are still under investigations in medicine, transportation, science, space, military and sport industries.

This study will mainly focus on two major application fields of luminescence – **dosimetry** (use of materials for storage of some of the energy acquired from ionizing radiation with the ability to “trigger” the energy release by a specific process thus determining the acquired dose) and **long-lasting luminescence** (use of materials for storage of some of the energy acquired from external sources for a subsequent gradual release of it in a form of light). While in-depth explanation is required to properly describe both fields, it is important to note that both fields are application-driven and therefore are widely used in industry for decades.

First PEO coatings with the specific purpose of studying their luminescence properties were created in 2015 (Smits et al.); however, while other studies were performed later to investigate luminescence of different ions in PEO (e.g. (S. Stojadinović et al.) (Stevan Stojadinović et al.)), no real application-driven studies were performed until recently (2018, (Bite et al.)), and no real study got the PEO luminescence further than TRL4 yet. This shows the relative novelty of the field with large potential for rapid development and adaptation.

3. Results and discussion

3.1. Methodology

3.1.1 *Characterisation*

Throughout the studies, various setups were used for evaluation of crystalline structure, analysis of elements in the coatings as well as morphology and coating thickness. Although reader is advised to check the publications associated with “Results” chapters, main devices are as follows:

X-Ray diffraction (XRD) was measured using two setups: a table-top device Rigaku MiniFlex 600 and more advanced device PANalytical X’Pert Pro diffractometer with Cu K α radiation (1.5418 Å).

SEM top-view and cross-section images were taken using either table-top SEM Phenom Pro or a Tescan Lyra SEM equipped with energy dispersive X-ray spectrometer (EDX) operated at 15 kV for element mapping.

Transmission electron microscopy (TEM) measurements in Al₂O₃:C and strontium aluminate coatings were done on Tecnai G2 F20, FEI operated at 200 kV. The samples for TEM studies were scratched from coating using diamond pen and placed on a lacy carbon coated grid AGS166-4 (Agar Scientific).

Although most PEO studies use the wide range of mechanical and chemical testing equipment to evaluate the performance of the coating from a structural stand point, the studies in this work disregarded those measurements as the focus was set on enhancing the luminescence properties. However, the assumption of good mechanical resilience can be made from the large thickness of the coatings and the harder crystalline phases of alumina present in some coatings.

For luminescence measurements, two setups were used: Andor Shamrock SR-303i spectrometer coupled with Andor iDus401 charge coupled device (CCD) was used for the acquisition of photoluminescence spectra, TSL studies and XRL. Additionally, Horiba iHR320 imaging spectrometer coupled with SampleMax sample chamber and Jobin Yvon/Horiba TRIAX320 excitation monochromator was used for photoluminescence and luminescence decay kinetics. This spectrometer is coupled with photomultiplier tube (PMT) and CCD. Spectra measured with CCD in PL, XRL and TSL were not corrected to accommodate differences in detection at different wavelengths as only the comparison study was performed. For a precise specification of hardware used for luminescence measurement please refer to the corresponding papers of research presented in this work.

3.1.2 PEO setup

To successfully perform PEO research a three-component system is required: reaction chamber, power supply and PC. The configuration is shown on fig. 3.1.

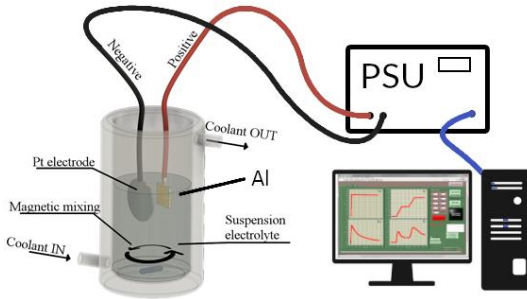


Figure 3.1 The overview of the PEO setup – reaction chamber with two electrodes is connected to the PSU, which is managed using a PC.

The setup uses double-walled glass beaker with 1L volume. Water inlet and outlet are used to provide constant flow of low-quality cold water (tap water) thus preventing contamination of the electrolyte. Inside glass surfaces are easily cleaned and are chemically inert as opposed to copper or aluminium heat collectors used in the industry. Use of glass chamber also provides the ability for using the magnetic stirrer - a better solution for improving convection of electrolyte than widely used bubble stirrer technique.

To minimize the generated hydrogen explosion probability above the electrolyte a high air flow is ensured to vent out the hydrogen and prevent bubbling. For this purpose, an attachment was developed and manufactured with electric ventilators blowing air to the electrolyte surface and appropriately sized venting holes for effective removal.

A custom power supply unit (PSU) for PEO was developed by Latvian LLC “Applied Electronics Labs”. The total output power of PEO PSU is 10kW – max current of 10A and voltage of 1000V can be achieved. An important property of the PSU is the ability to precisely control electrical parameters in various regimes (unipolar, bipolar, pulsed) with current and voltage limits in place. The precise modulation of high power square pulses allows pulse durations as small as 1 μ s. The PSU is fully automated through MODBUS communication protocol. The PC control also allows linear parameter change throughout the process enabling in-depth research of discharge characteristics. A PC software package was developed for control of the device.

3.2. Doping of PEO coatings

The modification of the PEO coatings by changing their chemical composition is of interest in various applications as it might affect all properties commonly associated with the PEO – high coating hardness, crystalline structure, wear resistance, chemical stability and others. With every changing parameter of the process there is a possibility to modify the coating and influence its structure and/or composition. Moreover, known mechanisms of PEO coating growth agree that formation occurs in the presence of four parts – substrate, electrolyte, previously formed oxide and plasma. First two of them are obvious candidates for the implementation of the foreign atoms – dopants – in the coating.

3.2.1 Alloying the aluminium with dopant atoms

Without a doubt, the metals present in the substrate – be it pure metal or alloy – will participate in the formation of the coating creating the metal-oxide. Therefore, a very first method that was realized to produce a coating with the specific purpose of enhancing its luminescence properties was done by using alloyed metal. The study was then considered as a proof of concept without the particular application in mind, therefore a well-known ion in alumina matrix should be chosen as a dopant. The rare-earth element europium fits well – Eu^{3+} exhibits very distinctive luminescence in red region of spectrum – sharp lines representing transitions from ${}^5\text{D}_0$ to ${}^7\text{F}$ levels with the most intense line observable at 613 nm (transition ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$). The lines are quite distinctive and the position varies only slightly with the different crystalline matrices. In addition, it is known that the Eu atom can incorporate in alumina matrix in Eu^{2+} state exhibiting blue luminescence that can be separated from intrinsic luminescence of the alumina.

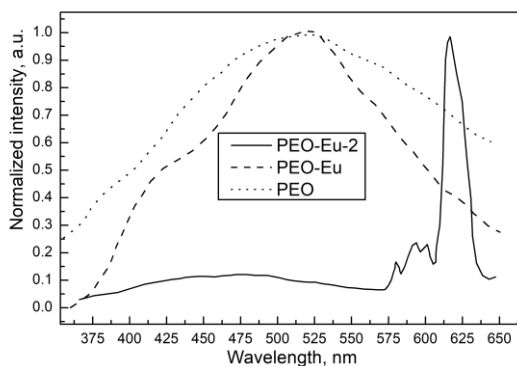


Fig. 3.2. Normalized photoluminescence spectra of PEO, PEO-Eu and PEO-Eu-2 samples.

The resulting photoluminescence spectra under 266nm laser irradiation are shown in fig. 3.2. The undoped coating (PEO) exhibits only the alumina intrinsic green luminescence band peaking at 500nm. On the other hand, doped coatings (“PEO-Eu” and “PEO-Eu-2”) with two different PEO processes (9 times higher current density of in positive pulses for “PEO-Eu-2” sample) both have significant changes in the spectral distribution and intensity of the luminescence – sample “PEO-Eu” exhibits increased luminescence in the blue region of spectrum – a possible Eu^{2+} ion in alumina matrix. It is well-known that Eu incorporates in a divalent configuration in various aluminates (Ravichandran et al.) (Stevens) (Peng et al.). On the other hand, coating with the greater current density (“PEO-Eu-2”) exhibits luminescence in the red region of spectrum – sharp lines, although overlapping and not clearly resolved, indicate the presence of Eu^{3+} in the coating. The difference of luminescence between samples “PEO-Eu” and “PEO-Eu-2” indicate the possibility of Eu recharging in the coating, thus the presence of Eu^{2+} in the coating should be explored in detail. First factor confirming the presence of Eu^{2+} in the “PEO-Eu” coating is the greatly increased photoluminescence intensity – the maximum intensity is approx. 50 times higher than that of sample “PEO”.

This first of its kind study was performed as a proof of concept – indeed, luminescence output of PEO coatings can be altered by doping of the coating through one of the routes – use of specific alloy to bring needed atoms in the coating structure. In addition, study shows the ability to alter the luminescence of the coating by changing PEO parameters – voltage, current, pulse width and process time can all change structure of the coating thus changing the luminescence output. Complimentary, the luminescence of the doped PEO coatings can be used to better understand coating formation mechanisms and adjust theoretical approaches with the obtained information.

It should be noted that the use of Eu containing aluminium alloy will not be commercially viable in most of the cases due to the high cost of alloy preparation. Moreover, if other dopants or concentrations are needed in the coating for a specific application, preparation of new alloy will be necessary making research and production expensive and labor intensive.

It is evident that other doping possibilities should be explored unless the luminescence of the coating is based on a dopant already present in readily-available aluminium alloys (like Cr, Mg, Mn and others often present in industrial-grade aluminium alloys).

3.2.2 Pore filling method

A range of studies indicates the benefits of the use of “slurry electrolytes” (Borisov et al.) – electrolytes with high concentration of insoluble micro- or nano-particles. Some studies indicate the increased growth rate of the coatings

with nanoparticles acting as the reinforcement of the coating, especially when particles with high hardness are used. Some of the properties of the particles will be transferred to the coating. (Malyshev and Zorin) This confirms the inclusion of solid particles in the formation process of the coating; therefore, the same principle can be used to alter the luminescence properties of the coating.

The present study is based on the two main concepts – firstly, only the particles in a near vicinity of the plasma discharge participate in the formation of the coating and can be implemented in the structure; secondly, pores of the PEO coating can be filled with some sort of material. Therefore, the aim of this study is to create highly-porous coating on the surface of the aluminium, fill pores with appropriately-sized powder of RRE oxide and perform the PEO on the porous filled coating fusing the oxide in the structure. The schematic representation of the process is shown on figure 3.3. This approach could minimize the required amount of often expensive powder by placing it in the discharge channels directly rather than relying on the electrolyte to bring the powder to the coating.

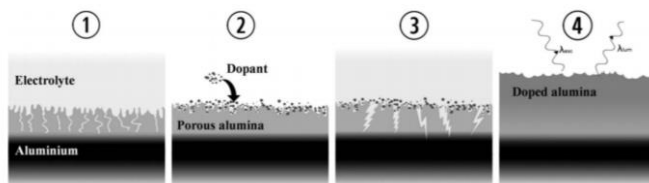


Fig.3.3 Schematic illustration of sample preparation stages: 1 – production of porous coating, 2 – filling the pores with powder, 3 – PEO processing, 4 – resulting doped oxide layer exhibiting luminescence.

First stage in achieving the goal is to find the best parameters to produce homogeneous porous structure. It is well-known that pores are naturally occurring during PEO process due to the formation of discharge channels; however, the increase of porosity of the coating still proposes a challenge that can be solved by altering power supply parameters and initial surface morphology.

Second stage is to fill the pores with $\text{Eu}(\text{OH})_3$ powder. To insert the $\text{Eu}(\text{OH})_3$ powder in the pores, it was first ground in a mortar for 10 minutes with addition of ethanol to prevent the agglomeration of the particles. The resulting highly concentrated dispersion of particles in ethanol was dripped on the porous alumina coating. The SEM image (fig. 3.4. B) gives an overview of the distribution of the Eu powder on the coating. One can see that the size of the powder grains is in range of 300 nm to 2 μm – mostly significantly smaller than the pores of the PEO coatings. This allows the grains to stay in the pores even after rinsing with water, during immersion in the constantly flowing electrolyte in the third stage and during the plasma discharges in the oxidation process.

Third, and final stage is a final PEO process – porous coating filled with the powder containing the desired dopant (Eu in this case) is submerged in the simple

electrolyte of 1L deionized water with 2gL^{-1} of KOH and unipolar DC 530V voltage-limited regime is applied for the extended periods of time. Current density is set at 0.15 A/cm^2 . Uniform plasma discharges are achieved on the surface of the sample, fusing the oxide with the powder in the pores and implementing the dopant atoms in the oxide structure.

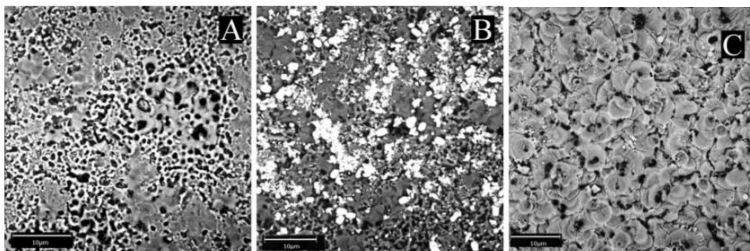


Fig. 3.4. SEM top view images of each stage of the process – A – first stage porous coating, B – filled porous coating after second stage, C – PEO-processed coating after third stage

To verify and control the presence of Eu ions in the pores in stage 2, a photoluminescence measurement was used in addition to SEM. The luminescence was excited with a 266nm UV laser with the average output from all sample surface accumulated in spectra. Figure 3.5 (left) summarizes the spectra. A distinct Eu^{3+} luminescence (red) was observed from the $\text{Eu}(\text{OH})_3$ powder - the transitions from level $^5\text{D}_0$ to ^7F in Eu^{3+} ion. The most intense line, which is observable at 613 nm marks the transition $^5\text{D}_0 \rightarrow ^7\text{F}_2$. A combination of broad intrinsic alumina band peaking at 450nm and Eu^{3+} bands is observable from porous alumina filled with $\text{Eu}(\text{OH})_3$ powder, as expected.

The application of a high voltage (third stage) leads to the plasma electrical discharges leading to the almost immediate Eu^{3+} luminescence disappearance from the spectra. However, a new broad band of luminescence appears in the blue region. The same observation was made in (Smits et al.) where it has been reported as Eu^{3+} recharging to Eu^{2+} . The recharge of the Eu could be linked to oxygen vacancies: Eu incorporates in the divalent state to compensate the charge difference. The luminescence of Eu^{2+} in blue region of spectrum was also observed in other alumina materials like translucent ceramics (Yang et al.) and alkaline-earth aluminates (Singh et al.) (Ueda et al.). Fig. 3.5 (right) presents a summary of the spectra obtained from the samples after the 3rd stage.

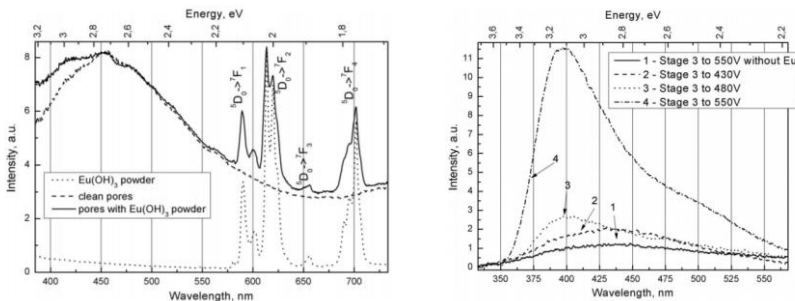


Fig. 3.5 –Left - normalized photoluminescence spectra of $\text{Eu}(\text{OH})_3$ powder, clean porous coating (first stage) and filled pores with $\text{Eu}(\text{OH})_3$ powder (second stage); Right - luminescence of coatings after third stage with varying voltage in third stage.

A tenfold increase in the photoluminescence intensity at 400 nm compared to the undoped alumina (pores were not filled in stage 2) was achieved for the 550V sample.

In conclusion, the developed pore filling method is a valid approach for doping of PEO coatings. The results clearly demonstrate the successful implementation of Eu ions in the coating structure. However, several drawbacks of the technology still persist: the high dependence on the initial surface quality – vigorous polishing is required prior to the PEO for the production of high quality pores. Powder grain size also should be controlled to meet the pore size of the coating after first stage. Most importantly, the process is performed in three separate stages, which limits the applicability of the technology in the industrial setting. All these factors and complications, however, might still be ignored due to the main advantage of the approach – minimum amount of wasted powder. Pore filling technique offers extremely efficient use of dopant-containing powder in comparison with widely used suspension or slurry electrolytes, where the concentration should be factored for the whole volume of the electrolyte. With industrial processes often using tens of liters of electrolyte per coating with frequent changes due to the degradation, the approach could offer a feasible way for better resource management.

This chapter demonstrated experimental process for altering the luminescence properties of PEO coatings using two completely different methods. In combination with the previously known data from the literature, the following thesis is therefore drawn:

Thesis 1: The doping of alumina PEO coatings to alter their luminescence properties can be achieved in three ways: alloying the metal substrate; using three-stage pore filling process and by adding dopants to electrolyte.

3.3. Dosimetry of PEO coatings

Radiation protection and monitoring will always be an important field of research, especially due to the rapidly growing use of radiation in medicine, nuclear powerplants and countless industrial applications of ionizing radiation. Big part in personal and industrial radiation protection is the use of solid-state dosimeters – devices for detection and quantification of the acquired ionizing radiation dose. Lately, interest in 2d dosimeters emerged for applications in medicine (De Deene)(Stathakis et al.)(Chung et al.)(Davis et al.)(Archer et al.) motivating further research of possible materials for emerging technologies. In addition, a scaling of the already developed and widely used ceramic or crystalline dosimeters possesses a challenge due to the large cost of production and lack of repeatability between the samples preventing the use of dosimeter arrays. With other drawbacks like low spatial resolution and small detection area (Chung et al.), the need for unconventional production methods is needed. Since many of the already developed dosimeters are based on the metal oxides, PEO stands as a promising technology since it produces a thick coat of oxide on metal surfaces that is easily scalable and manufacturable to specs required for the particular application. This chapter will explore the two possible PEO alumina-based dosimeters: carbon-doped Al_2O_3 and chromium-doped Al_2O_3 . Both dosimeters will be TSL-based. The schematic representation of the proposed technology is shown in fig. 3.6.

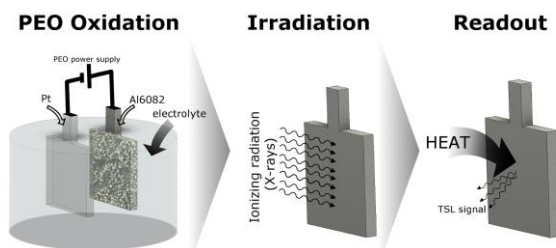


Fig. 3.6. Schematic representation of the production and use of TL-based PEO dosimeter.

Couple of factors will be kept in mind: both studies will be performed on a conventionally available aluminium alloys (Al6082 and Al1052) and will be considered as a single-step process with one electrolyte composition to fit industrial setting and make the process commercially-viable.

3.3.1 $Al_2O_3:C$ coating

Historically, one of the main materials for PEO processing is aluminium and its alloys. Naturally, for production of PEO coating based dosimeter, an obvious

idea is to mimic the already used dosimeter of similar structure. The conventional and readily available dosimeter based on Al_2O_3 is TLD-500 – carbon doped alumina. The replication of the material using PEO possesses a row of challenges, with the major one being the source of carbon. Conventional PEO is performed in electrolyte containing KOH, on aluminium alloy surface with no intentional carbon doping, therefore carbon atoms will have to be implemented manually. A reliable source of carbon is needed – highly soluble substance, like ethanol; however, other carbon-based chemicals can be used. To keep the research as close as possible to real application, a single step synthesis is required with the same electrolyte kept throughout the process.

Al6082 aluminium alloy is used in this study. Simple, 3-component electrolyte was used – deionized water, 2 gL^{-1} KOH and 60ml/L ethanol. Square voltage-limited non-symmetrical 5 ms pulses were used with the voltages of +700 V and -233 V. 1 ms pauses were set in-between pulses. Current density was 0.6 kA m^{-2} with minimal decline over 15 minutes of processing time. The AC regime with the 1/3 ratio of positive and negative pulses was chosen to reduce porosity (Xin et al.).

The TEM EDX study was performed to verify the amount of carbon in the coating. Figure 3.7 shows the analysis of two samples – carbon-doped coating (with ethanol in electrolyte as described previously) and undoped coating – same parameters except no ethanol in the electrolyte. The $K\alpha$ line of the carbon at 0.277 KeV shows that the ethanol in the electrolyte does indeed result in a significant amount of carbon atoms in the coating, with the inset demonstrating the repeat measurement of five samples. The variation in C/Al line ration is quite high – probably due to the combination of factors like inhomogeneity of carbon distribution in the coating and specifics of sample preparation for TEM measurements.

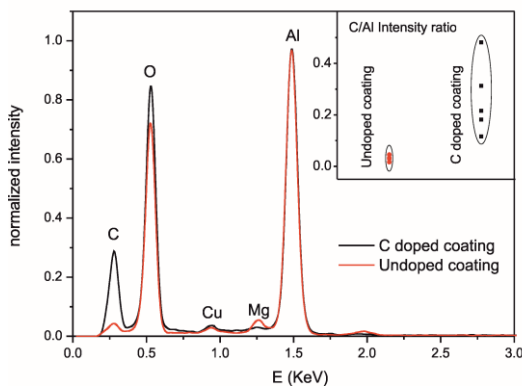


Fig. 3.7. TEM EDX measurements of two coatings – with and without ethanol in the electrolyte. Inset shows repeated measurements from 5 samples.

Next, TSL measurements were performed and compared to the signal from commercially available TLD-500 sample. The samples were irradiated with X-Ray lamp with W anode operating at 30kV and 10mA. The results are shown on fig. 3.8 (left) – carbon-doped PEO coating demonstrates a wide TSL peak from 300K to 630K while TLD-500 sample maximum occupies much smaller temperature range. The signal from TLD-500 is in a good agreement with other studies of the material (Kalita and Chithambo, “Comprehensive Kinetic Analysis of Thermoluminescence Peaks of α -Al₂O₃:C,Mg”) (PALAN et al.) (A. Weinstein et al.). The broad TSL maximum of PEO coating indicates the wide distribution of activation energies of traps – a characteristic of disordered crystalline structure and large amount of defects in the structure. Although the width of the maxima is much larger for PEO coating, the maximum occurs at the same temperature – this leads to believe that the same recombination centers are participating in the luminescence in both samples. To verify that, the spectral distribution of TSL as well as X-ray excited luminescence was measured for both samples and results are shown in fig. 3.8 (right).

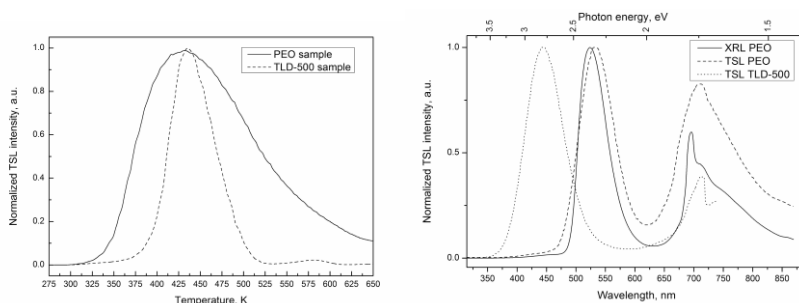


Fig. 3.8. Left - TSL glowcurves of the obtained carbon-doped coating and TLD-500 sample; Right - spectral distribution of TSL and XRL signal for carbon-doped PEO coating as well as TLD-500.

The analysis of spectral distribution of both samples shows that main luminescence of TLD-500 sample is located at 420nm and is described as the F⁺ center that is charge compensated by C²⁺ ions in trigonal crystalline lattice of alumina in α -phase (Akselrod and Kortov). Additional complex luminescence band of TLD-500 in red region of spectrum that is also present for PEO coating is described as various metal oxides present in the samples. It is well-known that Mg (Kalita and Chithambo, “On the Sensitivity of Thermally and Optically Stimulated Luminescence of α -Al₂O₃:C and α -Al₂O₃:C,Mg”), Mn (Martínez-Martínez et al.) and Cr (Salek et al.) oxides exhibit luminescence in the red region of spectrum; however, due to the mix of the metals as traces in both samples the distinction between the each band is impossible (apart from intense Cr³⁺ R-line doublet at 693-694nm). However, main band for the TSL in

PEO samples is located at 530nm. With the amount of tracing oxides that were brought from the aluminium alloy, the identification of this line is challenging. Similar luminescence band was found in alumina doped with Mg and C (M.G. Rodriguez et al.), where F_2^{2+} ($2Mg$) center is a result of charge compensation for the substitutional Mg^{2+} ion in Al^{3+} site.

Both the TSL glowcurve and signal distribution studies indicate the irregular structure of the alumina – to verify that the XRD spectra were registered for undoped (without ethanol in the electrolyte) and doped (with ethanol in the electrolyte) coatings. The eta- or gamma- phase alumina maxima are present in the “undoped” coating, while same lines are absent in the coating prepared with ethanol.

In conclusion, this study shows a valid approach to create a PEO coating with TL sensitivity for ionizing radiation. The resulting coating exhibits a range of drawbacks preventing its use as a dosimeter at room temperatures – the large width of the TSL peak allows the trapped electrons to recombine at room temperature leading to quick fading of acquired signal. Other drawbacks include the non-uniform distribution of TSL intensity on the surface of the coating, evaporation of ethanol from electrolyte and requirement for short PEO processing times preventing the synthesis of harder, desired alumina phases. Some of the drawbacks can be addressed by the use of other carbon sources in the PEO – replacing the ethanol could not only add a more controllable way of doping of the oxide, but also extend the PEO processing time to acquire at least some crystalline structure.

3.3.2 $Al_2O_3:Cr$ coating

The carbon doped alumina is, although most popular, not the only alumina-based material exhibiting intense TSL signal. One of such materials is chromium-doped alumina – however, previously noted by Akselrod et. al. that the use of Chromium dopant, although increasing the sensitivity, shifted the TL glowcurve maximum to 580K and 699nm – “inconvenient for reading” with the devices available in 1990. (M.S. Akselrod, V.S. Kortov, D.J. Kravetsky) Nowadays, the red region of spectrum is easily detectable by the conventional, cheap and readily available CCDs (Oxford Instruments Group) making $Al_2O_3:Cr$ as a viable option for dosimetry.

During our previous PEO dosimetric studies the increase of “red” luminescence from oxides was noticed with increased acidity of the electrolyte. This led us to believe that acidic electrolytes can produce coatings with increased dopant concentration in the oxide coating without any other dopant needed in the electrolyte itself or without the use of pore-filling method. This motivated the search of a particular electrolyte that will bring alloying elements from commercial aluminium alloy to the coating (e.g. Al1052 with alloying elements of Cr, Cu, Fe, Mg, Mn, Si, Ti, Zn and other metals with concentrations of up to 0.4%) in the coating thus altering the luminescence properties.

In this study, a 2mm thick Al1052 aluminium sheet was cut into samples $25 \times 25 \times 2 \text{ mm}^3$ in size, each having the total surface area of approx. 14 cm^2 (used in calculations of current density, a bit less than geometric value due to the non-constant waterline). No special treatment, apart from rinsing with water, was implemented before the PEO process.

The electrolyte for “doped” sample consisted of 3 components: deionized water, 1 g L^{-1} KOH (Stanlab) and 10 g L^{-1} citric acid. For comparison, the second sample (marked “undoped” in this chapter) was prepared without the addition of citric acid in the electrolyte. The pH of the electrolyte before the PEO process was 3.7 and 12.2 for doped and undoped samples, respectively. The temperature of the electrolyte was maintained at $30 \pm 5^\circ \text{C}$.

DC constant voltage electrical parameters were chosen and kept constant throughout the whole process. The total process time was set to 30min. Voltage was set to 700V while current density remained mostly constant (178 mA cm^{-2}) in the first half of the process and declined in the second half to 121 mA cm^{-2} . The current density for the undoped sample (without citric acid in the electrolyte) was approx. 25 mA cm^{-2} larger throughout the whole synthesis. This approach leads to the formation of two main crystalline phases– $\alpha\text{-Al}_2\text{O}_3$ rhombohedral and $\gamma\text{-Al}_2\text{O}_3$ cubic, which was verified by XRD.

To study the effect that citric acid inclusion in the electrolyte has on the concentration of impurity metal ions in the resulting coating, XRF measurements were performed and presented in fig. 3.9. One can clearly see that although some concentrations of Cr, Mn and Fe are present in the coating even without the citric acid in the electrolyte, the addition of it increased Cr content drastically.

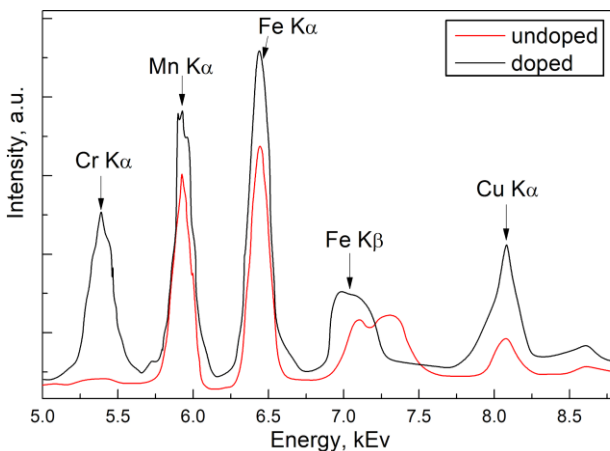


Fig. 3.9 Minor bands of XRF measurements of the undoped and doped PEO coatings.

Sample luminescence consists of three major parts – blue, green and red, representing visible light spectrum parts, as seen on fig. 3.10.

Blue luminescence (maximum at 425-450nm) appears only under UV irradiation in both samples and it relates to alumina F and F⁺ (oxygen vacancies with one or two electrons) centers and are often observed in anodic aluminium oxide films. Both F⁺ and F centers are present, and the maxima are overlapping thus producing a broad emission band (Kong).

Green luminescence band with maximum at 525nm is present under both UV and X-ray irradiation and in both samples. Well-known band in amorphous and crystalline alumina is due to intrinsic defects of alumina matrix, specifically F₂ centers. The band is observed in alumina prepared by a wide range of methods. (de Azevedo et al.; Baronskiy et al.; Gorbunov et al.; M. G. Rodriguez et al.)

Red luminescence is a complex band consisting of two sharp peaks (679nm and 693nm) and a broad-band covering the whole red part of the spectrum. The sharp peak at 679nm is interpreted as a result of the ²E_g→⁴A_{2g} transition in Mn⁴⁺ ions incorporated in alpha-alumina (Berezovskaya; van Die et al.). The presence of this peak confirms the inclusion of Mn ions in crystalline lattice of the coating. The 693nm sharp line dominates the XRL spectrum completely quenching the Mn⁴⁺ luminescence and is associated with widely studied and abbreviated in literature as R1 and R2 line doublet of Cr³⁺ ions in Al sites of the α-Al₂O₃ matrix (fig. 3.10 bottom half).

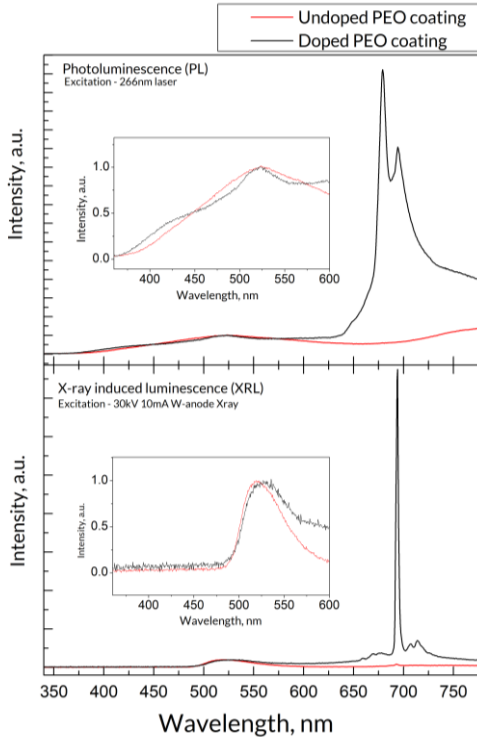


Fig. 3.10 Top half - PL spectra of undoped and doped samples, inset – intrinsic defect range 340-600nm; bottom half - XRL spectra of undoped and doped samples, inset - intrinsic defect range 340-600nm.

The TSL glow curve and 3d matrix is presented in fig. 3.11. Only Cr^{3+} luminescence is observed in TSL, meaning that any energy traps present in the lattice recombine exclusively on Cr atoms, which correlates well with previous observations even in other matrices. By analyzing only the 693nm line, one can observe that the Cr doped sample exhibits intense TSL signal in temperature ranges above room temperature consisting of two or more overlapping maxima. Low temperature maximum (centered at about 375K) is producing afterglow at room temperature and its intensity relates to the delay between the “impact” ionizing radiation dose and the measurement itself. The most intense glow curve maximum (at 442K with FWHM of 60K) represents the trap center with an activation energy of approximately 1eV (estimated Randall-Wilkins equation (J.T. Randall and Wilkins, “The Phosphorescence of Various Solids”; J.T. Randall and Wilkins, “Phosphorescence and Electron Traps - I. The Study of Trap Distributions”; J. T. Randall and Wilkins)). The intensity of this maximum might correlate with the acquired radiation dose, so long as the center is stable

enough at room temperature. Additionally, high temperature complex maximum is observed (from 575K and up).

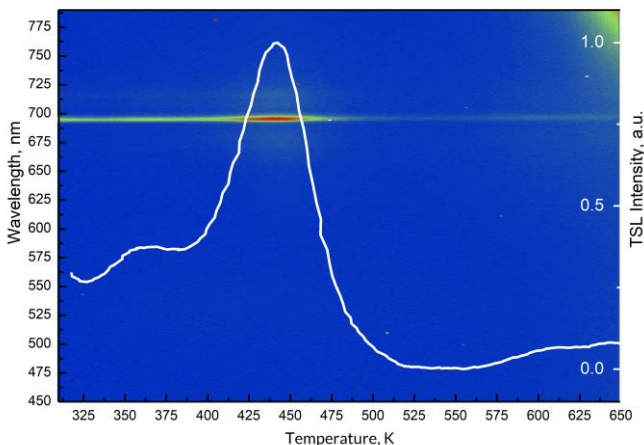


Fig. 3.11 TSL glow curve at 693nm (white line, right Y scale) overlaid on top of full measurement matrix (left Y scale). X-scale is joint between overlay and matrix. Color represents the intensity of the 2d graph (temperature to wavelength).

To conclude, obtained material exhibits outstanding luminescence properties promising for use in detection and quantification of ionizing radiation. Strong Cr^{3+} emission is observed in PL, XRL and TSL, providing basis for a range of sensor applications.

Since the proposed technique does not require an artificial dopant to be added to the electrolyte and rather uses the atoms already present in most aluminium alloys, this method is easily and inexpensively scalable and is more environmentally friendly than conventional Cr-based electrolytes.

The research presented in last two chapters is a basis for the thesis 2:

Thesis 2: The PEO process is applicable for the doping of alumina coating with carbon or chromium atoms thus making the material promising for applications in detection of ionizing radiation.

3.4. Phosphorescent coatings

One of the materials often used for “glow in the dark” devices is rare-earth doped SrAl – a $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+} matrix that, when prepared correctly, can exhibit long afterglow (> 10 h (Clabau et al.; Chander et al.; Rocío Estefanía Rojas-Hernandez et al.; Pan et al.)) and high quantum efficiency (Chen et al.; Liepina et al.; Xue et al.), good thermal and chemical stability (Choubey et al.; Bisen and

Sharma), environmental friendliness and no signs of toxicity (Terraschke et al.; Wu et al.; Bisen and Sharma). However, the production of SrAl is complicated, and if the intended use of material is to create any type of surface for illumination or signage (Anesh et al.; Xue et al.) (R. E. Rojas-Hernandez et al.; Bisen and Sharma), the material then should be prepared in powder form and mixed with lacquers or paints. This action creates a row of complications both in material performance (powder will not perform as well in any medium for coating) and manufacturing (additional production step is required). PEO might be the answer for that – it is used for production of alumina on flat metal surfaces and the oxide can be doped using various methods. The idea therefore is to develop a process for the creation of rare-earth doped SrAl using single step PEO process.

The method of doping from suspension electrolyte was chosen, and the appropriate electrolyte should be prepared: strontium carbonate (SrCO_3 , 6 gL^{-1}), europium oxide (Eu_2O_3 , 0.5 gL^{-1}), dysprosium oxide (Dy_2O_3 , 1 gL^{-1}) were used as the starting materials, all obtained from the Alfa Aesar. All three components have low solubility in deionized water, therefore an addition of 1 gL^{-1} of KOH was used to create needed ions in the electrolyte. As a substrate, Al6082 was used.

A voltage-limited (with voltage 700 V and a current density around 0.18 A cm^{-2}) unipolar regime was applied. The image of the uncoated, coated and emitting sample is shown in fig. 3.12.

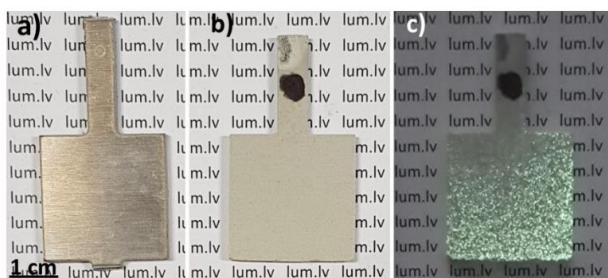


Fig. 3.12 – The photo of uncoated sample (a), PEO-processed sample in normal lighting (b) and PEO-processed sample after irradiation with UV light in low-light environment (c).

Right away one can observe that indeed, after 60 min long PEO processing time the coating visually looks similar to the conventional coatings. After short irradiation with 405nm UV light, the luminescence from the sample in a dark environment is observed for a couple of minutes indicating the formation of long-lasting luminophore.

Firstly, cross-section of the sample was prepared to analyze the thickness of the coating as well as perform EDX analysis to verify the distribution of the elements

(fig. 3.13). The thickness is approximately 40 μm – the expected value for the electrolyte and processing time.

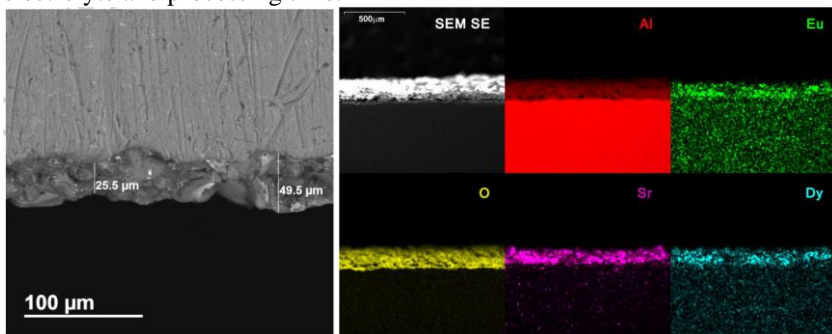


Fig 3.13. Left - cross section SEM image of the coating with two extreme values of thickness marked; right - EDX map of the elements present in the coating.

Finally, XRD pattern as well as EDX pattern from the top of the coating was measured – presented in fig 3.14. The XRD pattern reveals several peaks corresponding to γ -alumina crystalline structure as well as monoclinic SrAl_2O_4 phase. Another strontium aluminate phase was also detected – $\text{SrAl}_2\text{O}_{19}$. No crystalline phases of rare-earth (“dopant”) oxides were detected, therefore one can assume that the atoms are incorporated in the SrAl or alumina matrix. EDX revealed the approximate ratio of elements as 67% Al, 22% Sr, 4% Eu and 7% Dy at. % - a combination fitting with the intended composition of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{2+} .

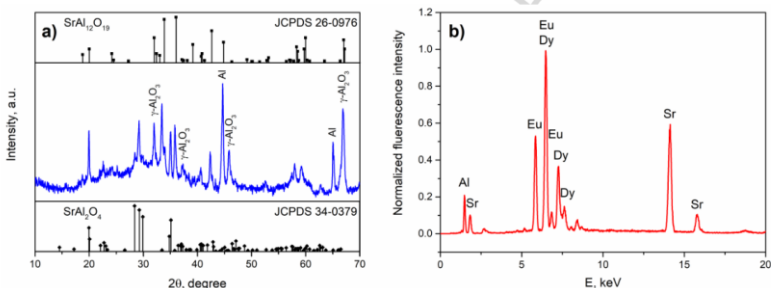


Fig. 3.14 a - XRD spectrum of obtained coating and b – EDX spectrum of the coating.

To further analyze the luminescence properties of the coating, the excitation-emission spectrum was recorded and is shown on fig. 3.15. For a comparison, a commercially available SrAl was used as a reference (obtained from Sigma Aldrich). Firstly, the afterglow of the obtained coating and commercial SrAl do

match indicating the same recombination centers responsible for afterglow in both samples. This luminescence is a 5d-4f emission of Eu^{2+} (Katsumata et al.) – therefore, a correct incorporation of Eu in the structure of PEO coating occurred due to the reduction of Eu^{3+} from the powder. The similar process did occur in the PEO pore-filling study described in section 3.1.2. The second maximum in the photoluminescence emission spectrum of the coating under UV irradiation at 455nm is associated with the Eu^{2+} incorporation in another Sr position in SrAl matrix (Nazarov et al.) with some contribution from the intrinsic amorphous alumina luminescence (Li and Huang; Li et al.). Although some reports suggesting that this maximum is quenched above 150K (Aitasalo et al.; Liepina et al.), the peak can also be explained with other SrAl phases present in the coating (Dutczak et al.) (as observed in XRD spectra in fig. 3.14). Other aluminate matrices can also exhibit Eu^{2+} luminescence in blue region of spectrum (e.g. barium-magnesium aluminates BaMgAl or barium-europium aluminates BaEuAl) (Yen et al.; Van den Eeckhout et al.).

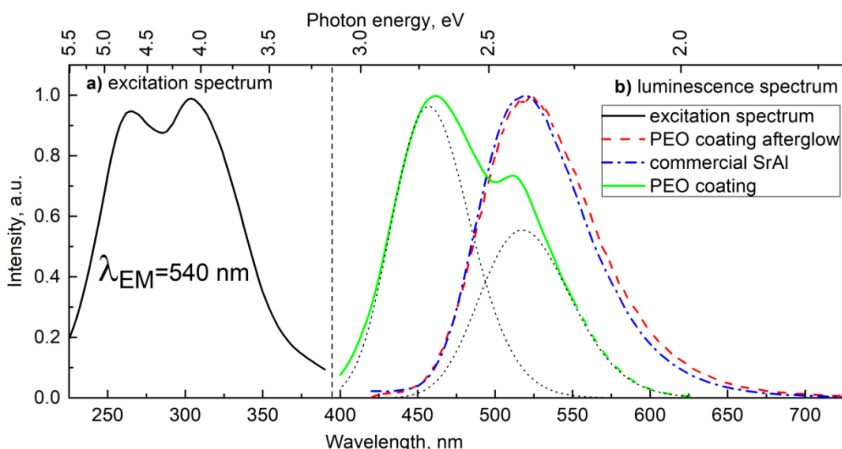


Fig. 3.15. Excitation and emission spectrum obtained from the coating and reference sample. a – excitation spectrum measured at 540nm emission and b – emission spectrum for PEO sample (green line) and afterglow spectrum of PEO coating and commercially available SrAl.

Thus, a novel approach for production of SrAl coatings is presented. Although certain optimization routes should be explored to make the performance of the phosphorescent coating comparable to the commercially available powder samples, the approach exhibits a row of crucial advantages. When compared to most popular SrAl production method – solid-state reaction – PEO process offers much smaller processing time, no need for pre- and post-processing to obtain material in a coating form, the ecological friendliness of the process, less energy requirements and efficient use of materials. The approach is also easily scalable

and transferrable to the industrial setting to produce a range of products like vehicle body panels, road and emergency signs and others.

The research of a production of strontium aluminate coating in a single-step PEO leads to the third thesis of this work:

Thesis 3: PEO process is a viable alternative to the solid state reaction in production of complex oxide phosphorescent coatings.

4. Conclusions

PEO is a complex process with the large number of varying parameters, therefore for a successful application of the technology the great care should be taken in choosing of the material, electrical parameters and electrolyte. However, the number of variable parameters can also be used as an advantage – for a controlled implementation of atoms in small concentration (dopants) in the structure of the oxide coatings. The role of dopants in luminescence materials is crucial, and many of the materials used for various luminescence applications are based on metal oxides; therefore, a PEO process can be used to produce coatings with a specific luminescence output. A set of PEO studies with the aim of altering the luminescence properties of the coatings is thus performed.

By implementing europium in the alloy, its luminescence can be observed from the coating after PEO processing. Moreover, the Eu ion in the lattice undergoes the transition from Eu^{3+} charge state to Eu^{2+} . However, the creation of specific alloys is often expensive, and the mechanical properties can be altered to disadvantage, therefore other methods for implementation of ions should be considered. One of these methods is the use of suspension electrolyte – the insoluble powder is mixed in a PEO electrolyte. This approach, although effective, has one crucial drawback often preventing the commercial application possibilities – the use of large amount of powder is necessary, and with large electrolyte volume the cost becomes high very quickly, especially so in production of luminescence coatings where high cost rare earth elements are used. One of the solutions to this problem is the developed pore-filling approach – this work demonstrated that by filling the pores on the PEO coating with a Eu-containing powder one can achieve the same effect as in the use of suspension electrolytes – the powder particles participate in the formation of the coating with the same effect of Eu charge state change that was observed in a study with Eu-containing alloy. The pore-filling approach can significantly reduce the amount of powder needed to achieve some sort of doped PEO coating, although a minor drawback can be defined – with prolonged PEO processes that are required to obtain hardest alpha-phases of alumina the amount of Eu in the coating will reduce minimizing the effect of the doping. To mitigate that a repeated pore-filling should be performed adding additional steps in the process – an undesired factor for commercial applications.

To further explore the possibilities of PEO to create coatings with luminescence-based applications, the enhanced thermostimulated luminescence signal was obtained from two different coatings – $\text{Al}_2\text{O}_3:\text{C}$ and $\text{Al}_2\text{O}_3:\text{Cr}$ coatings on aluminum surface. The carbon-doped coating was used by implementing the organic soluble additive in the electrolyte, while the chromium was implemented from the alloy itself, similar to the Eu implementation from the Eu-containing alloy previously. Both coatings exhibit

enhanced thermostimulated luminescence intensity, however, with different spectral and thermal distribution. Both studies describe a viable approach to produce dosimetric coatings, and with combination of other PEO advantages (low cost, scalability and energy efficiency) they present an interesting proof of concept for further research: the performance of both approaches should be improved and re-evaluated. Additional TSL, dose response curve and OSL measurements should be performed to fully understand the mechanisms, drawbacks, and applicability of the technology.

The attempt at replicating of another type of luminescence-based material using PEO was made in the field of long-lasting luminescence. Previous knowledge was used to create a complex suspension electrolyte and an electrical parameter set that enabled the synthesis of a PEO coating with strontium aluminate structure exhibiting observable long-lasting luminescence. This is a unique approach to create a complex crystalline structure of strontium aluminate doped with europium and dysprosium. Notable advantages of the PEO process to create phosphorescent coatings when compared to the conventional approaches include the single-step nature of the process, energy efficiency and great adhesion of the coating to the part. Despite the success of the research, the coating luminescence output should be optimized (afterglow is observed for 10 minutes after the end of UV irradiation while the similar material created by other synthesis methods demonstrates tens of hours of afterglow) before any commercial application. Nevertheless, the research demonstrated the possibility of PEO process to create not only doped metal-oxide coatings, but also complex, multi-component doped oxide structures enabling further search of other PEO applications.

5. Thesis

Thesis 1: The doping of alumina PEO coatings to alter their luminescence properties can be achieved in three ways: alloying the metal substrate; using three-stage pore filling process and by adding dopants to electrolyte.

Thesis 2: The PEO process is applicable for the doping of alumina coating with carbon or chromium atoms thus making the material promising for applications in detection of ionizing radiation.

Thesis 3: PEO process is a viable alternative to the solid state reaction in production of complex oxide phosphorescent coatings.

6. List of conferences and publications

6.1. Publications connected with the thesis

Thesis 1:

- K. Smits, D. Millers, **A. Zolotarjovs**, R. Drunka, M. Vanks, Luminescence of Eu ion in alumina prepared by plasma electrolytic oxidation, *Appl. Surf. Sci.* 337 (2015) 166–171. doi:10.1016/j.apsusc.2015.02.085.
- **A. Zolotarjovs**, K. Smits, A. Krumina, D. Millers, L. Grigorjeva, Luminescent PEO Coatings on Aluminum, *ECS J. Solid State Sci. Technol.* 5 (2016) R150–R153. doi:10.1149/2.0401609jss.

Thesis 2 :

- **A. Zolotarjovs**, K. Smits, K. Laganovska, I. Bite, L. Grigorjeva, K. Auzins, D. Millers, L. Skuja, Thermostimulated luminescence of plasma electrolytic oxidation coatings on 6082 aluminium surface, *Radiat. Meas.* 124 (2019) 29–34. doi:10.1016/j.radmeas.2019.02.020.
- **A. Zolotarjovs**, K. Smits, I. Bite, K. Laganovska, K. Auzins, E. Einbergs, V. Vitola, D. Millers Chromium luminescence in plasma electrolytic oxidation coatings on aluminium surface. In publishing.

Thesis 3:

- I. Bite, G. Krieke, **A. Zolotarjovs**, K. Laganovska, V. Liepina, K. Smits, K. Auzins, L. Grigorjeva, D. Millers, L. Skuja, Novel method of phosphorescent strontium aluminate coating preparation on aluminum, *Mater. Des.* 160 (2018) 794–802. doi:10.1016/j.matdes.2018.10.021.
- K. Auzins, **A. Zolotarjovs**, I. Bite, K. Laganovska, V. Vitola, K. Smits, D. Millers, Production of Phosphorescent Coatings on 6082 Aluminum Using $\text{Sr}_{0.95}\text{Eu}_{0.02}\text{Dy}_{0.03}\text{Al}_2\text{O}_4-\delta$ Powder and Plasma Electrolytic Oxidation, *Coatings.* 9 (2019) 865. doi:10.3390/coatings9120865.

6.2. Other authors publications

As of writing, author of the thesis is the main or co-author of 30 other (not connected with the thesis) publications (h index: 9). Full list of publications and other metrics can be found in WoS/Scopus databases.

6.3. International conferences in chronological order

The author of this work participated in over 10 international conferences and training courses/summer schools. The non-exhaustive list is as follows:

- «New materials for radiation detectors» in Peter the Great Saint-Petersburg Polytechnic University (SPbPU) (29.06.2015 – 3.07.2015)
- COST Training School on "Upconverting nanoparticles in bioaffinity assays - from bioconjugation to luminescence readout" in Turku, Finland, 3. - 5. April 2017
- RACIRI Summer School 2017 "Grand Challenges and Opportunities with the Best X-ray and Neutron Sources" in Ronneby, Sweden. 19-26 August 2017
- A number of "Functional Materials and Nanotechnologies FMNT" conferences in years 2013-2020
- „1st Conference and Spring School on Properties, Design and Applications of Upconverting Nanomaterials UPCON-2016"
- "Luminescent Detectors and Transformers of Ionizing Radiation LumDeTr" 9-14 September 2018, Prague, Czech Republic
- Various workshops and meetings in frame of COST action CM1403
- Various workshops and meetings in frame of COST action PortASAP CA16215

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