Analysis of metal surfaces
coated with europium-doped titanium dioxide
by laser induced breakdown spectroscopy

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The surface passivation with titanium sol-gel coatings is a frequently used technique to control the adsorption of selected biological mac-romolecules and to reduce the exposure of the bulk material to biological matter. Due to the increasing number of new coating-preparation methods and new gel compositions with various types of additives, the quality and homogeneity determination of the surface covering is a critical factor affecting performance of any implanted material. While coating thickness is easy to determine, the homogeneity of the surface distribution of coating materials requires more elaborate methodologies. In the paper, the laser induced breakdown spectroscopy (LIBS) based method, capable to quantitate the homogeneity and uniformity of the europium in titanium dioxide sol-gel coatings on stainless steel surfaces prepared with two different procedures: spin-coating and dip-coating, is presented. The emission intensity of titanium has been used to determine the coating thickness whereas the relative values of europium and titanium emission intensities provide data on the coating homogeneity. The obtained results show that the spin-coating technique provides better surface coverage with titanium dioxide. However, when the surface coating compositions were compared the dip-coating technique was more reliable.

Key words: *europium/titanium dioxide mixture LIBS spectra, LIBS, quality and composition of thin layers*

1. Introduction

Covering surfaces with thin layers or small particles is a commonly used technological approach when fine-tuning surface properties, protection from aggressive environmental factors is required or when the biological material needs to be protected from the potentially harm-ful exposure to the metal surface. For example, having low toxicity and high corrosion resistance, titanium di-oxide in combination with various additives is routinely used to cover implants surfaces [7], [12], [15], [18]. Since TiO_2 combined with various additives is exten-sively used in biomedical devices, methods enabling determination of its composition and homogeneity in situ are needed. Surface coverage using the sol-gel method is frequently used due to its convenience, economic effec-tiveness and simplicity of introducing additives such as titanium dioxide. In addition, the application of sol-gel does not require application of high temperatures, so the body of the coated device remains unaffected. There are different ways of applying sol-gel material onto the sur-face amongst which the most popular are dip-coating, spin-coating and spraying [6], [11], [20], [21]. From the functional point of view, uniformity of the coating and its compositional homogeneity are the most critical technological parameters. To monitor covering quality a number of analytical techniques have been devel-oped or adopted from other industrial applications. To study surface coverage quality in situ techniques such

as: X-ray photoelectron spectroscopy (XPS or ESCA) [17], auger electron spectroscopy (AES) [13], secondary ion mass spectrometry (SIMS) [10] and sputtered neutral mass spectrometry (SNMS) [8] are frequently used. The measuring principle of these techniques is to expose the surface to a beam of particles or radiation so the ejected/excited matter can be detected and quantify. All of these methods need well-defined measuring conditions such as high vacuum and, in the most cases, they require bulky and expensive instrumentation. Consequently, they are not practical to use for high throughput screening applications and as a support of production processes [17]. Other approaches rely on the extraction of the coating by chemical or physical treatment of the surface and subsequent analysis using HPLC, MS-HPLC or GC-HPLC setups [3]–[5], [9], [22]. Despite the excellent resolutions, with respect to the chemical composition, these methods do not provide information on components spatial distribution or homogeneity. This is a result of the spatial averaging due to the sample collection and preparation process. The laser-induced breakdown spectroscopy (LIBS) is an analytical tool which utilizes the high-energy laser beam to ablate a small area (few hundreds of microns in diameter) on the analyzed surface. The quantity of evaporated material can be controlled with a laser beam geometry, power and exposure time. The chemical composition of the resulting plasma is then determined from its LIBS spectrum. This method has already been used in a variety of scientific, geological and industrial applications [14], [16], [19], [23], [25]. In this paper, we show that LIBS technique can be used to measure the quality and homogeneity of thin layer of europium doped TiO_2 deposited on the stainless steel surface. Moreover the distribution of europium additive in the deposited sol gel was also determined. In the course of the works the new europium emission wavelength was identified in the europium/titanium mixture. This allows determining the quality and composition of the stainless-steel surface covering.

2. Materials and methods

2.1. Sample preparation method

Sol-gel: Eu^{3+}:TiO_2 mixtures at molar ratios of 0.01 and 0.02 have been prepared by means of acid-catalyzed sol-gel method, using $Ti(OC_2H_5)_4$ as a precursor. Titanium dioxide sol was obtained by dissolving TEOT in 96% ethanol at molar ratio 1:40. Few drops of 67% nitric acid were added to provide the acidic environment (pH ~2). Next $Eu(NO_3)_3 \cdot 5H_2O$ aqueous solution of required stoichiometry was added drop-wise into titanium dioxide sol. The mixture was than vigorously stirred for 5 min at room temperature.

Surface coating: The obtained europium doped TiO_2 sol was deposited on 316L steel plates by either dip-coating or spin-coating method. Samples were covered with either 3 or 6 layers of Eu^{3+}:TiO_2. During dip-coating deposition the excess of sol was allowed to drop and each layer was left to dry for 90 sec at room temperature prior to subsequent treatment. Spin-coating film deposition was performed using Desktop Spin Coater. In this case 20 μl of titanium dioxide sol was deposited on the surface, then the sample was spin for 90 sec with 3000 rpm to ensure the surface covering.

Preparation of samples containing the europium salt suspension: $Eu(NO_3)_3 \cdot 5H_2O$ powder was weighted and suspended in UV stabilized gel, according to the method described in detail previously [2].

2.2. Laser-induced breakdown spectroscopy measurements

All measurements were performed using the PharmaLIBS™ 250 instrument. The instrument was equipped with the high power Nd:YAG pulse laser (10 Hz, 190 mJ, 3–5 ns at 1064 nm). The energy of the laser pulse was measured with a joulemeter, positioned behind the beam splitter. The laser beam focused on the sample's surface ablates a spot of 200 μm in diameter. To collect plasma emission signal a spectrograph in the Czerny–Turner configuration, with the focal length of 300 mm and the operating range: 320–1100 nm (0.1 nm resolution), was used. The spectra were collected with the progressive scan (interline) scientific grade CCD detector. Each scan was of 1392 × 1040 imaging pixels where size of each pixel was 6.45 × 6.45 μm and the imaging area size was 8.77 × 6.6 mm. The linear range of energy detected was 16 000 e- with the read noise of 6 e-rms@10 MHz and the nonlinearity < 1%. The readout bits/speed and dark current were equal to 12 bits@20 MHz and 0.05 e-/p/s @ −30 °C, respectively. The sample was excited with 100 mJ pulses of 2 Hz repetition and the emission scans were taken with 1 μs delay time after the exposure of 2 μs and grating 600 g/mm blaze 1.0 μm.

The ablation was repeated 30 times at each location so the in-depth sample composition could be examined. The variation of the measured spectra, due to the instrumental factors alone, was evaluated for a series of ablations performed on the untreated stainless steel surface. The standard deviation of emission

intensity has been determined to be 8.5% for emission peak at 505.88 nm.

3. Results

To obtain detailed characteristic of the coating distribution, in terms of its spatial, depth and composition uniformity, series of spectra were acquired in 40 nm-wide spectral windows as demonstrated in Fig. 1. Spectra obtained for a stainless steel plate alone (Fig. 1B), pure titanium (Fig. 1B) and $Eu(NO_3)_3 \cdot 5\,H_2O$ (Fig. 1A), served as a guide for the selection of a detection window. Presented spectra are the average of 18 independent ablations performed at different locations on the sample surface. Figure 1A demonstrates spectral window between 440 and 480 nm acquired for $Eu(NO_3)_3$ mixture in solidified polymer according to method described by Borowik et al. [2] with, not reported previously, characteristic peak for europium (III) at 461.57 nm. Europium (I) in water emmits at 462.722 nm [1]. Figure 1B shows spectra emitted during a single ablation for the mixture of $Eu: TiO_2$ (1) and TiO_2 alone (2) deposited on the stainless steel surface. The panel C shows that the LIBS spectra collected for $Eu:TiO_2$ mixture suspended in the solidified gel is not different from that obtained for the mixture deposited on the stainless steel surface. Data presented in Fig. 1 shows that the peak at 461.57 nm was detected in all samples contaning europium regardless on their state therefore it has been used for all subsequent quantitative analysis. The dotted line in Fig. 1 highlights the spectral region where the europium (III) emission pick is located.

In order to correlate the Eu and TiO_2 emission peaks with their quantities a calibration experiment was performed. Figure 2A shows an example of the LIBS spectra of a $Eu: TiO_2$ mixture suspended in the solidified sol. In this case the europium-doped titania sol, prepared as described in previous section, was poured into 4 ml-cuvettes and left to solidify in the air for 24 h. The ratios of emission peaks for various Eu^{3+}/TiO_2 mixtures as a fuction of their predicted value are plotted in Fig. 2B. Measurements were conducted on the samples with Eu^{3+}/titanium molar ratios equal to 0, 0.01, 0.02, 0.04, and 0.05 with all other parameters remaining unchanged.
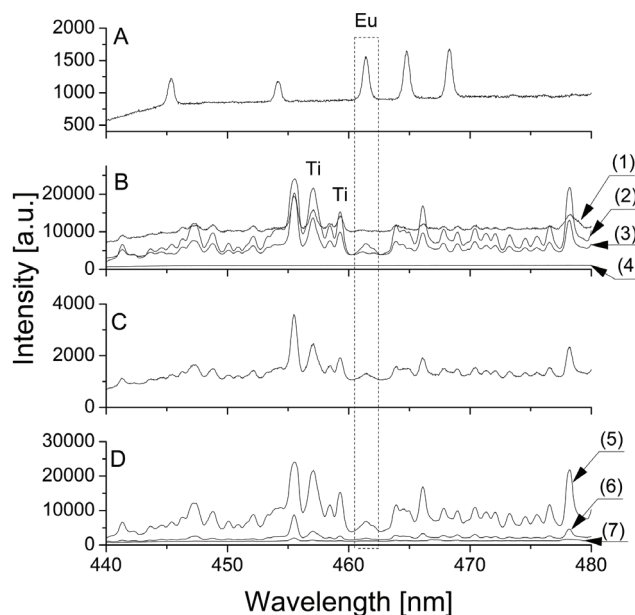

Fig. 1. Panel A shows emission spectra of $Eu^{3+}(NO_3)_3$ suspended in the solidified polymer. Panel (B) demonstrates emission spectra of (1) TiO_2 in sol-gel matrix, (2) $Eu:TiO_2$ and (3) TiO_2 deposited on stainless steel surface, and (4) stainless steel surface alone. Panel (C) presents spectra of $Eu:TiO_2$ mixture at molar ratio of $Eu^{3+}(NO_3)_3:TiO_2$ equal to 0.05. The mixture was suspended in the solidified polymer. Panel (D) presents emission spectra of the stainless steel surface covered with the $TiO_2:Eu$ coating obtained after 1st (5), 2nd (6) and 3rd (7) ablation
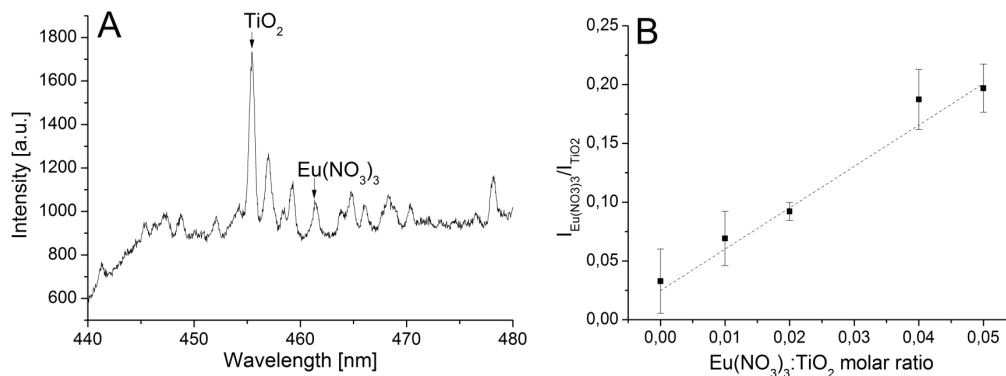

Fig. 2. Panel (A) presents an example of the emission spectrum of $Eu:TiO_2$ mixture in solidified sol. Molar ratio of $Eu^{3+}(NO_3)_3:TiO_2$ was equal to 0.05. Panel (B) shows the dependence of emission intensities ratio (at 461.57 nm ($Eu(NO_3)_3$) and 455.31 nm (TiO_2)) on the amount of europium and titanium present in the sample

Based on LIBS spectra obtained for samples containing various quantities of europium and titanium the dependence of the ratio of their emission intensities at predetermined wavelengths on their theoretical molar ratios were determined and plotted in Fig. 2B.

Using the intensity of the emission wavelength for titanium (at 505.88 nm) and stainless steel (at 497.84 nm) it was possible to evaluate the quality of surface covered with sol-gel using different deposition methods. For that purpose, two LIBS spectra collecting procedures have been adopted. In the first procedure a series of consecutive ablations have been performed at each location so the in-depth analysis was possible. Examples of such spectra are presented in Fig. 1D. In the second procedure spectra have been acquired at various locations on the sample surface so the lateral distribution of coating material can be determined. Using these two protocols the quality of surface coverages obtained with spin-coating or dip-coating methods were evaluated.

When the intensity values for selected peaks heights for each ablation are averaged over the whole surface area of the sample then the averaged surface titanium quantity and its averaged in-depth distribution can be determined. Representative plots for the four different samples are presented in Fig. 3. When the quantity of titanium is determined for each surface coverage procedures than the following conclusions can be made: there is no difference between methods used for surface coverage and the number of cycles of each procedure does not result with the increase of the quantity of titanium deposited onto the surface (actually the amount of deposited titanium decreases with the increasing number of cycles). Therefore, three cycles of the coating procedure is sufficient to reach maximum covering efficiency with sol-gel containing Eu^{3+}:TiO_2 mixture. The averaged titanium distribution profile measured along the surface normal allows for the evaluation of the total titanium quantities deposited at each location on the surface. To illustrate this, the quantitative assessment of the relative quantity of titanium, deposited onto the surface at each location, has been performed. It was assumed that the relative quantity of titanium deposited onto the surface (m_{Ti}) is proportional to the sum of intensities detected at 505.88 nm along the surface normal (I_{tot}) (formula (1)).
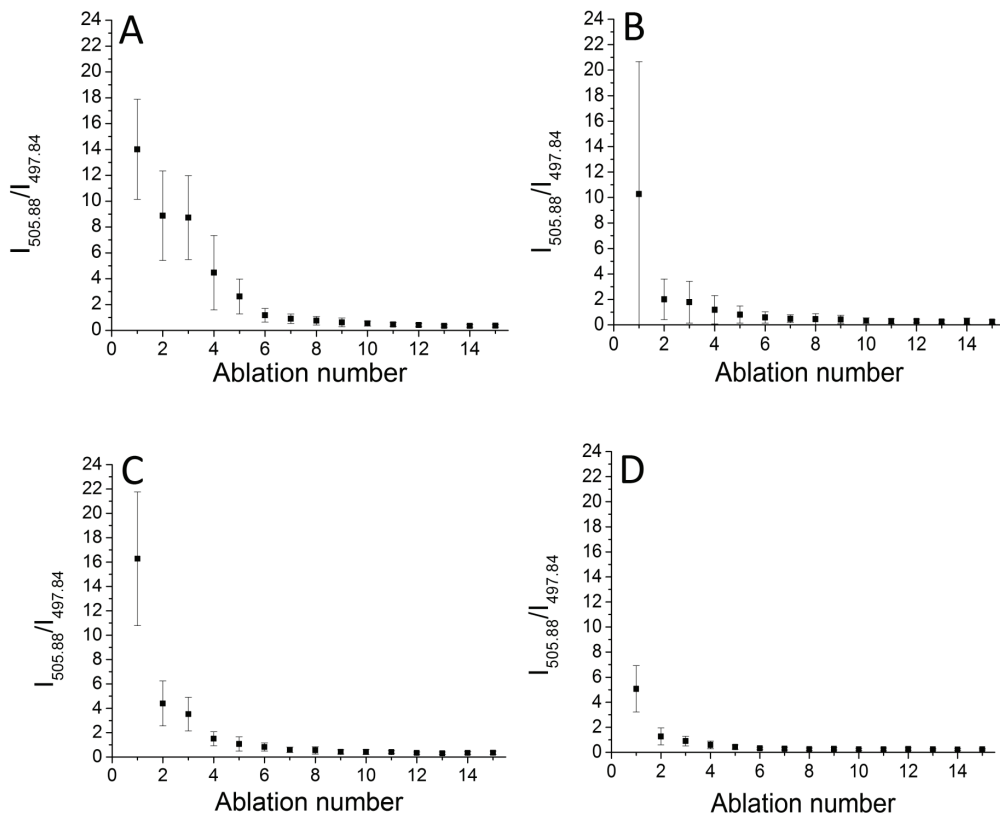

Fig. 3. The ratios of emission intensities at 505.88 nm and 497.84 nm obtained for samples exposed to 3 (A) and 6 (C) cycles of spin-coating treatment using the sol-gel doped with Eu^{3+}:TiO_2 mixture. Panels B and D have been obtained for samples exposed to 3 and 6 dip-coating procedure, respectively. The presented values are an average of emission intensities obtained from a series of ablations at 18 locations on each surface
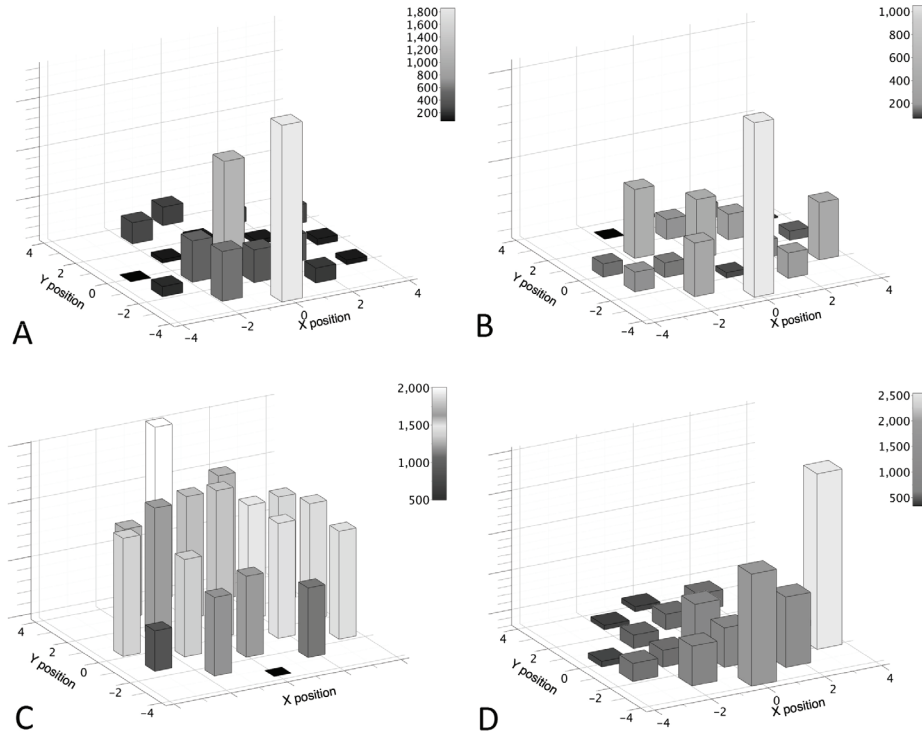
Fig. 4. Graphical representation of the surface distribution of the relative titanium quantity determined for the surface covered using the dip-coating method (A – 3 cycles – left , B – 6 cycles right) and spin-coating method (C – 3 cycles – left , D – 6 cycles right). The height of each bar was determined from the emission spectra of the second ablation. The emission intensity is indicated by the color code

$$m_{Ti} \approx I_{tot} = \sum_{k=1}^{m}\sum_{i=1}^{n}(I_{505.88}^{i,k} - I_b) \qquad (1)$$

where n is a number of points on the surface, m is a number of ablations performed at a single location, $I_{505.88}$ and I_b stand for emission intensities of the titanium and the background, respectively. For samples prepared with the spin-coating method I_{tot} equals 2.22×10^5 [a.u.] for three and 1.90×10^5 [a.u.] for six coating cycles, while samples prepared with dip-coating technique resulted with 1.12×10^5 [a.u.] for three and 0.70×10^5 [a.u.] for six coating cycles, respectively. The total quantity of deposited titanium, expressed in terms of the total intensity, shows that, as in the case of the distribution profile (Fig. 3), the increased number of technological cycles actually reduces the quantity of titanium deposited onto the surface. However, when the two deposition techniques are compared, with respect to the amount of titanium present on the surface, the spin-coating is twice as efficient as dip-coating method.

Furthermore, due to the localized probing, the LIBS technique allows for the determination of the surface distribution of the deposited material. Examples of such distributions are presented in Fig. 4. Here the bar height is proportional to the quantity of titanium detected at selected locations. In this case

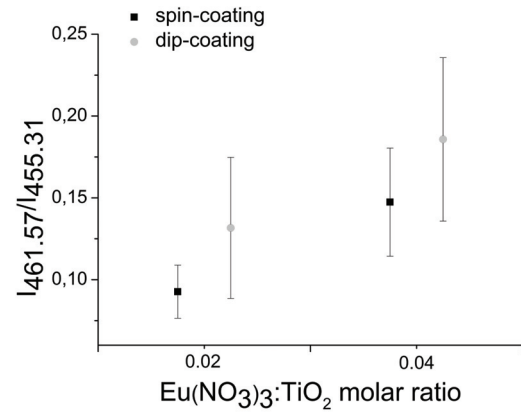the quantity of titanium was determined from the LIBS spectra collected during the second ablation.

Fig. 5. Ratio of Eu(NO$_3$)$_3$ intensity peak to TiO$_2$ intensity peak for emission spectra obtained for stainless steel surfaces covered with sol-gel doped with Eu(NO$_3$)$_3$:TiO$_2$ mixture using the dip-coating and the spin-coating techniques. Mean values and standard deviation have been calculated for emission spectra generated in the second ablation at 9 different locations

Figure 5 shows the relative values of measured emission intensities of europium and titanium (461.57 nm for Eu(NO$_3$)$_3$, 455.31 nm for TiO$_2$). In this case the measured relative quantity of the europium, with re-

spect to the titanium, was higher by almost 50% when the dip-coating method was employed. However, the coverage uniformity with respect to the relative quantities of europium and titanium, was better for the spin coating method.

4. Discussion

Laser Induced Breakdown Spectroscopy is a powerful tool for the quantitative characterization of solid-state surfaces. This is due to the capability to analyze small surface areas (100 μm in diameter) and no need for any sample preparation prior the measurement. The small surface needed for analysis enables the detailed characterization of the surface uniformity, whereas no need for sample preparation makes the method a convenient tool for *in situ* measurement regardless of the study object size or topology. Therefore, in studies presented, LIBS was used for the characterization of metal surfaces coated with complex materials. Stainless-steel samples were covered with sol-gel doped with a mixture of europium and titanium. Whereas the presence of titanium is not difficult to quantitate, thanks to the large number of emission peaks, the detection of europium is not straightforward. There are no reported emission bends for Europium in the spectra range available for analysis. To select the detection wavelengths both elements were analyzed individually and mixed together without the presence of any solid support. Because LIBS measurements using powders or liquid are not possible due to technical limitations we have used the methodology presented elsewhere [2]. Specifically, metal salts suspended in the polymer or material, which can be solidified, so the splashing effect during ablation can be eliminated. Using this procedure the LIBS spectra for titanium, europium and their mixtures have been collected and suitable detection widow selected (Fig. 1). Identified emission lines assigned to titanium and europium were confronted with the National Institute of Standards and Technology (NIST) database [24]. Interestingly, the NIST database does not provide any clear indication of the emission peaks for europium in the spectral range used in presented studies. The identified emission peaks for europium, titanium and stainless-steel support were subsequently used for the evaluation of the metal surface coverage with the sol-gel doped with europium and/or titanium. In order to assess the quality of the surface coverage several parameters have been selected: the relative thickness, its variation over the covered surface, the quantity of

titanium deposited on the surface and the surface uniformity of the titanium, europium and their ratio deposited. In order to evaluate the quality of the surface coverage a representative number of locations for repeated ablations have been selected on all analyzed surface. The thickness of the sol-gel coverage was evaluated with the amount of ablations needed to evaporate the surface deposited titanium. The quantity of titanium was evaluated with the ratio of two peaks, at 505.88 nm and 497.84 nm characteristic of titanium and stainless-steel, respectively. Figure 3 shows representative results obtained for surfaces covered using different procedures. The determined thickness of the coverage depends, in this case, on titanium and sol-gel quantities at the analyzed location. The quantity of titanium deposited on a surface, and its homogeneity are another technologically relevant parameters available from the LIBS spectra, as demonstrated in Fig. 4. Data presented in Fig. 4 shows that the quantity of deposited titanium dioxide using spin coating methods is much higher than that obtained using dip-coating method, whereas the quality of the surface coverage does not depend on the method used except for the procedure where the number of the repetition of spin-coating procedure is low (Fig. 4C). The measured uneven titanium distribution likely results from the lack of the proper balance between the flow of the sol and its drying process during the sample preparation procedure.

Whereas the quantity of the major component (titanium) of the deposited material can be used as an indication of the uniformity of surface coverage, the ratio of emission intensities of europium and titanium provides data on the variation in the lateral composition of the deposited layer. This ratio is especially important from the physicochemical point of view, since any difference in local electrochemical potentials (caused by differences in surface composition) may initiate and/or facilitate the corrosion processes [10], [19]. To determine the homogeneity of the titanium and europium mixture on the surface, stainless steel plates have been covered with sol-gel containing two different mixtures of europium and titanium at molar ratio 0.02 and 0.04. Examples of results are presented in Fig. 5. Presented data shows that the relative amount of europium deposited onto the surface depends on the coverage method used. Specifically, the quantity of europium detected on the surface was 2–3 times higher for dip-coating method than for spin-coating methods. In addition, the increased quantity of europium in the deposited mixture does not result from the same rise in the deposited layer. It has been also observed that the lateral variation in the

europium/titanium ratio for both preparation methods is very high (about 20%) showing that the surface coverage is very uneven with the respect to its composition. The measured variations are real since in the control experiment, where europium and titanium mixed together and suspended in solidified material, show excellent correlation between the intensities ratio measured at 461.57 nm and 455.31 nm, and the value of the europium to titanium molar ratio (the correlation coefficient equal 0.993) (Fig. 2B). Figure 5 shows two parameters, important for the surface coverage quality, the dependence of the surface coverage composition and uniformity on the coverage method used. The average composition of the deposit was evaluated with the value of ratio of emission intensities specific for titanium and europium collected at various surface locations. The uniformity of the surface distribution can be evaluated with the standard deviation calculated for a set of LIBS spectra obtained at various locations along the analyzed surfaces. The fraction of europium deposited on the surface increases with the number of repetition of each procedure and was higher for the dip-coating method. However the uniformity of the surface coverage was better for spin-coating method.

5. Conclusions

Laser Induced Breakdown Spectroscopy has been used to collect the LIBS spectra of titanium and europium mixture, deposited in sol-gel onto the stainless steel surface. The emission wavelengths for titanium, europium and stainless-steel have been identified and used for the quantitative analysis of the deposited thin layer quality. In the course of the studies we observed that the plasma produced by the laser ablation of the titanium/europium mixtures had emission maximum at 461.57 nm, the wavelength not listed in the NIST database. We have shown that this emission wavelength correlates with the quantity of europium present in the sample by measuring the europium salt LIBS spectra in solidified medium. Using those characteristic emission intensities the uniformity of the surface coverage produced with different protocols has been determined and evaluated. We have demonstrated that the deposition processes result in the uneven distribution of the matrix (i.e., sol-gel) as well as doped additives. The evaluation of the local quantity of deposited material shows that the spin-coating method is more effective than the deep-coating method. The spin-coating method also produced lesser variation in compositional uniformity of the coverage, whereas the dip-coating method deposited larger relative quantity of europium.

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