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Encapsulation of Al and Ti-Al alloy 1-D nanorods into oxide matrix by powerful pulsed discharge method.

Aleksey D. Lisenkov^{1*}, Sergey K. Poznyak², Claudio M. R. Almeida³, Mikhail L. Zheludkevich^{1,4}, Mário G. S. Ferreira¹

¹Department of Materials and Ceramic Engineering/ CICECO, University of Aveiro, 3810-193, Aveiro, Portugal

²Institute for Physical Chemical Problems, Belarusian State University, 220050 Minsk, Belarus

³REQUIMTE, Departamento Engenharia Química, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465, Porto, Portugal

⁴Institute of Materials Research, Helmholtz-Zentrum Geesthacht, 21502 Geesthacht, Germany

**corresponding author*

Email: lisenkov@ua.pt

Phone: +351935665746

Abstract

Encapsulated metal nanostructures were prepared using the powerful pulsed discharge method. Metal nanorods were obtained in porous titania and alumina matrix by direct electrodeposition from 1-ethyl-3-methylimidazolium chloride-based ionic liquids. The deposition process was characterized by cyclic voltammetry. Morphology of the

encapsulated structures was studied by SEM and EDS for morphological and elemental analysis. It was found that the most efficient method for electrodeposition of pure aluminium into titania nanotubes is the potential cycling method, while for deposition of the Al-Ti alloy in alumina pores a pulsed method with three different steps is preferable. Closing the titania nanotubes was found to be possible both with empty and metal-filled pores, whereas in alumina matrix this procedure can be performed only when pores are filled with a conductive material.

The obtained results throw light on the mechanism of porous film encapsulation under high-voltage pulses and allow preparing encapsulated nanostructures in the oxide films.

Keywords: metal encapsulation, titania nanotubes, porous alumina, ionic liquids, electrodeposition

1. Introduction

Core-shell nanostructures that consist of an inner core and an external shell of the different chemical composition is part of the family of nanomaterials, which attract increasing research interest due to their unique structural properties [1-8]. These structural features allow the possibility of combining various properties of several materials [8]. Core-shell nanostructures show improved physical, chemical and mechanical properties in comparison to their single-component counterparts [4]. The created core-shell nanostructures are of great importance to a wide range of applications including electronics, magnetism, optics and catalysis [2,4]. A wide variety of core-shell nanostructures have been successfully fabricated using different methods, ranging from laser ablation and high-temperature evaporation to carbothermal reduction and hydrothermal methods [6-8]. Structural characterization of these nanostructures and determination of their unique properties for various applications have been well documented [7].

One of the methods for core-shell nanostructures preparation is based on the deposition of metals into a porous matrix. This method allows preparing metal particles coated with shells of the oxide of different metals. In contrast to the physical methods, during electrodeposition the metal fills the oxide pores from the bottom filling the whole volume.

Recently a new electrochemical technique, namely powerful pulsed discharge oxidation of metals, has been suggested [9-11]. In this technique, the electrochemical reaction occurs at the metal-electrolyte interface under action of single high-voltage (> 1 kV) pulses. The powerful pulsed discharge method could be also used to melt the surface of the porous alumina and titania resulting in closing the pores [9,10]. In previous work a two-stage mechanism of powerful discharge for film growth was

suggested. The full ionization of the film occurs in the first step during a few microseconds followed by a slower anodic Faradaic process of film growth [9,10]. The fact that the entire film is fully ionized during the first step leads to vanishing out the difference between different zones of the surface and allows the formation of a very uniform layer. However, mechanistic details of the process, which occur on the surface during the pulse and the main factors affecting the process are not yet clear.

The main aim of the present work was to develop methods that allow preparing 1-D metal nanostructures encapsulated into oxide matrixes. Porous titania and alumina films were treated by the powerful pulsed discharge method to study the possibility of pore sealing. To understand the mechanism of pore sealing, studies were carried out with empty and metal-filled pores. A set of electrochemical methods were used to clarify the effect of applied voltage on the kinetics of ionization, film morphology and level of pore sealing.

2. Experimental

2.1 Pore preparation

Both aluminium and titanium substrates were mechanically polished using abrasive papers up to grid 4000. Then Ti electrode was chemically polished in a HF:HNO₃ (1:3 by volume, HF(Sigma-Aldrich, 97%), HNO₃ (Sigma-Aldrich, ACS reagent, 70%)) mixture, while Al was electrochemically polished in a C₂H₅OH:HClO₄ (4:1 by volume, C₂H₅OH (Panreac, 99,8%), HClO₄ (Sigma-Aldrich, 70%)) electrolyte in potentiostatic regime at 20 V to mirror finish. After polishing, the electrodes were rinsed with

deionized water. Two-step anodization was used to form a well-ordered alumina template. The first and second anodization steps were performed at a constant voltage of 40 V in 0.3 M oxalic acid solution (Sigma-Aldrich, $\geq 99\%$) for 1 h at a temperature of about 3 °C. Between them the pre-structured alumina surface was chemically dissolved in a mixture of phosphoric acid and CrO₃ (Sigma-Aldrich, 99,9%) at 70–80 °C for 5 min. At the end, the pores were enlarged in a separate solution of 0.3 M oxalic acid solution at 40 °C for 2.5 h without application of the potential. Titania templates were prepared by anodization of titanium (99.9%, Goodfellow) with a platinum counter-electrode in an electrolyte containing 0.75% NH₄F (Sigma-Aldrich, $\geq 98\%$) and 2% H₂O in ethylene glycol (Sigma-Aldrich, 99,8%). The potential was increased from 0 to 20 V with 0.1 V/s rate, followed by anodization at a constant potential of 20 V for 20 min. In both cases, vertical nanopores were formed with a length of ~ 1 μm .

2.2 Metal deposition

All experiments of metal deposition from ionic liquids were carried out in a glove box filled with nitrogen (concentration of O₂ and H₂O < 5ppm). Anhydrous aluminium chloride (Sigma-Aldrich, >99.9%) and anhydrous titanium (II) chloride (Aldrich, 99%) were used as received. The ionic liquid 1-ethyl-3-methylimidazolium chloride, EMIM, (Fluka, $\geq 99.0\%$) was heated to 140 °C under dynamic vacuum during 24 h in order to dry it. The electrolyte was prepared by addition of 1.7 mol of AlCl₃ to 1 mol of 1-ethyl-3-methylimidazolium chloride and stirred for 24 h [12-14]. The reaction of AlCl₃ and EMIM-Cl is highly exothermic, therefore the temperature was controlled below 70 °C to avoid decomposition of the ionic liquid. A 0.5 M solution of TiCl₂ in the EMIM-

AlCl_4 ionic liquid was used as the electrolyte for Ti-Al alloy deposition[15,16]. Electrochemical deposition was performed in a three-electrode cell. Aluminium wire (Alfa Aesar, 99.999%) and glassy carbon rod were used as reference and counter electrodes correspondently. Deposition and cyclic voltammetry studies were carried out using a Bio-Logic SP-300 potentiostat.

2.3 Sealing of the pores

The electrochemical cell used for the pulsed discharge sealing was made of high-impact polystyrene and consisted of Ti or Al coated respectively with porous titania or alumina (dimensions: 100x8x10 mm) with a working surface of 4.4 cm² placed inside a cylindrical Ti cathode (Alfa Aesar, 99.7%) with about 20 times larger surface area. Titanium was chosen as a cathode material due to its high strength and chemical stability. An aqueous solution of 0.1 M ammonium pentaborate ($(\text{NH}_4)\text{B}_5\text{O}_8 \cdot 8\text{H}_2\text{O}$ (Sigma-Aldrich, $\geq 99\%$)) was used as the electrolyte for pore sealing of both substrates. Electric discharges between the electrodes were generated using a low-inductance 100 μF capacitor bank, charged to a fixed voltage (1000-1800 V). The capacitor was commutated to the cell using a low-inertial relay triggered by a synchronizing pulse.

2.4 Electron microscopy studies

Surface topography and composition of the films were investigated using a Hitachi SU-70 scanning electron microscope (SEM) coupled with a Bruker high-resolution XFlash silicon drift detectors for energy dispersive spectrometer (EDS). Spectra were

analysed using Bruker Quantax 1.6 software, P/B-ZAF standardless analysis was used for quantification of the obtained X-ray spectra.

3. Results and discussion

3.1 Deposition of the metals into pores

To study the behaviour of the metal-filled titania and alumina nanotubes two types of electrodes were prepared: aluminium deposited into the titania film and aluminium-titanium alloy deposited into the porous alumina.

Al deposition in titania

Electrodeposition in the potentiostatic mode results in slow deposition of the aluminium into titania pores. After filling the pore bulk, aluminium nanostructures start to grow on the top of the nanotubes (Fig. 1A) eventually covering the entire surface with bulky deposits. To avoid the growth of metal deposits on the surface electrodeposition of aluminium into the titania tubes was performed using potential cycling. Vertex potentials were chosen in the range of -0.5 V and +0.35 V vs. Al quasi-reference electrode to avoid decomposing the ionic liquid from the cathodic side and significant metal dissolution from the anodic one. Typical cyclic voltammograms for a different number of cycles are shown in Fig. 2.

Fig. 2 shows typical cyclic voltammograms (CV) of titania nanopores in $\text{AlCl}_3/\text{EMIM}$ electrolyte started at 0.1 V (vs Al) and cathodically polarized. Careful analysis of the process evolution reveals it changes during potential cycling. In the first cycle (Fig. 2A, black solid line) the oxidation process is diffusion limited since the ingress of chloride anions in the pores is restricted and thus the possibility of

aluminium dissolution is limited (eq. 1-3). The anodic oxidation can be described by the following processes[12]:



etc.

An increase of the ionic liquid anion size (eq. 1-3), with a corresponding increase of the number of Al atoms in it, results in the drop of its solubility and polymeric aluminium chloride structures deposit on the metal, preventing its dissolution in the pores. In the following cycles, the anodic current limitation becomes less distinct and almost disappears after the 20th scan (Fig. 2A, green dotted line). The increase of the aluminium amount on the porous titania surface, where oxidation of the metal is not limited by diffusion and its dissolution is easier, results in a rise of the anodic current. In the case of the cathodic reduction process, there are almost no diffusion limitations taking into account that the ionic liquid contains aluminium chloride ions.

The sweep rate is a very important parameter for the aluminium deposition in the pores. Aluminium deposition was studied at the following sweep rates: 20, 50, 100, 200 and 500 mV/s. It was found that metal particles are deposited on the top of TiO₂ films when a sweep rate of 20 mV/s is applied, and the fill factor remains low (Fig. 1B). Deposition at higher sweep rates, 50 and 100 mV/s, results in good filling of the pores with aluminium without further growth of metal structures on the surface (Fig. 1C). In this SEM image one can see that there is no nanostructures growth on the surface of the pores at 50 mV/s, while pores are filled with metal. With the increment

of the sweep rate to 200 and 500 mV/s the number of empty pores increases and the deposition of metal on the surface arises.

Al-Ti deposition in alumina

The possibility of aluminium-titanium alloy deposition from the solution of TiCl_2 in AlCl_3 -EMIM-Cl (2:1) mixture was demonstrated earlier [17]. The composition of the alloy is highly dependent on the applied potential. Deposition using the potential cycling method in this case can produce variations in the nanorods' composition. Recently Perrie et al. [18,19] have proposed a method based on pulsed deposition. It was shown that two pulses are important for metal nanowires formation: the first one with cathodic polarization for metal deposition and the second one, anodic, for relaxation processes in the pores. To avoid the formation of metal structures on the surface of the porous layer, we used a modified pulsed method, and three pulses instead of two were applied (Fig. 2B). The first one, which corresponds to metal growth, was applied for 50 ms at a potential of -0.3 V vs Al quasi-reference electrode. Partial dissolution of the deposit was performed at +0.2 V for 40 ms, and the final pulse at 0 V for 150 ms was used for the sake of ion migration and electrolyte renewal in the pores. When the third pulse is not applied results in a significantly lower fill factor of the obtained nanowires.

The results of EDS analysis obtained for the alloy nanostructures in the pores show the presence of about 13% Ti in the deposit (Table 1).

3.2 Sealing of empty nanoporous alumina and titania films under action of Powerful Pulsed Discharge

Nanoporous alumina and titania films have essentially different nature. While aluminium oxide demonstrates hexagonal structure with a pore in the centre and no space between cells, titanium oxide mainly consists of nanotube shaving thin walls in the top and thicker ones closer to the metal substrate, which can be even separated [20,21]. The conductivity of the porous oxides is also different since TiO_2 is known as a wide-bandgap semiconductor, while Al_2O_3 films can be considered as a dielectric material and have higher resistance.

To estimate the possibility of closing the oxide pores, the titania and alumina films were studied under action of discharge pulses before deposition of the metals into the pores (Fig. 3 A, B). Fig. 3 C and D show the structure of the porous oxides after 5 pulses at 1600 V. The morphology of the discharge-treated titania film (Fig. 3 C) seems to be different from the not treated one. The cross-section (Fig. 3C insert) of this film shows that the top part of the pores was melted, resulting in sealing of the nanotubes. According to the processes described in previous works [9,10], it can be suggested that plasma is formed on the top of the pores, resulting in their melting. The behaviour of the alumina films under the same conditions was found to be different. After application of 5 pulses at 1600 V, cracks in the film can be observed (Fig. 3D). Action of 40 pulses with lower potential (1200 V) leads to changes of the film structure, and at high magnification a minor melting of the pore walls can be seen (not shown). Examination of the coating cross-section reveals signs of the wall melting near the substrate and some sealing in the lowest part of the pores (10-25 nm). Thus, closing of the alumina pores under powerful pulsed discharges is incipient,

and only minor part of pores can be closed. It can be suggested that the electrical conductivity of the alumina is insufficient to transport charges through the oxide to the upper part of the film for a further melting process.

3.3 Sealing of the alumina and titania filled nanopores by applying Powerful Pulsed Discharge

The metal-filled porous oxide structures were further treated with high voltage pulses. Analysis of the current vs time plots can throw light on the mechanism of processes that occur under action of such discharges. As previously studied [9,10], the discharge process contains two steps. During the first, short one, which is characterized by relatively high currents, ionization and melting of the oxide occur. In the second one with a significantly higher duration, the main process is the growth of the film. The key factor that corresponds to the charge distribution ratio between the first and second step is the amount of defects in the coating. Fig. 4 shows typical discharge curves obtained for porous titania and alumina electrodes filled with aluminium and titanium-aluminium alloy, respectively. In comparison to the plots recorded on the pure metal electrodes, the shape of the discharge profile is closer to that obtained on aluminium [10], which oxide can be characterized by high resistance and low amount of defects. These plots contain a short first ionization part and a relatively long second one, and the two steps are well separated. However, detailed analysis of the plots reveals that the charge passed through the cell during the second period, which

corresponds to the film growth, is negligible and consists only of about 1% of the capacitor charge. Moreover, according to the current integration, only 30% of charge is consumed by the ionization processes. It can be suggested that in such systems growth of the oxide does not occur, and the only process is ionization of the oxide with its further melting. An increase of the discharge voltage does not result in changes in the plot shape, and only a current increment in the first step of the process can be observed.

Inspection of the electrode surface after applying the discharges reveals the dependence of its morphology on the applied potential. In all the cases, the discharge curves have a shape different of that obtained previously, and further investigation by SEM shows a big number of cracks on the porous oxide surface. Increasing the voltage up to 1600 and 1800 V leads to the sealing of the pores (Fig. 5). EDS analysis of the cross-section (Table 2) revealed that alumina is the main material of the melted part of the pore. Taking into account that the coating contains titanium-aluminium alloy inside, it can be assumed that the main source of the material for the sealed part of the pore is alumina from the nanotube walls. In contrast to action of discharge on the empty pores, in this case encapsulation of the pore content takes place. Thus, filling the channels of alumina with conductive material opens the possibility to close the pores in the same way as it occurs on titania.

Application of powerful pulsed discharges to the aluminium-filled titania pores also causes pore closure. Discharge pulses at the potential to 1600 V result in the total encapsulation of the pore content (Fig. 6A). It was also found that the molten material on the surface of the nanotubes consists mainly of titania, what is in good agreement with our previous assumption. Further increase of potential leads to the formation of islands of surface castings and most pores remain open (Fig. 6B).

4. Conclusions

The Powerful Pulsed Discharge method offers an unconventional approach not only for electrochemical synthesis of thin oxide layers, but also for modification of the oxide morphology. In the present study, this method is proposed for efficient encapsulation of metal nanorods preliminarily deposited into vertically aligned titania and alumina nanopores. Under action of the discharge with voltages less than 1600 V, the top part of the titania tubes melts, resulting in closing of the pores. Closing the titania nanotubes by this method is possible irrespective of the pore content. In the case of alumina nanoporous layer, only a small part of the pores can be sealed if they are empty. However, filling the pores with conductive metal gives them the possibility of being closed from the top.

Studies of the kinetics of the discharge process on the metal-filled porous titania and alumina electrodes show that the shape of the temporal current evolution profile does not depend on the oxide matrix composition. Increasing the applied voltage results in a current increment without changing the profile shape. Analysis of the current *vs* time plots show that only a small part of the charge is spent on the oxide growth and the principal process occurring is ionization of the oxide with its further melting.

It was also demonstrated that the potential cycling method is efficient for electrodeposition of aluminium into titania nanotubes. In the case of Al-Ti alloy deposition into alumina pores, a pulse method, where the potential is reversed during deposition, can be applied to avoid the growth of structures on the oxide surface and provide a high fill factor of the pores with metal.

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6. References

1. Chang N, Zhang H, Shi M-S, Li J, Shao W, Wang H-T (2017) Metal-organic framework templated synthesis of TiO₂@MIL-101 core-shell architectures for high-efficiency adsorption and photocatalysis. *Mater Lett* 200:55-58.
2. Krysiak E, Wypych-Puszkarcz A, Krysiak K, Nowaczyk G, Makrocka-Rydzik M, Jurga S, Ulanski J (2015) Core-shell system based on titanium dioxide with elevated value of dielectric permittivity: Synthesis and characterization. *Synth Met* 209:150-157.
3. Maia F, Tedim J, Lisenkov AD, Salak AN, Zheludkevich ML, Ferreira MGS (2012) Silica nanocontainers for active corrosion protection. *Nanoscale* 4 (4):1287-1298.
4. Park J-B, Ham J-S, Shin M-S, Park H-K, Lee Y-J, Lee S-M (2015) Synthesis and electrochemical characterization of anode material with titanium-silicon alloy solid core/nanoporous silicon shell structures for lithium rechargeable batteries. *J Power Sources* 299:537-543.
5. Zhao L, Sun C, Tian G, Pang Q (2017) Multiple-shell ZnSe core-shell spheres and their improved photocatalytic activity. *J Colloid Interface Sci* 502:1-7.
6. De Bonis A, Santagata A, Galasso A, Laurita A, Teghil R (2017) Formation of Titanium Carbide (TiC) and TiC@C core-shell nanostructures by ultra-short laser ablation of titanium carbide and metallic titanium in liquid. *J Colloid Interface Sci* 489:76-84.
7. Jiang J, Zhou H, Zhang F, Fan T, Zhang D (2016) Hydrothermal synthesis of core-shell TiO₂ to enhance the photocatalytic hydrogen evolution. *Appl Surf Sci* 368:309-315.

8. Kim GH, Park SH, Birajdar MS, Lee J, Hong SC (2017) Core/shell structured carbon nanofiber/platinum nanoparticle hybrid web as a counter electrode for dye-sensitized solar cell. *J Ind Eng Chem* 52:211-217.
9. Lisenkov AD, Poznyak SK, Montemor MF, Carmezim MJ, Zheludkevich ML, Ferreira MGS (2014) Titania films obtained by powerful pulsed discharge oxidation in phosphoric acid electrolytes. *J Electrochem Soc* 161:D73-D78.
10. Lisenkov AD, Salak AN, Poznyak SK, Zheludkevich ML, Ferreira MGS (2011) Anodic Alumina Films Prepared by Powerful Pulsed Discharge Oxidation. *J Phys Chem C* 115:18634-18639.
11. Poznyak SK, Lisenkov AD, Ferreira MGS, Kulak AI, Zheludkevich ML (2012) Impedance behaviour of anodic TiO₂ films prepared by galvanostatic anodisation and powerful pulsed discharge in electrolyte. *Electrochim Acta* 76:453-461.
12. Endres F, Abbott A, MacFarlane D (2017) *Electrodeposition from ionic liquids*. John Wiley & Sons.
13. Jiang T, Chollier Brym MJ, Dubé G, Lasia A, Brisard GM (2006) Electrodeposition of aluminium from ionic liquids: Part I—electrodeposition and surface morphology of aluminium from aluminium chloride (AlCl₃)–1-ethyl-3-methylimidazolium chloride ([EMIm]Cl) ionic liquids. *Surf Coat Tech* 201:1-9.
14. Jiang T, Chollier Brym MJ, Dubé G, Lasia A, Brisard GM (2006) Electrodeposition of aluminium from ionic liquids: Part II - studies on the electrodeposition of aluminum from aluminum chloride (AlCl₃) - trimethylphenylammonium chloride (TMPAC) ionic liquids. *Surf Coat Tech* 201:10-18.
15. Endres F, Zein El Abedin S, Saad AY, Moustafa EM, Borissenko N, Price WE, Wallace GG, MacFarlane DR, Newman PJ, Bund A (2008) On the electrodeposition of titanium in ionic liquids. *Phys Chem Chem Phys* 10:2189-2199.
16. Andriyko Y, Nauer GE (2007) Electrochemistry of TiCl₄ in 1-butyl-2,3-dimethyl imidazolium azide. *Electrochim Acta* 53:957-962.
17. Tsuda T, Hussey CL, Stafford GR, Bonevich JE (2003) Electrochemistry of Titanium and the Electrodeposition of Al-Ti Alloys in the Lewis Acidic Aluminum Chloride–1-Ethyl-3-methylimidazolium Chloride Melt. *J Electrochem Soc* 150 :C234-C243.
18. Perre E (2010) *Nano-structured 3D Electrodes for Li-ion Micro-batteries*. Uppsala University, Uppsala
19. Perre E, Nyholm L, Gustafsson T, Taberna P-L, Simon P, Edström K (2008) Direct electrodeposition of aluminium nano-rods. *Electrochem Commun* 10:1467-1470.
20. Liu N, Mirabolghasemi H, Lee K, Albu SP, Tighineanu A, Altomare M, Schmuki P (2013) Anodic TiO₂ nanotubes: double walled vs. single walled. *Faraday Discuss* 164:107-116.
21. Macak JM, Tsuchiya H, Ghicov A, Yasuda K, Hahn R, Bauer S, Schmuki P (2007) TiO₂ nanotubes: Self-organized electrochemical formation, properties and applications. *Curr Opin Solid State Mater Sci* 11:3-18.

Table 1.

Results of EDS analysis of Ti-Al alloy deposited into alumina pores.

| Element | concentration, at.-% |
|---------|----------------------|
| Ti | 12.7 \pm 1,4% |
| Al | 73.8 \pm 3,4%* |
| O | 9.6 \pm 2,1% |
| Cl | 3.9 \pm 1,1% |

* sample holder and alumina nanotubes can influence to the concentration of aluminium

Table 2.

Results of EDS analysis of cross-section of the sealed part of alumina o .

| Element | concentration, at.-% |
|---------|----------------------|
| Ti | 1.1 ±0,7% |
| Al | 61.6 ±8,5% |
| O | 37.3 ±5,1% |

* Signal of Ti can be explained by influence of scattered electrons which give signal from the pore deposit. Nonstoichiometry of alumina can be explained by low thickness of the film resulting in low signal.

Figure and table captions

Fig. 1. SEM image of the titania pores filled with aluminium in potentiostatic mode for 15 min (A) and by potential cycling at sweep rate 20 mV/s (B) and 50 mV/s (C)

Fig. 2. Cyclic voltammogram of aluminium deposition into titania nanopores at a sweep rate of 50 mV/s (A). Scheme of the pulse electrodeposition for Al-Ti alloy (B).

Fig. 3. SEM images of the pure porous titania (A, C) and alumina (B, D) before (A, B) and after (C, D) application of 5 discharge pulses with a potential of 1600 V. Insert of Fig. 3 C shows the cross-section.

Fig. 4. Discharge plots of the nanoporous alumina (A) and titania (B) filled with Ti-Al and Al, respectively.

Fig. 5. Cross-section of the film (A) and top view (B) of the alumina pores filled with Ti-Al alloy after action of 10 discharge pulses applied at 1600 V (A) and 1800 V (B).

Fig. 6. Surface of the titania nanotubes filled with aluminium after action of 10 discharge pulses at 1600 V (A) and 1800 V (B).

Table 1. Results of EDS analysis of Ti-Al alloy deposited into alumina pores.

Table 2. Results of EDS analysis of the cross-section of the sealed part of alumina.