ANODIC TITANIUM OXIDE WITH CONTROLLABLE OPTICAL PROPERTIES FOR BIOMEDICAL APPLICATIONS

V. Gritskov[1], E. Gvozdoyskaya[1], G. Rabatuev[1], S. Lazarouk[1], O. Kupreeva[1],
A. Kurilenko[1], D. Isaev[2], F. Gorbachev[2], A. Lastovka[2], A. Mazurenko[3]
[1] Belarusian State University of Informatics and Radioelectronics, Minsk, Belarus
[2] Belarusian State Medical University, Minsk, Belarus
[3] State institution «Republican scientific and practical centre for traumatology and orthopedics», Minsk, Belarus

I. INTRODUCTION

Titanium oxide films have been intensively studied in recent years due to application of this material in medicine as coating for titanium implants [1-3]. The investigations of anodic titanium oxide fabrication and titanium oxide optical properties are presented in this work. In addition we have reviewed the possibilities of utilization of these oxide films in maxillofacial surgery for visualization and masking of titanium implants.

II. EXPERIMENTAL

The experiments were carried out on the samples of titanium foil of 99.9% purity with thickness of 50 μm and area of 0.8 cm^2. 1% citric acid ($C_6H_8O_7$) solution was used as electrolyte. The electrolyte temperature was kept in the range of 18–25 ºC. The anodization was carried out in a two stages: the first stage was the galvanostatic mode with the current density of I_f = 2 – 12 mA/cm^2 and anodic voltage (U_f) rising from 9 to 199 V with the rate of 1 V/s, and the second stage was the potentiostatic mode to provide a decrease in the current density by 10% of the initial value.

The thickness of the fabricated films (Lt) was evaluated using the Newton's color method [4] and SEM measurements.

Medical titanium implants were anodized in appropriate modes to fabricate contrast (for visualization) or near to skin (for masking) colored oxide films on its surface.

III. RESULTS AND DISCUSSIONS

During the investigation the anodic oxide films have been formed at forming voltages from 9 to 199 V. Table 1 shows the formation modes and corresponding film parameters. By varying forming voltage it is possible to grow barrier oxide films with a thickness from 30 to 300 nm and with different colors in the range of the entire visible spectrum from violet to red.

Photos of original sample and of samples with white, flesh (light orange), red, green and blue colored oxide films are presented on Figure 1. Coloring of titanium implants in the darkest colors, such as blue, to improve their visualization, and in bright colors, such as flesh and white, to mask the subcutaneous objects, is of special interest of medicine.

Since biological tissues have different optical penetration depending on the structure and thickness [5], the colored surface of titanium can be visualized at exhibiting light of the visible spectrum. But it has positive and negative aspects for different techniques of implantation of titanium structures. Metal structures (mounting plates and screws) of the maxillofacial area can be removed after the execution of their purpose in 10-12 months from surgical treatment. In this case, it is reasonable to cover the implant with the dark colored oxide film to simplify the visualization of the titanium object through the human tissue that allows to determine the exact location of the implant, to reduce the time of surgical treatment and to minimize operating injury. Such objects are clearly visible through the mucous membranes of the mouth and nose. They also are visible in case of surgical treatment in tissue layers that allows to carry out a surgical operation with minimal disruption of soft tissues. The results of investigations show that the visualization through human tissue is the best for titanium structures with oxide films formed at Uf=30±5V, which provides dark blue and blue-violet colors.

Titanium implants for reconstruction of the facial skeleton bones and for the face contouring imply a permanent presence in the body. In such cases, the implanted fastening plates should be masked. Therefore, it is reasonable to use implants with a near to skin colored oxide film with antireflective properties. Such implants are especially suitable in areas with a thin soft tissues: orbital area, nose bridge, oral cavity. Depending on the location and on the requirements of masking of the implantable fixing plates, preference is given to implants of yellow, pink, light golden, light orange, beige (flesh) colors.

Table 1 – The anodization modes and corresponding parameters of formed titanium oxide films

№	U_f, V	I_f, mA/cm^2	Sample color	Layer thickness (L_t), nm	Forming ratio ($F_r = L_t/U_f$), nm/V
1	9	2	beige	28	3,2
2	19	2	brown	40	2,1
3	29	2	blue-violet	57	2,0
4	39	2	blue	68	1,8
5	49	2	light blue	85	1,7
6	59	2	metallic	97	1,6
7	69	2	light golden	111	1,6
8	79	2	golden	128	1,6
9	89	2	orange	139	1,6
10	99	2	rosy-orange	154	1,6
11	109	2	violet-blue	171	1,6
12	119	12	blue-green	182	1,5
13	129	12	green	199	1,5
14	139	12	green-yellow	210	1,5
15	149	12	light orange	233	1,6
16	159	12	dark pink	239	1,5
17	169	12	violet-red	250	1,5
18	179	12	blue-violet	273	1,5
19	189	12	green-blue	284	1,5
20	199	12	green-violet	296	1,5

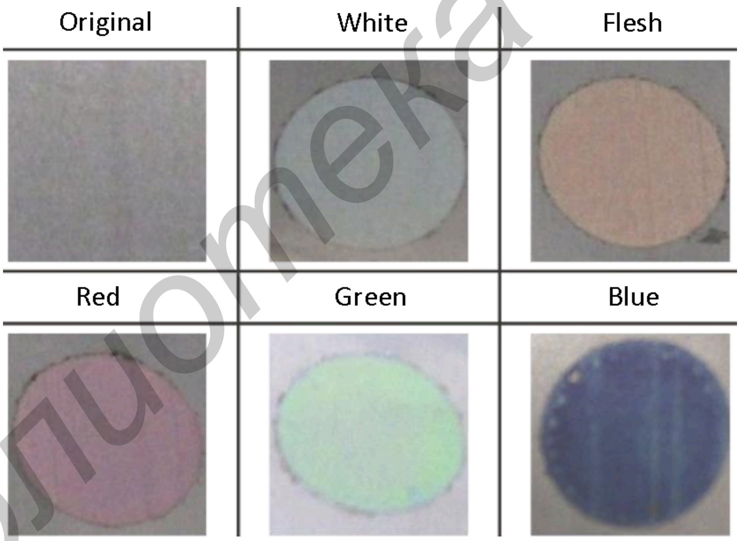

Figure 1 – The original and anodized samples of titanium foil

IV. CONCLUSIONS

The conducted investigations showed that oxide films with colors overlapping the entire visible range from red to violet and a thickness from 28 to 300 nm can be formed on the titanium surface by electrochemical anodizing. The obtained results are promising for using in maxillofacial surgery to fabricate titanium implants with strong, biocompatible coatings with required optical properties.

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