ANALYZE OF THE ANODIZING PROCESS PERFORMED ON TITANIUM ALLOYS SURFACE.

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Abstract. In the last few years, the anticorrosive research area of titanium used in medicine was focused on the improvement of the materials' quality surface, by different techniques as anodizing, and the examination of the electrochemical corrosion resistance. This study deals with the analysis of the anodizing process, equipments and techniques, used to perform the laboratory test. The results achieved by optical microscope techniques, show that the surface morphology of the oxide layer obtained after anodizing process, is strongly dependent on the process parameters like electrolyte chemical composition, cell voltage, temperature, time etc.

Keywords: Corrosion, electrolyte, anodizing, electrochemical cell.

1. INTRODUCTION.

Corrosion stands for material/metal deterioration or surface damage in an aggressive environment. Corrosion is a chemical or electrochemical oxidation process, in which the metal transfers electrons to the environment and undergoes a valence change from zero to a positive value. The environment may be a liquid, gas or hybrid soil-liquid. These environments are called electrolytes since they have their own conductivity for electron transfer. An electrolyte is a conductive solution, which contains positively and negatively charged ions called cations and anions, respectively.

Ti and Ti alloys offer many attractive properties (excellent specific strength, high corrosion resistance), which lead to an increasing interest in using them in different areas such as medical devices and automotive parts. Thus, the corrosion process which can be chemical in nature or electrochemical due to a current flow, requires at least two reactions that must occur in a particular corrosive environment (cathode reaction) [1].

The success of *biomaterials* in the body depends on factors such as the material properties, design, and *biocompatibility* of the material used, as well as other factors not under the control of the engineer, including the technique used by the surgeon, the health and condition of the patient, and the activities of the patient. Biocompatibility involves the acceptance of an artificial implant by the surrounding tissues and by the body as a whole. Biocompatible materials do not irritate the surrounding structures, do not provoke an abnormal inflammatory response, and do not incite allergic or immunologic reactions [2].

A variety of surface treatments and coatings have been developed for use with titanium and its alloys Anodization is one of the treatments used to form an oxide layer on the metallic anode. It has been found for a long time that metals can be colorized with anodization [3].

Titanium and its alloys serve for industrial interests both for the biomedical and space engineering usage, and their electrochromism phenomena have been examined quite intensively. NiTi possesses high corrosion resistance by virtue of a titanium oxide film naturally formed on its surface. Owing to these desirable thermomechanical properties and chemical stability, NiTi is becoming a popular biomaterial. The high Ni content in NiTi (about 50 at.%), however, has caused some concern of its safe use as an implant material because Ni is allergenic and toxic when its concentration exceeds a certain limit in the human body. In this respect, the native oxide on NiTi, which is very thin (less than 10 nm), is not adequately corrosion resistant by stringent medical standards.

In this paper, the anodization process on titanium alloys will be analyzed. Thus, the purpose of this paper is to provide a large understanding of the anodizing process of Ti alloys. The modification of the NiTi surfaces by ion implantation and analyze of the surfaces morphology will be assessed by optical microscope.

Below are shown a few applications for synthetic materials in the body. Note that metals, ceramics, polymers, glasses, carbons, and composite materials are listed according with the field research:

- *Dentistry* (influence of the biofilms in wear phenomena) - introduction of titanium implants has revolutionized dental implantology;
- *Orthopedic science* (hip and knee joints) - are fabricated from titanium, stainless steel, special high-strength alloys, ceramics, composites, and ultrahigh-molecular-weight polyethylene;
- *Skin repair template* – Silicone – collagen composite [4];
- *Contact lenses and ocular* - A variety of intraocular lenses (IOLs) have been fabricated of methyl methacrylate, silicone elastomer,

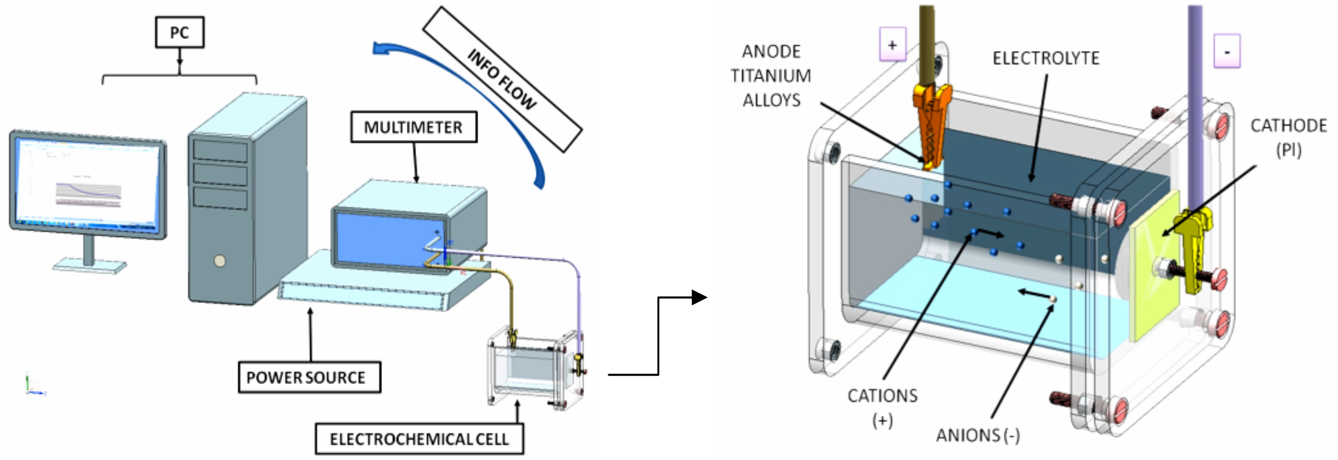


Figure 1: Equipments used to perform the anodizing process.

elastomer, soft acrylic polymers, or hydrogels and are used to replace a natural lens when it becomes cloudy, due to cataract formation [5];

- *Wear of replacement heart valves* - There are many types of heart valve prostheses and they are fabricated from carbons, metals, elastomers, plastics, fabrics, and animal or human tissues chemically pretreated to reduce their immunologic reactivity and to enhance durability [6].

Thereby, the biomaterials deterioration in an aggressive environment is encountered in a wide variety of applications.

2. EXPERIMENTAL.

2.1 EQUIPMENT USED TO PERFORM THE ANODIZING PROCESS.

In Figure 1 is presented the 3D view of the equipment used to perform the anodizing process. The images are designed in Unigraphics NX 5 (3D software used for design). The main components of the equipment are:

- *Electrochemical cell* – the place where the anodizing process takes place, requires 200ml solution, distilled water with different quantities of chemical component which will be implemented on Ti surface when the anodizing process will start. In Figure 1 is presented the electrochemical cell;
- *Power source* – the voltage and the current intensity influence the layer characteristics obtained on the biomaterial surface by the anodizing process;
- *The Multimeter* reads the process and sends to PC info with the reactions intensity.
- *PC* – using a special program to collect the anodizing process data. The software used will generate charts for each anodizing phenomena during the real time process. These charts show the evolution of the process and help us to understand the intensity reactions involved there.

2.2 PROCESS

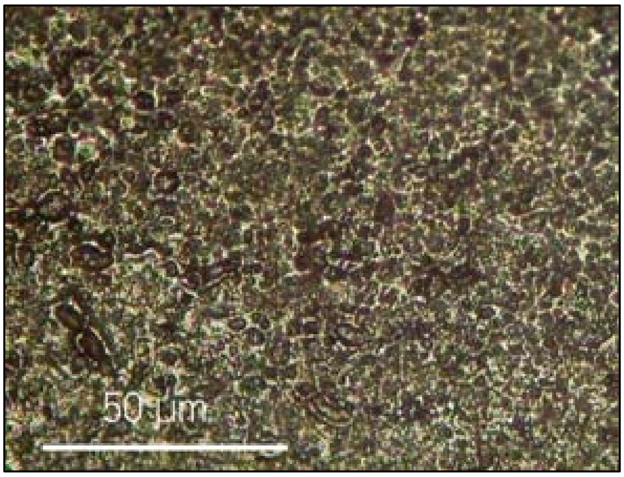
The samples (NiTi) will be used as an anode and should be assembled to the positive connector on the Power Source. As a Cathode will be used a Pl sample connected to the negative source. The anions that are leaving the Pl surface are the ions with more electrons than protons, giving them a net negative charge. The ions with fewer electrons than protons and a positive charge are called cations due, to the fact that the anode electrode is attracting them.

Ionization begins with changing the number of electrons equal with the number of protons in the nucleus. Performing this reaction, the Ti ions are leaving the crystalline structure, passing as hydrated ions into the liquid corrosive and leave in solid phase electrons equivalent amount. As specified in existing literature, on the sample surface of Ti will be formed an anode film which is increasing as a result of cations transfer.

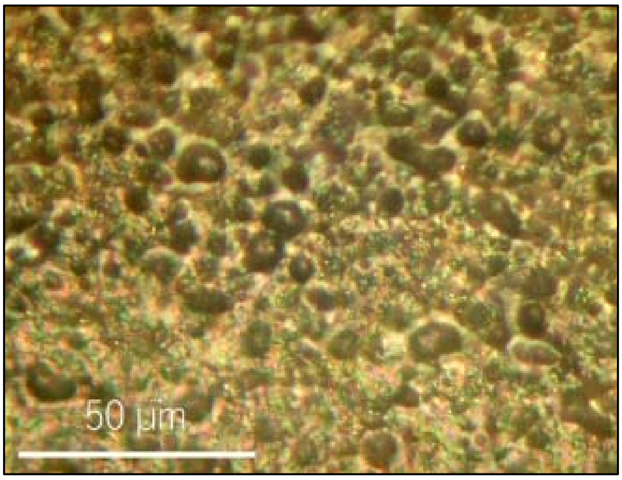
The electrolyte will have different chemical composition. The components added on the distilled water, due to the anodizing process, will be implemented on the biomaterial oxide layer.

Table 1. *Electrolyte components.*

Component description	*Chemical formula*	*Molar concentration*	
		a.)	b.)
Sodium Silicate	Na_2SiO_3	0.5	0.6
Sodium Borate	KOH	0.25	0.04
Potassium Hydroxide	$Na_2B_4O_7$	0.04	0.25
Glycerin	$C_3H_8O_3$	0.05	0.05



a.) 0.5 M Na_2SiO_3 + 0.25M KOH + 0.04M $Na_2B_4O_7$ + 0.05M $C_3H_8O_3$



b.) 0.6 M Na_2SiO_3 + 0.04M KOH + 0.025M $Na_2B_4O_7$ + 0.05M $C_3H_8O_3$

Figure 2: ***OM images of surfaces anodized in different electrolyte composition***

3. RESULTS AND DISCUTIONS.

The current density vs. time plots obtained during the anodizing processing in Silicate electrolytes are shown in Figure 3. In the case of silicate based electrolyte, the initial dissolution/passive film formation was observed in the first 7s and the barrier layer break down begin at lower current density. The final current registered at the end of 25 min process duration in Si electrolyte was 32.5 mA/cm^2.

The surface micrographs showed that the film morphology becomes uniform due to the fast current decrease this is gradually stabilized at a low current value which can be observed in the curve in electrochemical transient. During the decrease of current density a large number of small size sparks was observed as a white light scanning over the electrode surface rapidly and randomly but distributed evenly over the whole surface.

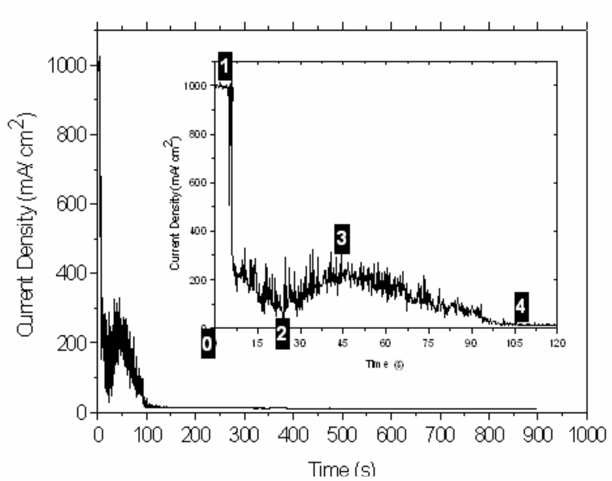


Figure 2: ***Current transient during anodizing of NiTi vs. time plot of a typical anodic deposition cell***

The surface morphology can be observed in Figure 2. In the ***optical microscope*** (***OM***) images (50µm) is shown the surface of the NiTi anodized in different electrolyte compositions. It can be seen that the electrolyte composition influence the structure of the oxide layer obtained at low current intensity (32.5mA).

In order to achieve a better understanding of the anodizing process, in Figure 3 is shown the intensity of the reactions that occurred during the 2 min of the process. The most important stages of the process are:

- ***Between 0-1*** the current increases monotonically;
- ***In point 1*** a continuous barrier layer is formed over the anode surface (NiTi sample);
- ***Between 1-2*** the current decreases as layer thickness;
- ***In point 2*** the barrier layer break down begins;
- ***Between 2-3*** the current increases as breakdown of barrier accelerates;
- ***Between 3-4*** the current decreases until reaches a constant value (32.5mA/cm^2).

4. CONCLUSIONS.

In order to achieve a better understanding of the anodizing process, the behavior of the NiTi surface morphology immersed in different electrolytes pH concentration, was revealed. In the experimental study, it was used samples of nickel titanium (NiTi) alloy.

NiTi alloy reached the attention from his unique properties such as shape memory effect (SMA), superelastic and corrosion resistance.

In order to highlight the equipments used in anodizing process, were designed 3D images in Unigraphics NX5, a special soft used in industry execution design.

The anodic treatment of NiTi was carried out in different molar concentration solutions and with low voltage applied in the electrochemical cell. The results show that the dissolution of the metallic surface and deposition of the chemical components added in the electrolyte in order to protect the oxide film from corrosion phenomena, occur simultaneously.

According to the results obtained by OM analyze technique, the surface morphology of the oxide layer is strongly dependent on the process parameters like electrolyte chemical composition, cell voltage, temperature, time etc.

Thus, the formation of a stable titanium dioxide layer on NiTi alloy is desired in order to increase the corrosion resistance and decreasing nickel ion release. The modification of the NiTi surfaces by ion implantation and analyze of surfaces morphology by OM method is the subject of the present study. Thereby, the main purpose of this paper is to achieve a better understanding of the anodizing process performed on the titanium alloys.

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