Nanostructured Titania Coatings on Electrolytic Plasma-Polished Titanium Alloys

A. Stanishevsky, University of Alabama at Birmingham, AL; & A. Parshouto & A. Mahiout, VTT Manufacturing Technologies, Espoo, Finland

Titanium and its alloys are common materials used for biomedical implants. These materials are valued for their overall mechanical properties, and generally little adverse reactions in a biological environment. Functionalisation of the biomedical alloys by depositing nanostructured oxide coatings dramatically effects the biological response of implants, and often improve their biocompatibility. Nanostructured coatings mask the difference in the chemical composition of the substrates, and impose an additional surface topography at nanoscale. It has also been demonstrated that the success or failure of these materials as implants is very strongly connected with the adhesion, composition and structure of the oxide layers, surface contamination, and surface topography. Surface treatment of biomedical alloys before coating plays often a crucial role in the coating's performance. First results of the chemical solution deposition of nanostructured TiO_2 coating on the electrolytic plasma polished (EPP) titanium alloys are presented in this work. The capabilities of the electrolytic plasma to polish and modify the surface of titanium alloys are demonstrated. The EPP method is based on the chemical and physical processes occurring at the electrode surface immersed in a low-concentration non-acid electrolyte, during applying the direct current voltage in the range of 100 – 600 V. Chemical solution deposition with and without the electric field has been utilized for synthesizing titania based coatings from solutions of alcoxides or inorganic salts, followed by thermal annealing to crystallize the coating material. Our preliminary results show that chemically deposited and annealed dense 100-200 nm thick titania coatings on EPP titanium exhibit smaller grain size and better adhesion than the coatings on mechanically polished substrates. The coatings have favorable for biomedical applications rutile structure, however further studies of the corrosion and wear resistance, as well as the cell response are needed to optimize the both processes of electrolytic plasma treatment and titania coating deposition.

For more information contact:
Prof. Andrei Stanishevsky
Department of Physics
The University of Alabama at Birmingham
CH310, 1300 University Boulevard,
Birmingham, AL 35294-1170
Tel: +(205)-934-8030
Fax: +(205)-934-8042
E-mail: astan@uab.edu

Introduction

Titanium and its alloys (Ti-Ni, Ti-6Al-4V, Ti-6Al-7Nb, Ti-5Al-2.5Fe, Ti-Mn6, etc.) are common materials used for various bio-medical applications, particularly for artificial heart valves, orthodontic and orthopedic implants. The biocompatibility of titanium and its alloys has been attributed to the presence of stable oxide layers instantly formed on the surface. It has also been demonstrated that the success or failure of these materials as implants is very strongly connected with the surface properties including composition and structure of the oxide layers, surface contamination, and surface topography. These properties influence the interaction of the implants with the biological environment.

The relationship between the surface state and biocompatibility of engineered biomaterials is not well understood yet. The knowledge about which surface properties are the most critical, and how these properties of the implant material are transferred to the biological environment is currently a subject of extensive studies [1-3]. Over past years numerous studies were conducted to address the problems concerning the influence of biomedical implant surface properties on biological response [4-7]. Among physical parameters affecting cell response surface topography at micro- and nano-scale, surface energy, and surface charge seem to be the most important. Cells use the morphology of the substrate for orientation and migration. It is known that surface modification of biomaterials induced by a finishing technique can promote desirable reactions (e.g. an increase in cell adhesion) or prevent undesirable effects, change cell or soft tissue attachment kinetics, change the healing process that result from the presence of the an implant, prosthesis or artificial organ; cause a tissue inflammatory and/or foreign body response in the tissue surrounding the biomedical implant [8-10].

There are several methods to treat the surface of metallic materials for biomedical application, including mechanical or electrochemical polishing, chemical or plasma etching, ion irradiation, and coatings deposition. Each of these methods can affect the material structure, composition, and surface topography in one or another way [11-16]. The results of the surface treatment depend also on the history of the implant fabrication process (e.g., machining, thermal processing).

Among all surface treatments of biomedical alloys, electrochemical polishing is so far the most critical in the final surface appearance. This method utilizes concentrated acid-based electrolytes, and it is commonly used for steel and titanium based materials. The traditional electrochemical polishing is carried out at low DC voltages (Figure 1, regime I) and current density in the range of 0.1-1.0 A/cm^2. The isotropic surface topography of complex shape articles can be easily reached [11-14].

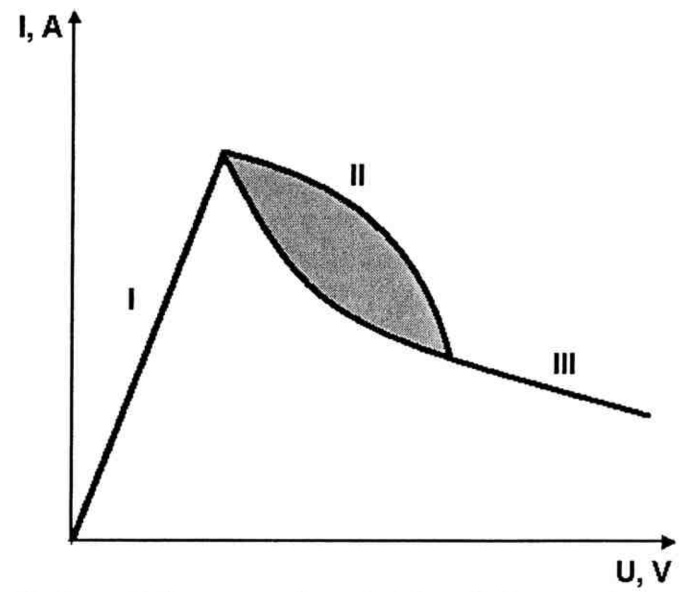

Fig.1. Volt-ampere characteristic of the electro-chemical polishing processes: I – ordinary electrolysis, II – transient stage, III – steady electrolytic plasma stage.

Another kind of the electrochemical polishing that can potentially be very efficient for surface engineering of biomedical alloys, takes place at higher voltages (usually 100 – 600 V, Figure 1, regime III). Low-concentration aqueous electrolytes are used [17,18], which makes this method attractive also from the environmental point of view. The method is characterized by formation (Fig.1, regime II) and maintaining (Fig.1, regime III) at the surface of an article (anode) a stable vapor/gas (plasma) layer separating the surface from the liquid electrolyte, and promoting intense chemical and electrochemical reactions between the materials of the article, and the electrolyte vapor. We will further refer this method to as electrolytic plasma (EP) treatment. The EP treatment can dramatically change the surface properties of metal substrates and affect the processes of formation of functional coatings. The goal of this work is to develop the deposition processes of biocompatible nanostructured titania thin-film coatings with controlable properties on biomedical titanium alloys polished with electrolytic plasma.

Electrolytic plasma polishing (EPP)

The EP treatment involves electrolysis and electrical discharge phenomena and it is an emerging, environmentally friendly surface engineering technology. This method is a part of several electrochemical processes that have been categorized in a recent review under the generic title of "Plasma electrolysis" [19]. Although the discharge phenomena associated with electrolysis were discovered more than a century ago, and were studied in detail over past several decades, their practical benefits were first exploited only in the 1960s. Various realizations of plasma electrolysis have been elaborated since that including nitriding, nitrocarburizing, oxidation, etching, coating removal and deposition, and polishing of metal surfaces [17,18,20-27]. Oxidation of metal surfaces is currently is one of the most used applications of plasma electrolysis. Yerokhin et al [20] utilized AC electrolytic plasma for oxidation of a Ti-6Al-4V alloy. They found good corrosion resistance of the oxidized material in physiological solutions. Meletis et al [21] have demonstrated that EP treatment can effectively clean steel surfaces. The produced surfaces are nanocrystalline and exhibit a passive behavior. The latter is a direct outcome of physics involved in the process, and results in significantly improved corrosion resistance compared to the base steel. This is important when considering biomedical applications or subsequent coatings deposition.

A number of electrolytic plasma polishing (EPP) processes have been developed [17,18]. The polishing processes are carried out in neutral (pH 5.5 – 8.0) low-concentration (2.0 – 6.0 %) aqueous solutions of inorganic salts such as sulfates or chlorides of ammonia and sodium. The EPP offers cleaning, rounding the sharp edges, deburring, the surface preparation to a subsequent application of diverse coatings. It has been proven to be a good alternative to traditional electrochemical polishing for stainless and low-carbon steels, copper, and aluminum [18]. It has been also shown that EPP of brass can result in selective etching of alloy surfaces. The modification of the elemental composition of the surface layers of alloys during EPP is not well studied so far. Competing processes of etching and oxidation also complicate the EPP of commercially pure titanium and its alloys. Although some good preliminary results have been achieved for pure titanium and Ti-6Al-4V, the detailed process understanding is still lacking, and its parameters are far from optimum.

A basic schematic representation of the electrolytic plasma treatment method realization is presented in Figure 2. The surface of the anode material is modified by a combination of chemical and physical processes that occur in a thin (1 – 100 μm) plasma layer (often called a vapor – gaseous blanket) surrounding the electrode as shown in the insert in Fig.2. A general description of the process has been given in several publications [19,21,24], and it is briefly outlined below.

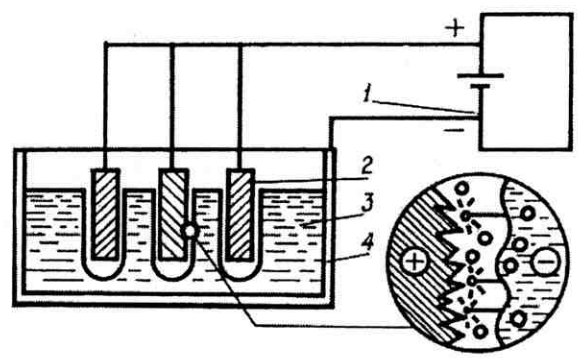

Fig.2. Schematic representation of electrolytic – plasma (EP) treatment: 1 – DC power supply, 2 – sample, 3 – electrolyte, 4 – bath.

According to available data, a DC potential rise leads to current oscillation, increase of current density, local boiling of the electrolyte adjacent to the electrode, and light emission due to spark discharges. This happens in the voltage range of 80 – 200 V depending on the particular process [28]. An intensive heating can occur at this process stage, which can sometimes melt the processed articles. Such heating can also cause modification of near-surface chemical and phase composition of the materials.

Upon progressing to a maximum of current density (Fig.1) a continuous vapor-gaseous layer is formed around the anode. Due to the hydrodynamic stabilization of the vapor layer the current drops by a factor of 3 – 5, and a stable EP polishing regime is established. The voltage range for this regime (150 – 600 V) depends on many factors but primary on the electrolyte concentration and temperature. Almost all of the potential drops in this continuous vapor-gaseous layer causing the electric fields in the range of $10^6 - 10^8$ V/m. Such a high electric field initiates the ionization process resulting in a uniform blue glow distributed throughout the vapor-gaseous layer. Azumi et al [29] have also observed the light emission when the temperature of electrodes in an electrolytic cell exceeded the boiling temperature of the electrolyte due to the intense cathodic polarization: a thin vapor layer was formed at the metal / electrolyte interface in which a high electric field ionized vapor molecules to generate the plasma state. The spectra of the emitted light were assigned to the constituents of the electrolyte solution, electrode material and gaseous hydrogen evolved at the electrode. Although there is also heating of the electrode due to plasma action, the integral substrate temperature remains relatively low in the range of 200 – 300 °C due to simultaneous cooling by the electrolyte. The local surface temperature can be very high that can lead to the material erosion and phase transformations. Further increase of the DC potential leads to local arcing that causes severe damage to the surface of the treated material.

A number of the EP treatment applications and equipment designs and processes are based on this representation of the process. Figure 3 shows a pilot

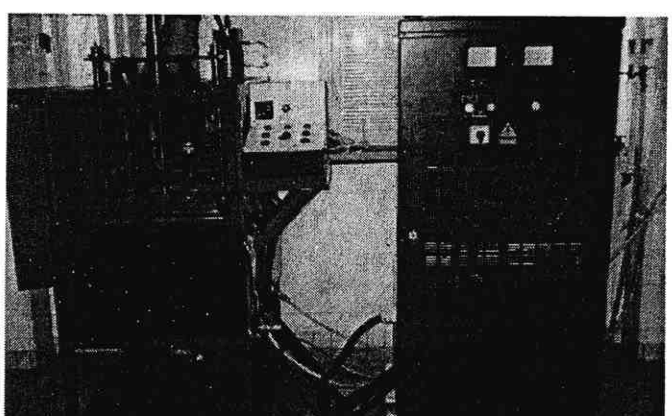

Fig.3. Pilot manual EP treatment system at VTT Manufacturing Technology, Espoo, Finland.

EPP apparatus capable to process surface area of ~ 0.2 m^2. A major drawback of the EPP is higher power consumption when compared to traditional electrochemical polishing. This disadvantage is compensated, particularly, by much lower electrolyte consumption, shorter process time due to higher material removal rate (Figure 4), and easy disposal of used electrolytes because of their low toxicity. Still, the power consumption is a limiting factor of the electrolytic plasma technology, and the processes have to be further optimized.

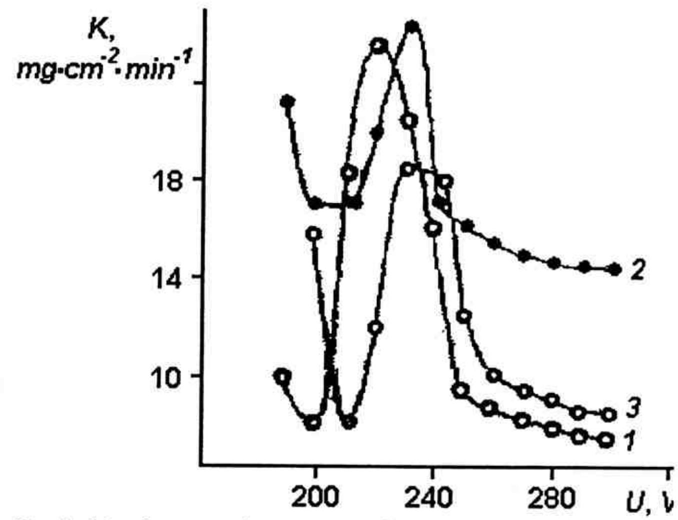

Fig.4. Metal removal rate as a function of DC voltage in 20% NH_4Cl: (1) – Cr, (2) – Mo, (3) – Ti.

Despite the significant progress achieved in electrolytic plasma processing of metal surface, it is little known on its feasibility for polishing the biomedical alloys based on titanium, and for surface finishing before deposition of a functional coating.

Nanostructured titania coatings on EP-polished titanium alloys

Functionalisation of the biomedical alloys by depositing nanostructured oxide coatings dramatically effects the biological response of implants due to formation of a specific surface topography at nanoscale. This kind of topography may control the patterns of cell motion and attachment, thus affecting local cell-implant interactions at the molecular level [30]. The oxide coatings on titanium-based biomedical alloys have been demonstrated to improve their biocompatibility [31,32].

Oxide formation of the titanium alloy surface occurs simultaneously with polishing during EP treatment in many experiments, however we were able to achieve a substantial progress in producing quality surfaces that were used for chemical solution deposition of the coatings. An example of EP polished Ti-alloy parts is shown in Figure 5.

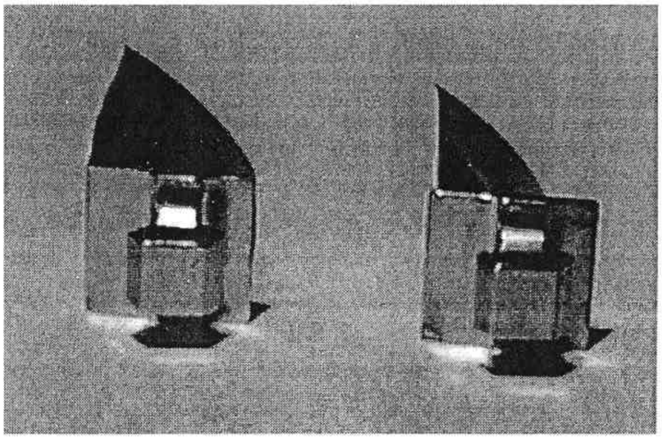

Fig.5. Electrolytic plasma-polished titanium alloy parts.

Chemical solution deposition of the titania coatings without applying an electric field was conducted by a sol-gel process using titanium iso-propoxide as a precursor. The precursor solution was spun on the EP-polished Ti-alloy substrates at 3000 rpm followed by drying at 100 °C. These operations were repeated for 5 times to obtain a thicker layer. The samples were annealed in a rapid thermal processing system at 650 °C for 1 min to crystallize the material. The structure of the resulting 150-200 nm thick coatings was rutile

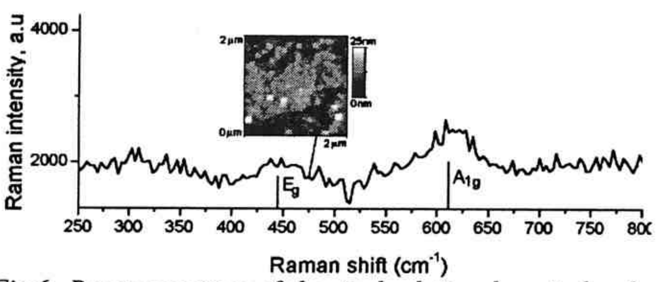

Fig.6. Raman spectrum of chemical solution deposited and crystallized TiO_2 rutile phase on a Ti-alloy substrate.

according to Raman studies (Figure 6). There was no substantial difference in the structure of the coatings prepared on EP-polished and mechanically polished substrates, although the preliminary results show that the sol-gel derived titania coatings on EP-polished titanium alloy exhibit smaller grain size when compared with those polished mechanically (Figure 7). It was also noted that the coating on the EP-polished substrates are more scratch and wear-resistant. The coefficient of friction of these coating was ~0.1 (~0.2 for the coating on the mechanically polished sample) during a micro-friction test in a contact with a steel ball at 1 mN load.

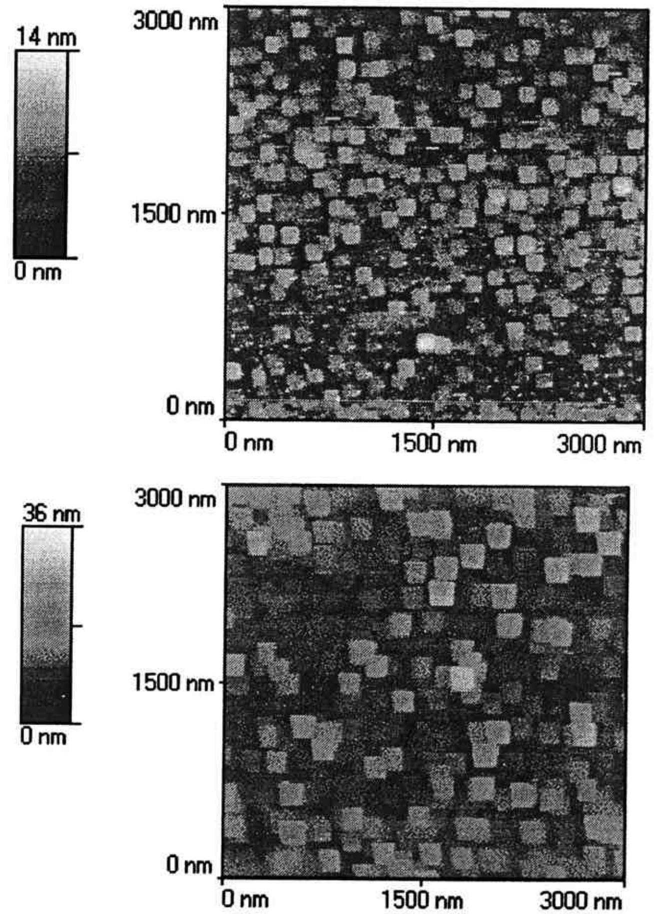

Fig.7. AFM images of the surface of TiO_2 coatings on mechanically polished (bottom) and electrolytic plasma polished (top) titanium samples.

Summary

Nanostructured titania thin film coatings were prepared on electrolytic plasma-polished Ti-alloy substrates using chemical solution deposition. These coatings have favorable for biomedical applications rutile structure and good mechanical properties. Further studies of the EP polishing and titania chemical deposition, corrosion and wear resistance, as well as the biological response of the coatings are needed to optimize the coating performance, improve the interface properties yet keeping full control over the coating crystallization process, its structure and surface topography.

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