The effects of growth TiO_2 nanotubes on forged $\text{Ti}_6\text{Al}_4\text{V}$ alloy and selective laser sintered $\text{Ti}_6\text{Al}_4\text{V}$ alloy surfaces for environment and medical applications

Luciana Laura Dincă (Shamieh) Boulven^{1,*}, Alexandra Banu¹, Gizem Nur Soylu², Gabriel Dobri¹ and Madalina Elena Mocirla (Mihai)¹

¹Politehnica University of Bucharest, Department of Manufacturing Technology, Splaiul Independenței no. 313, sector 6, Bucharest, RO-060042, Romania

²University of Kocaeli, Kocaeli, Umuttepe Yerleskesi, 41380, Turkey

Abstract. The paper describes the effect of growth TiO_2 nanotubes on titanium surfaces by anodic oxidation for environmental and medical applications. The importance of the metallurgical state of TiAl_6V alloy on the growing of TiO_2 nanotubes by anodization will be highlighted. Starting from the possibility of obtaining the TiO_2 nanotubes, the paper presents results on TiO_2 nanotubes grown by electrochemical anodization method, using a solution containing HF 0,4% and having as electrodes, graphite as cathode and titanium alloy specimens obtained by two technologies: by cold plastic deformation as well as by additive manufacturing process SLS, as anode. So, the nanotubes were produced by anodization and analysed by scanning electron microscopy. The aim of this paper is to compare the electrochemical formation of TiO_2 on the surface of both specimens knowing that the titanium alloys and its oxides are used in many biomedical and environmental applications, thus providing the importance of nanotubes and the fact that their properties open doors in these fields.

1 Introduction

TiO_2 nanotubes have benefited of a significant technological interest in the recent years thanks to the widely used in many areas [1].

To obtain TiO_2 nanotubes on titanium alloy surfaces, several processing methods have been used, but from these methods, electrochemical deposition of titanium dioxide presents on important interest, thanks to the capability to produce self-organized structures at ambient temperature [2].

TiAl_6V alloy, thanks to its biocompatibility, corrosion resistance and strength, is successfully used in medical prosthesis and orthopedic and dental implants [3]. Starting from the fact that, because the implants failure generally occurs between the implant and the underlying bone surface, one of the easiest ways of fixation of titanium implants to the human bone is the direct contact of the implant with the bone, their osseointegration, thus

* Corresponding author: lucianalaura_shamieh@yahoo.com

obtaining TiO₂ nanotubes have gained much concern over the last decade due to its characteristics on titanium alloy [3].

Considering the metallurgical state of TiAl₆V alloy, because of its dual phase α and β , the resulting nanotubes will have different dimensions that can be modulated for a wide variety of applications [4].

The titanium surface functionalization with the TiO₂ nanotube offers new solutions in environmental and medical applications, due to the fact that researchers are focusing on exploring particular properties of titanium surfaces for use in these areas [4].

The main objective of this paper is to establish the effect of growth TiO₂ nanotubes on TiAl₆V alloy surfaces for environmental and medical applications, with the aim of anticipating the importance of nanotubes and the fact that their properties open doors in these fields.

2 Experimental details

2.1 Materials

In order to illustrate the growth mechanism of TiO₂ nanotubes and observe the effect of growth TiO₂ nanotubes on titanium alloy surfaces, two different specimens were used.

The specimens used in this study, which are the anode, are obtained by two technologies: by cold plastic deformation and by additive manufacturing process SLS.

First sample of Ti₆Al₄V of (20×10×10mm) was obtained by cold plastic deformation, and then mechanically surface was grinded with sandpaper 400, 800 and 1200 successively. The another Ti₆Al₄V sample, of 10mm thickness was obtained by additive manufacturing process, using a EOS EOSINT M270 laser sintering machine, and was built horizontally onto a titanium substrate.

The surface of each sample was washed with acetone, ethanol and distilled water by ultrasonic for 15 min.

Electrolyte composition contains glycerol, water and fluoric acid.

2.2 Method

To obtain the nanotubes, anodization method was used, which consisted of using a solution containing HF 0,4% and having as electrodes, graphite as cathode and Ti₆Al₄V alloy specimens as anode. The anodization experiments were carried out at room temperature, the voltage applied was 25 V and 8 h of anodizing were applied for both specimens. After anodization, the samples were rinsed with deionised water and then dried.

The specimens were analyzed by a scanning electron microscopy (SEM) method.

3 Results and discussion

3.1 Metallurgical state of TiAl₆V alloy

This study started from the highlighting the importance of the metallurgical state of TiAl₆V alloy on the growing of TiO₂ nanotubes.

Starting from the fact that, metallurgical state is very important, the specimen's surfaces before and after anodic oxidation will be presented.

Usually the sintering temperature of conventional Ti-6Al-4V alloy was 1300°C, in the β phase region at a temperature well below the liquids temperature (~1660 °C for Ti-6Al-4V) [5], but in the case of laser sintered Ti-6Al-4V alloy, there is possibility that because of local overheating to temperatures higher than the liquids temperature of Ti-6Al-4V (~1660 °C) liquid phase sintering occurs. That liquid phase sintering provides the supplementary driving forces for sintering because of extra surface energies (from the liquid surface and from the liquid-solid interface) and implies different sintering mechanisms such as pore-filling, from the solid-state sintering [5].

Although the additive manufacturing is one of the most promising and interested technologies for many areas such as medicine, the additive manufacturing process still shows a series of issues among which the microstructural inhomogeneity in the built material [5].

The metallurgical state of Ti₆Al₄V alloy for both forged and sintered parts are shown in Fig.1. and Fig.2.

Fig. 1. The metallurgical state of Ti₆Al₄V alloy for forged specimen

Fig. 2. The metallurgical state of Ti₆Al₄V alloy for sintered specimen

3.2 Experimental procedure TiO₂ nanotubes formation mechanism

In this paper, the mechanism of the titanium nanotube formation during anodizing was studied. We produced and studied Ti₄Al₆V surface covered with TiO₂ nanotubes with the aim to obtain a material appropriate for biomedical applications and environment. Starting from the fact that electrochemical parameters and the electrolyte concentration, are very important in achieving TiO₂ nanotubes, our work consist in an anodization voltage 25V, and a intensity that stabilized after 13 minutes at I = 0.07A in the case of forged sample and after 20 min at I = 0.08A in the case of sintered sample. Electrolyte compositions contain glycerin, water and fluoric acid. The samples were introduced into a electrochemical cell containing HF 0.4% electrolyte and having as electrodes: graphite as cathode and titanium alloy specimen as anode (see Fig. 3).

Fig. 3. Electrochemical anodization

The distance between the two electrodes was kept at 3 cm in all anodizing process. After electrochemical anodization, the specimens were rinsed with deionized water and then ultrasonicated in ethanol for 3 min.

To detect the influence of metallurgical state on the morphology of nanotube, was performed to fabricate TiO₂ nanotubes on two different surfaces, obtained by cold plastic deformation as well as by additive manufacturing process SLS.

3.3 Morphology of TiO₂ nanotube growth

The morphology of the TiO₂ nanotubes on Ti6Al4V was observed using SEM method and are presented below.

In figure 4, in the case of forged specimen, the TiO₂ nanotubes have been grown on the surface of Ti6Al4V, they covered the whole surface and its diameter was approximately 80 nm.

Fig. 4. SEM images of anodized at 25V TiO₂ nanotube on forged sample

Fig. 5. SEM images of anodized at 25V TiO₂ nanotube on sintered sample

In figure 5, in the case of sintered specimen, the TiO₂ nanotubes have been grown on the surface of Ti6Al4V as are presented. With a scanning electron microscope (SEM) can be observed the fracture surfaces of sintered sample.

3.4 Application of TiO₂ nanotubes in environmental and medical applications

To make our life easier and more comfortable, many products appear in the last years but during the various steps to the final products, these cause many environmental problems and increase health human risks [6].

TiO₂ nanotubes have attracted much attention recently and play an important role in the new technologies developed to assure a good future for our world.

The importance of nanotubes in environmental technologies comes from their photocatalytic activity in the degradation of inorganic and organic pollutants, water splitting, photovoltaic devices. They are also candidates for use in sensitive sensors for trace compounds, because of their wide absorption spectrum [6].

The importance of nanotubes in medical field comes from their applicability, in vitro, they have been used to control cell activity, enhance the anti-bacterial activity, provide surface- induced mineralization, drug delivery, in vivo, TiO₂ nanotubes have been used to enhance osseointegration, biocompatibility, protein synthesis etc. [6].

4 Conclusions

Starting from the importance for environmental and medical applications of growth TiO₂ nanotubes on titanium alloy surfaces, on the basis of the analysis carried out in this paper, we can be highlighted next conclusion:

TiO₂ nanotubes were grown on titanium alloy surfaces through anodizing method trying two specimens obtained by two different technologies.

On both specimens TiO₂ nanotubes have been successfully growth and analysed with the SEM;

Importance of nanotubes comes from their applicability, in vitro, they have been used to control cell activity, enhance anti-bacterial activity, provide surface-induced mineralization, drug delivery, in vivo, TiO₂ nanotubes have been used to enhance osseointegration, biocompatibility, protein synthesis, etc. also

The results presented in this paper provide information on the importance of the of growing TiO₂ nanotubes on Ti₆Al₄V alloy surfaces for environmental and medical applications.

References

1. P. M. Perillo and D.F. Rodriguez, Growth control of TiO₂nanotubes in different physical environment, Comisión Nacional de Energía Atómica, CAC, Grupo MEMS, Av. Gral. Paz 1499 (1650) Bs. As., Argentina, (2012)
2. J. Wang, H. Li, Y. Sun, B. Bai, Y. Zhang, Y. Fan, Anodiz. of Highly Ordered TiO₂ Nanotube Arrays Using Orthog. Design and Its Wett. Laboratory for Biomechanics and Mechanobiology of Ministry of Education, China (2010)
3. M. Niinomi, in Encyclopedia of Biomedical Engineering, Handbook of Non-Ferrous Metal Powders,(2019)

4. K. Indira, U. Kamachi Mudali, T.Nishimura, N.Rajendran, A Review on TiO₂ Nanotubes: Inf. of Anod. Param, Form. Mech, Prop, Corr Behavior, and Biomedical Applic, Journal of Bio- and Tribo-Corrosion, Dec (2015)
5. M.Yan and P. Yu, An Overview of Densification, Microstructure and Mechanical Property of Additively Manufactured Ti-6Al-4V — Comp. among SLM, LMD and SLS, and with Conv. Powder Metallurgy, (2015)
6. Q. Zhou, Z. Fang, J. Li, M. Wang Review, Appl. of TiO₂ nanotube arrays in env. and energy fields:A review,College of Geosciences, China University of Petroleum Beijing, China, (2014).