Evaluation of Microstructure and Antibacterial Properties of TiO_2 Nanotube/CuO Composite Coating Fabricated Using Combination of Magnetron Spattering and Electrochemical Anodizing

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Abstract

A nanocomposite coating including titanium oxide nanotube and CuO is synthesized on the commercially pure titanium using electrochemical anodizing at 30V for 2 hours in an electrolyte containing Ethylene glycol, water and ammonium fluoride in combination with a magnetron spattering process to produce a thin layer of copper. A thin layer of copper deposited on the titanium prior to anodizing as well as after the anodizing process and then the samples were thermally oxidized under pure oxygen atmosphere at 300°C for 1 hour. Microstructural evaluations revealed that titanium nanotubes were formed over the metallic surface. In the case of the pre-coated sample, CuO particles were detected over and in the nanotubes and for the post-coated sample, a contiguous layer of copper oxide was formed over the nanotubes. Wettability of the produced samples improved in comparison with the sample without copper. Also, the antibacterial activity of the copper-containing samples was better than the raw materials and the sample without copper.

Keywords: Titanium Oxide Nanotube, Copper Oxide, Anodizing, Magnetron Spattering, Wettability, Antibacterial Activity.

1. Introduction

Titanium oxide nanotubes formed on titanium substrate during chemical anodizing is promising material for use in various applications specially photo catalysts, anti fog and self-cleaning glass and also in biomaterials applications[1-3]. In the case of biomaterials applications, various studies revealed the potentials for the use of TiO_2 nanotube as antibacterial and osteo-generation material. It is mainly attributes to the nano pros and wetting ability of this material as a coating on titanium substrate which can be improved by the addition of antibacterial agents such as antibiotics as well as minerals such as silver, zinc and copper ions [4-8].There are two main risks in surgical procedures for the replacement of an implant; first, the risk of inflammation and second the osteo-generation on the surface of implant. Recent researches reported the ability of copper as an antibacterial agent and also the use of copper oxide as osteo-generation material. Copper can be introduced in the chemical composition in various ways and there are many reports that apply copper and copper oxide by the use of coating techniques. Magnetron spattering may be used as a coating rout which is able to produce thin layer of a metallic coating with uniform distribution and flexibility. [7]
Different parameters concerning the anodizing process of titanium were reported by the researchers specially the applied voltage, procedure time and temperature as well as the electrolyte composition [9-11]. Also, application of a second phase to produce composite coating with functional abilities was reported in some applications such as gas sensors [12].In this research, a nano composite coating containing titanium oxide nanotubes and copper as an additive to the surface coating produces via magnetron spattering with two main different routs including copper pre anodized coating and copper post anodize coating was synthesized and then, wettability and antibacterial properties of the produced samples were compared.

2. Materials and Methods

A commercially pure titanium sheet with the dimension of 20×20×0.7 mm was used as substrate. Prior to the anodizing process, the surface of the samples was polished mechanically using abrasive paper and alumina suspension using emery paper. The samples were then ultrasonically cleaned in acetone to eliminate the contaminations. An electrolyte containing Ethylene glycol, water and ammonium fluoride (95:5 vol. with 0.5 wt.% ammonium fluoride) was used for anodizing process as reported in other researches [13-14] Anodizing process carried out using a potentiostat power source in an applied anodizing voltage of 30 volts for 2 hours with a graphite cathode to produce titanium oxide nanotube (TNT). In this study three different samples were prepared in three different routes; first, a sample were anodized without any copper additive. Second, a titanium substrate was

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first coated with a thin layer of copper via magnetron spattering and then thane sample was anodized, and the third sample was first anodized and then after the anodizing procedure, a thin layer of copper was deposited via magnetron spattering on the anodized surface. All three samples then were annealed at 300°C for 1 hour in a tube furnace under pure oxygen atmosphere. Microstructural investigations were carried out using field emission scanning electron microscope (FESEM). The wettability of the samples was measured using a droplet technique with deionized water. Also, antibacterial activity of the surface evaluated using a standard procedure based on ISO 22196 standards by the use of E. coli bacteria.

3. Results and Discussion

The microstructure of the sample anodized at applied voltage of 30 V for 2 hours without any copper coating is shown in Fig. 1. As shown here, titanium oxide nanotubes are formed on the surface of the titanium substrate and were grown normally to the substrate surface. The formation of titanium oxide nanotubes is due to surface oxidation and dissolution of the oxide layer in the presence of fluoride ions as previously reported by [9-11].

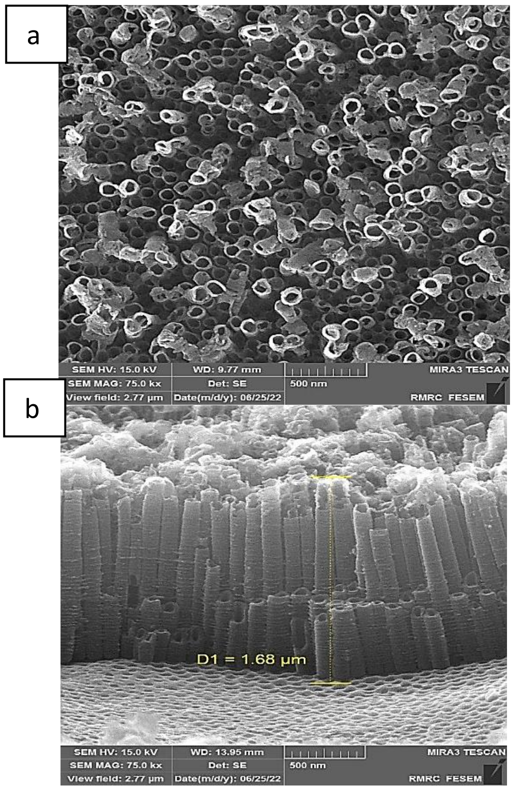

Fig. 1. FESEM micrograph of titanium oxide nanotubes on titanium substrate anodized at 30 V for 2 hours without copper.

A relatively uniform positioning of nanotubes on the surface is seen. The mean diameter of nanotubes is measured to be about 82 µm as well as the thickness of the oxide layer is 1.68 µm. previous studies reported that the pore size of 80 µm is appropriate for biomaterials application.

The Addition of copper to the coating structure and oxidation of the copper layer due to thermal oxidation in a pure oxygen atmosphere produces a copper oxide/ TNT composite layer on the surface.

Fig. 2. reveals the surface structure of the titanium sample coated with a very thin layer of copper and then anodic oxidized to produce TNT. The sample then was thermally oxidized at 300°C, so it is expected that copper layer converted to copper oxide. The particles mentioned with arrows in Fig. 2 are probably CuO particles. EDS microanalysis as well as X-ray mapping from the surface of the sample demonstrated that the particles containing copper and a fine distribution of copper containing particles is formed in TNT.

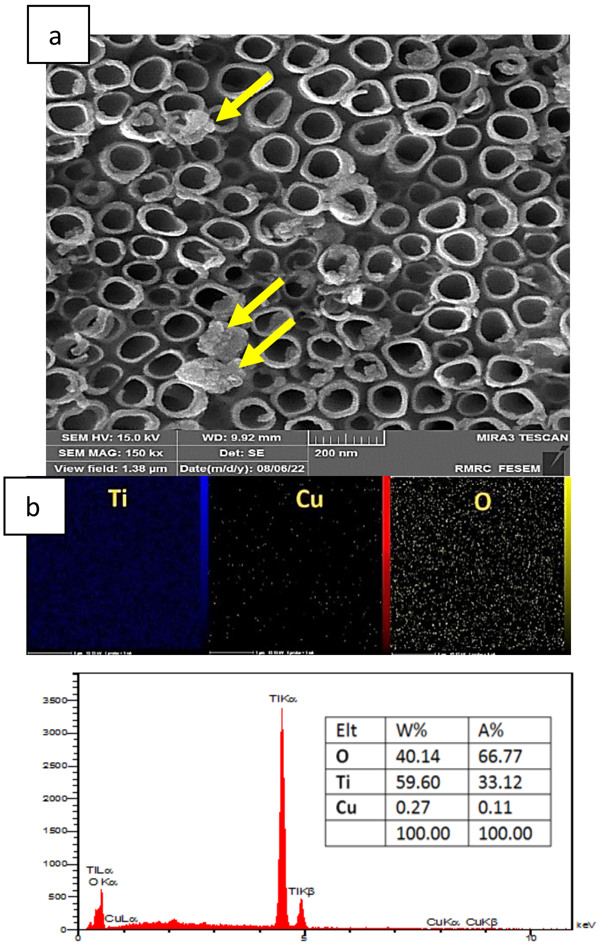

Fig. 2. a) FESM image of the sample anodized after copper deposition on the titanium surface and b) X-ray map and EDS microanalysis from the surface of the sample.

It is proposed that copper atoms positioned in the nanotube wall and also move to the top surface of the tubes as seen in Fig. 2. Although, the weight per cent of copper on the surface is only 0.27 wt.%., it was reported that the presence of about 0.3 wt.% of copper in the chemical composition is sufficient for antibacterial activity of the surface. [7,8]

In the case of the sample coated with copper after anodizing and then thermally oxidized, a layer of copper oxide with a thickness of about 300 nm is formed on the top surface of the sample as seen in FESEM image in Fig. 3.

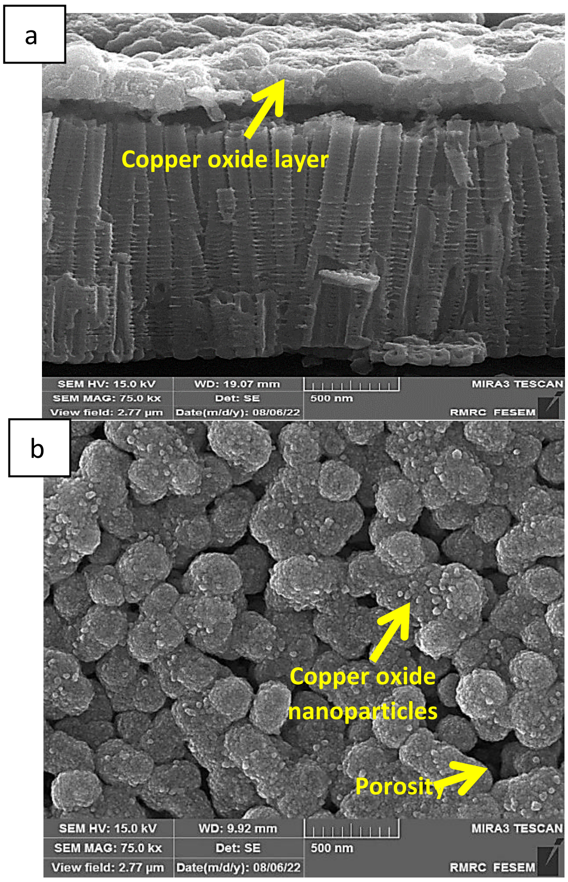

Fig. 3. a) Cross section FESEM image of the anodized sample and then coated with copper and then oxidized, b) the surface of the sample.

As seen in Fig. 3., semi-globular copper oxide nanoparticles are formed on the surface of the sample with pores between particles. Formation of a layer of copper oxide on the surface of the sample and the porosities in the structure can promote the formation of soft tissue in the case of implants. Also, as mentioned before, copper plays an important role in the antibacterial activity of the surface.

While, it was impossible to characterize the oxide with XRD because of the limitations of copper oxide layer thickness, the sample were thermally oxidized in the pure oxygen atmosphere, and therefore, it is probably that the oxides are CuO. EDS microanalysis and X-ray mapping from the surface of the sample is shown in Fig. 4. Because all of the copper coated on the TNT surface, weight percent of copper in the chemical microanalysis is about 27 wt.% which is comparable with the copper content in the later sample.

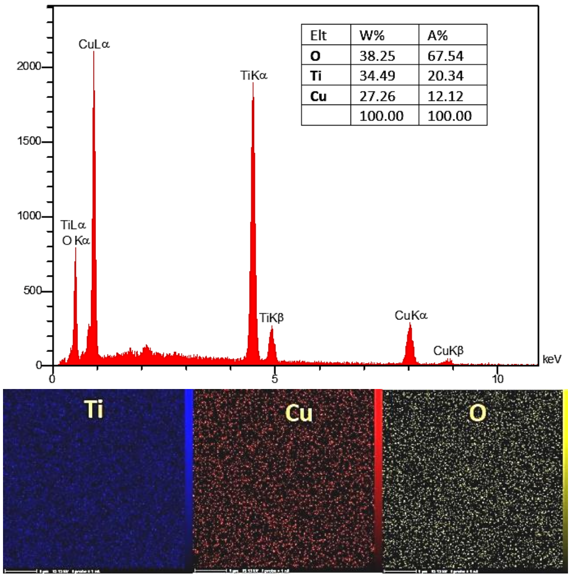

Fig. 4. EDS microanalysis and X-ray mapping from the surface of the sample anodized and coated with copper and then oxidized at 300°C for 1 h.

Existing of pores in the structure of the surface can cause capillary effects and therefore, wettability of the surface would be improved. Wettability of the samples in this study is compared in Fig. 5. As shown here, wetting angle of raw material without any surface coating is about 29°. In the case of the sample with surface coating, the wetting angle decreased to 14° for anodized sample without copper oxide and 4° and 3° for the samples pre-coated and post-coated, respectively.

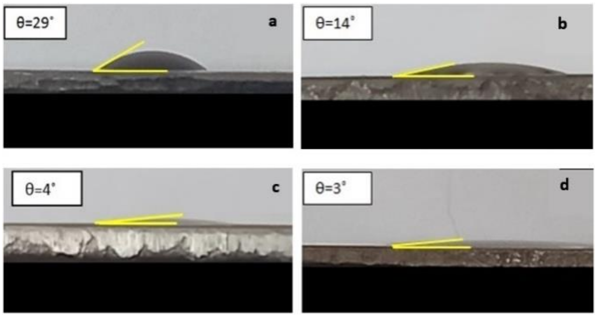

Fig. 5. wetting angle for the samples in this study. a) pure Ti, b) as anodized sample without copper, c) pre-coated anodized sample and d) anodized and post-coated sample.

Improvement of wettability of the sample anodized is related to the capillary effect of nanotubes or because of micro cracks in the surface coating. In the case of copper coated samples, existence of pores on the surface improves the wettability of the surface considerably. Better wetting properties of the surface improve the joining of the implants to the tissue in human body and also favor the drug doping in the structure of the surface. So, it would be considered that existence of copper oxide on the surface of the sample has two main functions for implants. First, copper oxide plays an important role in antibacterial activity of the surface and, secondly, it can improve osteogeneration and joining of tissue to the implant material.

The results for antibacterial activity of the surface are shown in Fig. 6. As shown in the fig. 6, in the case of pure titanium greater than 30 colonies are seen with unarmed eye. For the samples with TNT coating and also composite CuO/TNT coating, the number of colonies reduced considerably.

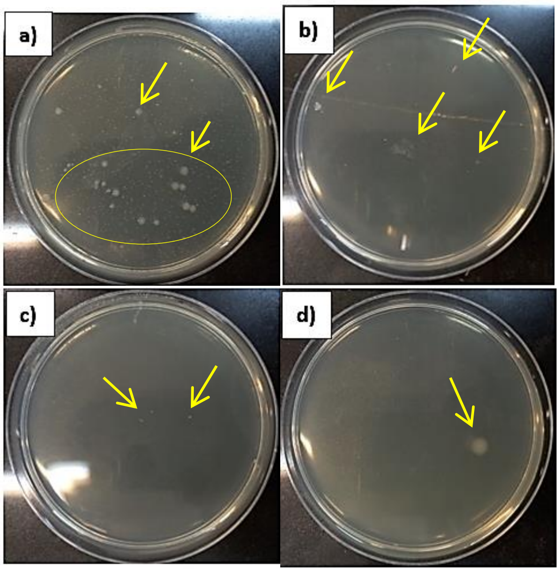

Fig. 6. the number of bacteria colonies cultured on the samples in this study. a) pure Ti, b) as anodized sample without copper, c) pre-coated anodized sample and d) anodized and post-coated sample.

4. Conclusion

Based on the results of this research the followings can be concluded:

1. Composite coating containing titanium oxide nanotubes and copper oxide were successfully synthesized using a combination of magnetron spattering and electerochemical anodizing at the applied voltage of 30 v and holding time of 2 h. nanotubes of about 82 nm in diameter and 1.68 µm was synthesized on the surface.
2. Application of copper using magnetron spattering and oxidation of the coating in pure oxygen at 300˚C produces a thin layer of CuO on the anodized surface. In the case of pre-coated samples, CuO particles were seen on the surface of the samples, but, here the content of CuO was fewer.
3. Wettability of copper containing samples improves considerably and the wetting angle decreased up to 3˚ in the case of post-coated sample.
4. Antibacterial properties of the copper containing surface in comparison with raw substrate and anodized sample without copper was increased considerably.

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