BACTERICIDAL PROPERTIES OF Cu DOPED TiO_2 FILMS DEPOSITED ON MEDICAL STAINLESS STEEL

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Introduction

Due to its photocatalytic activity under the effect of UV light, titanium dioxide (TiO_2) has been found useful in a scope of health care and environmental protection applications [1,2]. Recently, a number of reports also appeared where the matrix made of a thin TiO_2 film hosts minority metal additions [3-5]. It is mainly made in order to intensify the photocatalysis, to extend recombination times and to shift the excitation threshold energy towards visible light. Apart from that, a small supplement of bactericidal activity exhibiting metal (such as Cu) may additionally enhance material's microbiocidal properties and substantially reduce bacterial colonization of the surface coated [3,4]. In the majority of these publications, TiO_2 coatings are deposited onto glass or quartz substrates, either with magnetron sputtering or with the sol-gel method. There are also relatively rare reports dealing with the synthesis of such coatings on a polymer or steel support [6], a use of which allows one to broaden the scope of applications with prosthetic devices, implants and other medical appliances. This is particularly important today, in the times of excessive overuse of antibiotics and strong mutagenic disinfection chemicals bringing new microbiological hazards. Under these circumstances, a search for novel alternative means of bacterial prevention and control is well under way [1-3].

Materials and Methods

Copper doped TiO_2 coatings were produced with the help of the radio frequency plasma enhanced chemical vapor deposition (RF PECVD) method. Medical grade SANDVIK BIOLINE 316LVM (ISO 5832-1) steel was used to prepare substrates. Chemical composition of the coatings was determined with X-ray photoelectron spectroscopy (XPS), while their surface topography was assessed with atomic force microscopy (AFM). In addition, their phase composition was studied with the low angle X-ray diffraction (XRD) technique and chemical bonding was investigated with both Fourier transform infrared (FTIR) and Raman spectroscopies. Mechanical properties of the films, such as adhesion force, hardness and modulus of elasticity were assessed with the nanoindentation technique. Finally, bacteriostatic and bactericidic properties of the coatings as well as their water wettability under the effect of UV light illumination were also investigated.

Results and Discussion

The content of Cu in the coatings amounted to 0.38, 1.42 and 3.39 atomic percent. Due to an application of Cu (II) (6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate) as a copper precursor, fluorine is also incorporated into the material and since it is a light element, its incorporation proceeds substantially faster than that of copper. To illustrate this, one has to note that a coating containing 3.39 atomic percent of copper also comprises 9.43 atomic percent of fluorine. In other words, a presence of copper in this case is inseparably connected with an access of fluorine.

In the AFM image of the undoped coatings, one can observe a presence of globular forms of small dimensions as well as their agglomerates of sizes attaining 120 nm. An addition of the dopand brings about surface homogenization and small globules (grains) are only observed. Results of Raman studies, confirmed with those of XRD investigations, reveal a predominantly amorphous character of the coatings. The only maxima present in the Raman spectrum are broad and of low intensity which suggests sole low distance interactions. In any case, the highest intensity of the peaks is recorded for the coatings doped with small amounts of copper. At the highest Cu concentration, most of these maxima disappear.

FTIR studies of the coatings confirmed a presence of chemical moieties characteristic for TiO_2. Hardness of a plain titanium dioxide coating amounts to 8.9 GPa and the smallest addition of the dopand results in its increase to 11.2 GPa. Farther doping, however, brings about reduction of this parameter. Similar are the changes of Young modulus.

In order to assess bactericidity of the coatings, a number of *E. coli* strain DH5 α bacteria adhered to their surface was counted. On the surface of plain titanium dioxide coating, 19.7% cells were computed relative to the surface of 316LVM steel used as the control. A small increase of the number of bacteria was recorded in the case of the smallest addition of copper (0.38%) but the larger additions reduced that number to approximately 10%. This is an evidence of the fact that doping a TiO_2 coating with copper at its concentrations higher than 1% enhances the bacteriostatic effect of this material.

Conclusions

With a help of the RF PECVD technique, it is possible to produce copper doped TiO_2 coatings, with an addition of the dopand increasing the coating homogeneity. All the coatings are characterized by amorphous structure. An addition of small amounts of copper brings about an increase of the coating hardness and its Young modulus. Finally, a substantial increase of the coating bactericidity is observed for the coating containing 3.39 atomic % of copper.

References

[1] V. Binas, D. Venieri et al D. Kotzias, G. Kiriakidis, J. Materiomics 3 (2017) 3-16

[2] S. Sontakke, J. Modak et al., Chem. Eng. J. 165 (2010) 225-233

[3] V.I. Syngouna, C.V. Chrysikopoulos, J. Colloid Interface Sci. 497 (2017) 117-125

[4] A. Markowska-Szczupak, K. Ulfig et al., , Catal. Today 169 (2011) 249-257

[5] H. Wang, R. Zhang et al., Ceram. Int. 41 (2015) 11844-11851

[6] K. Hashimoto, H. Irie, A. Fujishima, Jpn. J. Appl. Phys. 44 (2005) 8269–8285.