Effect of TiN/TiO$_2$ multilayer coatings on the properties of stainless steel for biomedical applications

T Hikov$^{1,3}$, M Nikolova$^2$ and P Petrov$^1$

$^1$Acad. E. Dzakov Institute of Electronics, Bulgarian Academy of Sciences, 72 Tsarigradsko Chaussee, 1784 Sofia, Bulgaria
$^2$Department of Material Science, A. Kanchev University of Ruse, 8 Studentska Str., 7017 Ruse, Bulgaria

E-mail: thikov@ie.bas.bg

Abstract. A large number of research studies have been focused recently on possible methods for surface modification of metals and alloys. Titanium nitride (TiN) and titanium dioxide (TiO$_2$) films deposited on different substrates have found many applications because of their good mechanical properties, resistance to corrosion, and biocompatibility. The substrates for coating can consist of various kinds of metals and alloys used for manufacturing implants, and endodontic or rotary dental instruments. In this study, stainless steel 304L substrates and endodontic files were coated by a DC-magnetron-sputtered TiN/TiO$_2$ multilayer; the mechanical and biocompatible properties of the newly deposited films were explored.

The structure of the coatings was examined by X-ray diffraction (XRD), whereas the hardness was investigated by nanoindentation. The corrosion resistance was evaluated by potentiodynamic polarization tests in Ringer solution. Each endodontic file coated with TiN/TiO$_2$ was used for mechanical preparation of five root canals and, afterwards, their surface morphology was studied by scanning electron microscopy (SEM).

Our results confirmed that the TiN/TiO$_2$ multilayer coatings prepared had good stoichiometry and corrosion resistance. Moreover, the pre-coated instruments had a smoother surface and less debris and defects after mechanical preparation of five root canals compared to the non-coated ones. This indicated the usefulness of the coating formed in dental applications.

1. Introduction

Metal materials and alloys have been used in dentistry and medicine because of their specific mechanical properties and wear and corrosion resistance [1]. They are utilized for manufacturing a variety of devices, such as orthopedic prostheses, dental brackets, endodontic instruments, etc. [2]. The AISI grade 304L steel is one such material. Drawbacks of metal materials and their alloys are the poor binding ability to the bone tissue and the release of metal ions after prolonged exposure [3], which can be toxic. Therefore, many researchers have focused their efforts on using different methods for strengthening the surface of alloys. These modifications include deposition of coatings with wear-resistant micro- and nanolayers [4-7]. The purpose of applying coatings is to provide increased surface hardness, wear resistance, corrosion resistance, cutting efficiency, and can improve the interactions

3 To whom any correspondence should be addressed.
with the adjacent biological tissue and the material of the substrate [8, 9]. Titanium nitride (TiN) films deposited on different substrates have found many applications because of their exceptional mechanical properties, resistance to corrosion, and biocompatibility. Another multifunctional material that can be applied in the form of a coating is titanium dioxide (TiO$_2$). It has a number of applications as self-cleaning or biomedical coatings, or in bio-sensors [10, 11].

Among the various methods for deposition of the discussed coatings (sol-gel, ion implantation, physical vapor deposition (PVD), etc.), the magnetron sputtering technology (MS), which is type of a PVD technology, have advantages in controlling the deposition process. This guarantees the reproducibility of the film formation, as well as good control of its structure and properties. There are different kinds of magnetron sputtering: direct current (DC) MS, radio frequency (RF) MS, high-power pulsed MS [12-15].

The endodontic treatment requires proper cleaning and shaping of the root canal space and reducing the bacterial load in the case of infection, which is done through chemo-mechanical protocols [16]. Typically, the most widely used instruments for endodontic treatment are the stainless steel (SS) files. Stainless steel instruments have a natural tendency to straighten curved canals due to the inherent stiffness of the alloy and cannot follow the curvature even in moderately curved canals.

The aim of the present study was to evaluate the physico-mechanical, electrochemical and biological properties of a multilayer TiN/TiO$_2$ coating deposited on 304L stainless steel samples and files for dental applications.

2. Materials and methods

Samples of stainless steel and endodontic files were coated with thin layers of TiN and TiO$_2$ by DC magnetron sputtering in vacuum equipment with a rotating magnetron system. The cathode was made of pure Ti (99.8%) with a diameter of 100 mm and a thickness of 5 mm. The deposition of TiN was carried by a flow of a reactive (N$_2$) and an inert (Ar) gas at a working pressure of 1.2×10$^{-1}$ Pa. The ratio of Ar:N$_2$ was 23:1. The substrates were heated up to 350 °C. The coatings of TiO$_2$ were prepared in a pure O$_2$ environment at a working pressure of 6×10$^{-2}$ Pa and a substrate temperature of 180 °C. Each layer of the coatings was deposited for 120 minutes.

The coatings were characterized by X-ray diffraction using a URD6 Seiferd&Co diffractometer with Cu-K$_\alpha$ radiation. The measurements were conducted in a Bragg-Brentano symmetrical mode, from 20° to 80° 2θ at a step of 0.1° with a counting time of 10 s per step.

The electrochemical study was conducted in an experimental set-up comprising an electrochemical cell with a platinum counter electrode and a saturated Ag/AgCl reference electrode. Both electrodes and the working one with an exposed area of 0.2 cm$^2$ were immersed in 80 ml of naturally aerated Ringer-Braun’s solution at 37 ± 0.05 °C, pH 5.7. After the OPC carried out for 30 min, potentiodynamic polarization curves were recorded by sweeping the potential starting at a cathodic potential of about 250 mV below the OPC up to +2000 mV vs Ag/AgCl at a scan rate of 1 mV s$^{-1}$ using a potentiostat 263A (EG&G Princeton Applied Research) coupled to a PC by a controller.

The samples of endodontic files were used for shaping and cleaning tooth root canals. Forty extracted mandibular incisors were used to simulate a clinical situation. The teeth were decoronated at approximately 1 mm above the cementoenamel junction. The length was standardized at 15 mm. The root canals were shaped with K-files. During instrumentation, a 5.25% NaOCl solution was used as an intra-canal irrigant. Each file was used for mechanical preparation of five root canals without autoclaving.

After the root canal experiments, the surface morphology of the endodontic instruments was studied by SEM to evaluate the coatings’ influence.

3. Results and discussion

X-ray diffraction was used to obtain information about the multilayer TiN/TiO$_2$ coatings’ structure as deposited on a stainless steel substrate. The pattern is presented in figure 1.
The results show that multilayer coatings were formed successfully. Reflections corresponding to the substrate can be seen at 43.8°, 44.5°, 51°, 65° and 75°. Polycrystalline TiN and TiO₂ phases are registered. TiN has a face-centered cubic lattice (fcc) and space group Fm3m (225). Single-phase a-TiO₂ with a tetragonal structure and space group I41/amd(141) is detected. The identification of the phases was done according to the JCPDS database as follows: a-TiO₂ (JCPDS 21-1272), TiN (JCPDS 38-1420). It should be noted that these results are in agreement with those reported by other authors [12], who also obtained single-phase a-TiO₂ when heating the substrates. Usually, a mixture of anatase and rutile phases is observed after bias voltage is applied.

The corrosion parameters $E_{corr}$ (corrosion potential), $E_p$ (pitting potential) and $I_{corr}$ (corrosion current density) were obtained from the polarization curves (figure 2) by using the Tafel extrapolation method. The polarization resistance ($R_p$) was determined from the Stern-Geary equation. The values determined are given in Table 1. Another important parameter calculated in this study is the passivation index ($PI$) for both systems. It is given as the difference between the corrosion and the pitting potentials. As seen in figure 2, both samples exhibit a passive layer on the surface (increase in the potential with a slight increase in the current density). For the bare steel substrate, this can be explained by the formation of an oxide layer (Cr₂O₃ and spinel oxides [18]). The coated sample has a higher $PI$ (1132 V vs 480 V for bare stainless steel) due to the fact that it already has a passive oxide layer (TiO₂). That multilayer sample exhibits also a lower corrosion current density than bare SS, 10.85 nA/cm² and 49.8 nA/cm², respectively. The lower values for $I_{corr}$ and the higher values for $PI$ of the multilayer TiN/TiO₂ coated samples indicate a better corrosion resistance than pure stainless steel.

![Figure 1. XRD of multilayer TiN/TiO₂ coatings on stainless steel.](image1)

![Figure 2. Polarization curves of bare SS sample and multilayer TiN/TiO₂ coated SS.](image2)

| Sample                | $E_{corr}$, mV | $I_{corr}$, nA cm²² | $E_p$, mV | $R_p$, kΩ | $PI$, mV |
|-----------------------|----------------|---------------------|-----------|-----------|----------|
| 304L SS               | -28            | 49.8                | 534       | 3.65      | 480      |
| TiN/TiO₂ coated SS    | -65            | 10.85               | 1209      | 10100     | 1132     |

Table 1. Electrochemical corrosion parameters of bare and TiN/TiO₂ coated 304L stainless steel in Ringer’s solution at 37 °C (corrosion potential $E_{corr}$, corrosion current density $I_{corr}$, pitting potential $E_p$, polarization resistance $R_p$ and passivation index $PI$).

Figure 3a and 3b show the apical part of non-coated (figure 3a) and TiN/TiO₂-coated (figure 3b) files used for cleaning and shaping of five root canals. It can be seen that the non-coated sample’s surface is rough, with material missing at the right-hand side of the cutting edge. Moreover, the presence of debris in different areas of the non-coated files (the middle part not shown here) was established. This is an undesired effect because apically extruded necrotic debris might cause flare-ups and decrease the success rate of treatment [17]. On the other hand, the coated K-file has a relatively
smooth surface with no defects and very little to no debris are observed. Figure 3c and 3d show the apical part of the thinnest non-coated (figure 3c) and coated (figure 3d) files that were used for root canal shaping and cleaning. Again, the same tendency can be seen. The file that was not coated has more surface defects, fractures at the cutting edge and curvature at the very top. On the other hand, the coated instrument displays a smoother surface, although some defects can also be seen. No fractures or curves are found on its surface.

![Figure 3. SEM image of stainless steel endodontic files after cleaning and shaping of 5 root canal: without coating (a), (c) and with a coating (b), (d).](image)

4. Conclusions
The results of the present study show the effect of coating stainless steel with multilayer TiN/TiO2 coatings, deposited by reactive magnetron sputtering, on its physicochemical properties and biocompatibility.

The coatings contain polycrystalline single-phase α-TiO2 with a tetragonal structure. It is demonstrated that the coated samples are less likely to experience pitting corrosion in Ringer solution than uncoated steel.

Acknowledgements
This work was supported by the Bulgarian Ministry of Education and Science under the National Research Programme "Young scientists and postdoctoral students" approved by DCM # 577 / 17.08.2018. The authors also would like to thanks D. Dechev and N. Ivanov from the Institute of Electronics, Bulgarian Academy of Sciences for their help with the layers’deposition and Assoc. Prof. E. Radeva from the Dentistry Department, Medical University, Sofia, for her help with the K-files experiments.
References
[1] Mears D 1972 Materials and Orthopaedic Surgery (Baltimore: The Williams and Wilkins Company)
[2] Santonen T, Stockmann Juvala H and Zitting A 2010 Review on toxicity of stainless steel (Helsinki: Finnish Institute of Occupational Health) p 87
[3] Chew K-K, Zein S H S and Ahmad A L 2012 Natural Sci. 4 184
[4] Yao S H, Kao W H, Su Y L and Liu T H 2005 Mater. Sci. Eng. A 392 380
[5] Leng Y X, Sun H, Yang P, Chena J Y, Wana B J, Wana G J, Huanga N, Tian X B, Wang L P and Chub P K 2001 Thin Solid Films 398-399 471
[6] Subramanian B, Muraleedharan C V, Ananthakumar R and Jayachandran M 2011 Surf. Coat. Technol. 205 5014
[7] Jabbari Y S A, Koutsoukis T, Hadlaq S A, Berzins D W and Zinelis S 2016. J. Dental Sci. 11 48
[8] Jabbari Y, Fehrman J, Barnes A C, Zapf A M, Zinelis S and Berzins D W 2012 Coatings 2 160
[9] Pisarek M, Holdynski M, Roguska A, Kudelski A and Czachor M J 2014 J. Solid State Electrochem. 18 3099
[10] Pan D, Fan H, Li Z, Wang S, Huang Y, Jiao Y and Yao H 2017 Micro & Nano Lett. 12 82
[11] Kelly P and Arnell R 2000 Vacuum 56 159
[12] Arnell R and Kelly P 1999 Surf. Coat. Technol. 112 170
[13] Bohlmark J, Lattemann M, Stranning H, Selinder T, Carlsson J and Helmersson U 2006 49th Annual Techn. Conf. Proc. Soc. Vacuum Coaters 334
[14] Lattemann M, Ehiasarian A P, Bohlmark J, Persson P A O and Helmersson U 2006 Surf. Coat. Technol. 200 6495
[15] Sood K, Mohan B and Lakshminarayan L 2006 J. Endod. 18 34
[16] Gunes B and Yeter K Y 2018 J. Endod. 44 1191
[17] Guillamet R, Lopitaux J, Hannoyer B and Lenglet M 1993 J. Phys. IV Coll 03 349