J Mater Sci: Mater Med (2009) 20:1825–1830
DOI 10.1007/s10856-009-3757-6

Electrolytic deposition of hydroxyapatite coating on thermal treated Ti-40Zr

Hsueh-Chuan Hsu · Shih-Ching Wu · Chih-Hung Lin · Wen-Fu Ho

Received: 3 December 2008 / Accepted: 15 April 2009 / Published online: 29 April 2009

Abstract In this study, hydroxyapatite (HA) was coated on both thermal treated and untreated Ti-40Zr substrates by means of electrolytic deposition. It was predicted that the HA layer would increase the bioactivity and osteoconductivity of the Ti-40Zr substrate, and a thermal treatment would improve the bonding strength between the HA layer and Ti-40Zr substrate, and prevent the corrosion of the Ti-40Zr substrate. First, the Ti-40Zr samples were annealed at various temperatures (200, 300, 400, 500 and 600°C respectively). After annealing, samples were immersed in a $Ca(NO_3)_2 \cdot 4H_2O$ and $(NH_4)_3PO_4 \cdot 3H_2O$ solution for the electrolytic deposition of the HA coating. Various analyses of the coating were conducted, including surface morphology, phase structure, corrosion resistance, biocompatibility, and bond strength between HA and Ti-40Zr. Experimental results indicated that the bonding strength of the HA coating on the thermal treated Ti-40Zr was markedly improved when compared to that of the HA coating on an untreated Ti-40Zr alloy. The corrosion resistance of Ti-40Zr was also improved by the use of the thermal treatment, as shown by a potentiodynamic polarization test. Finally, osteoblast-like cells cultured on the HA coating surface were found to have proliferated on all samples.

H.-C. Hsu · S.-C. Wu
Department of Dental Laboratory Technology, Central Taiwan University of Science and Technology, Taichung, Taiwan, ROC

H.-C. Hsu · S.-C. Wu
Institute of Biomedical Engineering and Material Science, Central Taiwan University of Science and Technology, Taichung, Taiwan, ROC

C.-H. Lin
Department of Mechanical and Automation Engineering, Da-Yeh University, Changhua, Taiwan, ROC

W.-F. Ho (✉)
Department of Materials Science and Engineering, Da-Yeh University, No. 112, Shanjiao Rd., Dacun, Changhua 51591, Taiwan, ROC
e-mail: fujii@mail.dyu.edu.tw

1 Introduction

Titanium (Ti) and its alloys are widely used for medical and dental applications, largely because of their excellent biocompatibility, high strength to weight ratio, corrosion-resistance and low cost [1, 2]. Since unalloyed Ti is not strong enough for some dental purposes, many Ti alloys have been developed for dental use, and their properties have been studied [3–6]. A previous study by the authors indicated that the Ti-40Zr alloy has superior mechanical properties, excellent elastic recovery capability and improved grindability at low grinding speed and therefore has great potential for use as a dental machining alloy [4].

Much study has gone into the modification of metal surfaces to improve the osteointegration of implant-tissue [7–9]. Due to its good biocompatibility and osteoconductivity, HA is widely used as a bioceramic in orthopedic and dental surgery. Apparently, the HA layer facilitates direct bonding to hard tissues because it has a similar chemical composition to the inorganic components of natural bones and teeth [10, 11]. As a result, a number of researchers have attempted to combine the osteoconductive properties of bioactive ceramics with the favorable mechanical properties of Ti and its alloys for clinical applications [12–14]. HA coatings have shown good fixation to bone and various HA coating methods have been used to improve the bonding strength to metal substrates [10].

Recently, a thermal surface treatment has been developed and successfully used to improve the mechanical properties of Ti alloys. Significantly, this process leads to the formation of titanium dioxide (TiO_2) on the surface of Ti alloys [15]. More recently, it has been discovered that thermal treatment has great potential for applications in human implants and medical devices [16, 17]. This is because an oxide layer can facilitate direct bonding between the substrate and the HA layer. Therefore, in this study, we explored the modification of the surface properties of Ti-40Zr alloy by controlled thermal treatment which would lead to the formation a thin oxidized layer on the surface.

A previous study by the authors has shown that electrolytic deposition could successfully form ZrO_2/HA coatings on c.p. Ti [18]. In the current study, electrolytic deposition was used to fabricate HA coating on both thermal treated and untreated Ti-40Zr samples. After deposition, the structural, electrochemical and mechanical behavior of the coatings was analyzed.

2 Experimental

2.1 Preparation of substrates

First, discs (12 mm diameter, 1 mm thickness) of cast Ti-40Zr alloy were mechanically polished to a mirror finish in order to facilitate the thermal treatment process. Before thermal treatment, all specimens were also ultrasonically cleaned in double-distilled water and acetone for 10 min respectively. Thermal treatments were carried out in an air-circulating furnace at 200, 300, 400, 500 and 600°C for 1 h each.

2.2 Electrolytic deposition

Electrochemical deposition was carried out using a potentiostat (AUTOLAB PGSTAT 30, Eco Chemie BV, The Netherlands). The Ti-40Zr discs functioned as the working electrode, with a platinum wire as the counter electrode, and a saturated calomel electrode (SCE) working as the reference electrode. The HA coating was formed in a solution of $Ca(NO_3)_2 \cdot 4H_2O$ and $NH_4H_2PO_4$ in double-distilled water. After deposition, the specimens were dried for 24 hrs and then annealed at 350°C for 1 hr in an argon environment.

2.3 Characterization of the coatings

The SEM was used for the surface observation and microstructural analysis of the ceramic-coated specimens. The phase constituents of both treated and untreated samples were analyzed using an X-ray diffractometer with CuK_α radiation operated at 30 kV (voltage) and 20 mA (current) with a scanning speed of 1°/min. The various phases of the specimens were identified by matching each characteristic XRD peak with those in JCPDS files.

An ASTM C-633 adhesion test was used to test tensile bond strength of the coatings. The surface of the coatings was attached to the facings of the loading fixtures with METCO EP-15 adhesive. After curing and hardening of the bonding glue, the assembly was loaded into a universal mechanical tester (Instron, AG-IS, SHIMADZU, Japan) for measurement of the tensile bond strength. Six samples per coating type were used to determine tensile bond strength. This test was performed at a crosshead speed of 1 mm/min.

The electrochemical behavior of the specimens was tested using open circuit potential (OCP) and potentiodynamic measurement. The electrochemical cell consisted of a working electrode (specimen), a saturated calomel reference electrode (SCE), and a platinum counter electrode. The electrochemical tests of the specimens were conducted in artificial saliva at 37°C. The composition of the artificial saliva was: NaCl (400 mg/l), KCl (400 mg/l), $CaCl_2 \cdot 2H_2O$ (795 mg/l), $NaH_2PO_4 \cdot H_2O$ (690 mg/l), KSCN (300 mg/l) and $Na_2S \cdot 9H_2O$ (5 mg/l), with the addition of lactic acid to achieve a pH of 5.5. The electrochemical polarization curves were measured with a potentiostat and associated computer software for corrosion measurements. A scanning rate of 0.01 V/s was used in the range of −1.2 V to 2.3 V (SCE).

MG-63 osteoblast-like cells were used to test biocompatibility. These were first cultured in Dulbecco's Modified Eagle Medium (DMEM), containing 10% fetal bovine serum, 1% penicillin/strepmycin, 1% L-glutamine and 1% non-essential amino acids, in an incubator containing 95% air and 5% CO_2 at 37°C. Cells were then cultured and put in direct contact with the specimens. After they were co-cultured for 4 days, the specimens were fixed in 4% formaldehyde solution for 48 h and dehydrated in increasing ethanol concentrations (30–100%). Finally, the surfaces of the culture specimens were examined by SEM.

One-way ANOVA statistical analysis was used to evaluate the statistical significance of the bond strength and electrochemical data.

3 Results and discussion

3.1 Phase constituent and surface composition

XRD analyses of phases were conducted on the phase constituents of both treated and untreated samples. Figure 1 shows the XRD results of the Ti-40Zr substrate at various annealing temperatures; 200, 300, 400, 500 and 600°C. At annealing temperatures below 600°C only Ti

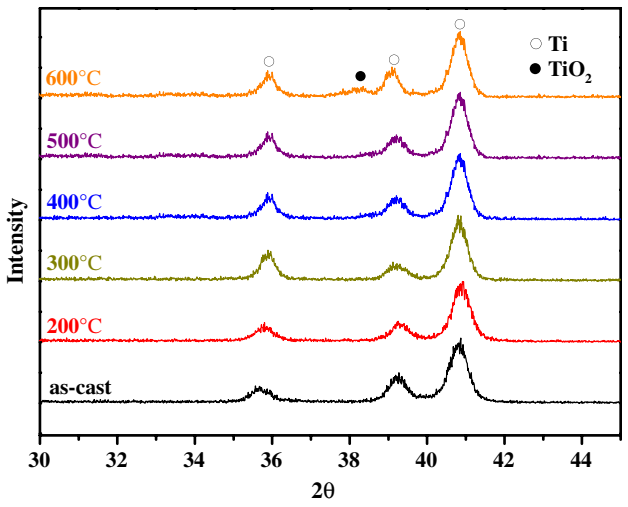

Fig. 1 XRD patterns of Ti-40Zr substrate at various annealing temperatures

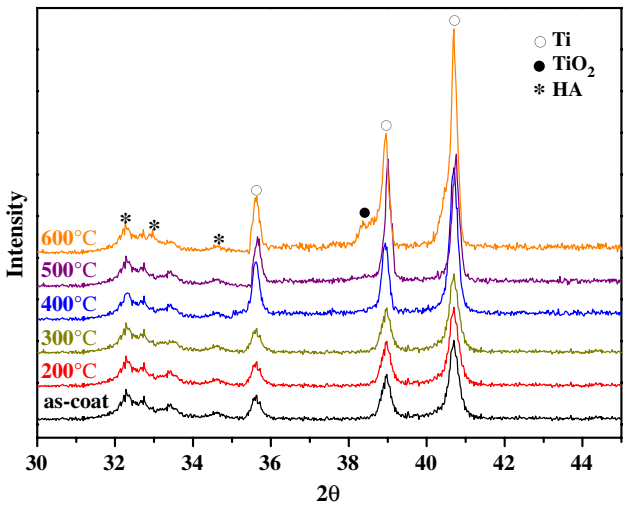

Fig. 2 XRD patterns of HA layer deposited on different Ti-40Zr substrates after annealing

was found, whereas, at 600°C both Ti and a surface compound layer of TiO_2 were found. This indicates that the Ti-40Zr substrate could be more easily oxidized at high temperatures.

Figure 2 shows the XRD patterns of the HA layer deposited on the Ti-40Zr substrates after annealing. Diffraction patterns for all samples below 600°C indicated the predominance of Ti and HA. In contrast, TiO_2 was only found in significant quantities after annealing at 600°C. These patterns also show that the HA peak was found at $2\theta = 32.3°$, 33° and 34.2°. Furthermore, XRD analysis of the samples revealed the low crystallinity of HA coatings, which could promote integration [19].

Figure 3a shows the SEM morphology of the HA layer coating on the Ti-40Zr substrate. After coating the HA over the thermal treated layer, the surface appeared to have a plate-like structure. SEM morphology of the coating (Fig. 3b) revealed that HA layer was composed of forms resembling fractal geometric flowers. Such fractal-like surfaces would be more active because they accumulate high surface energy. This leads to an increase in biological reactivity of the implant coatings with natural bone, resulting in stronger bonding between bone and implant [20]. The analysis of EDS showed the HA deposits had a Ca/P ratio of 1.7, which is in almost perfect agreement with the theoretical value of 1.67 for HA.

3.2 Characterization of surfaces

3.2.1 Bonding strength

Figure 4 shows the bonding strengths of the HA layers deposited on the Ti-40Zr substrates, as revealed by the tensile test. The bonding strengths of the HA layer coated on thermal oxidized specimens showed statistically significant differences ($P < 0.05$) compared to that of the untreated specimen. Bonding strengths of the six groups of samples ranged from 26.9 ± 2.3 to 43.1 ± 2.2 MPa. In

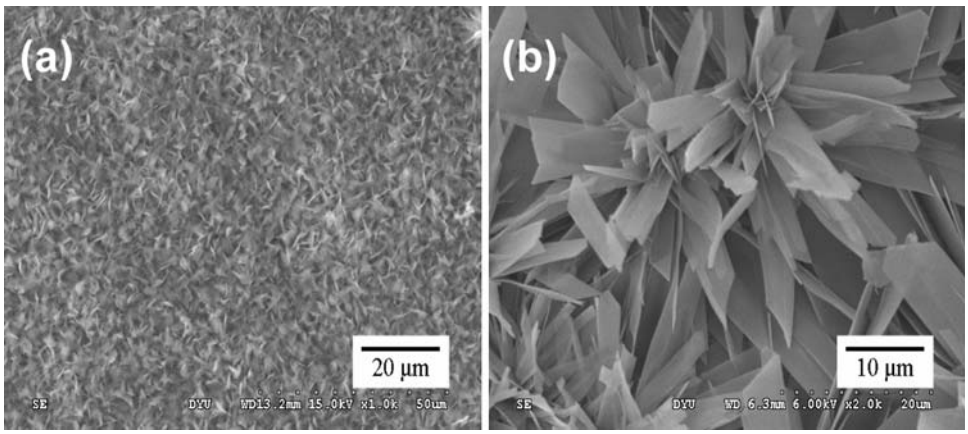

Fig. 3 SEM morphology of HA layer coating on thermal oxidized Ti-40Zr substrate at 600°C. **a** Magnification ×1000, and **b** magnification ×2000

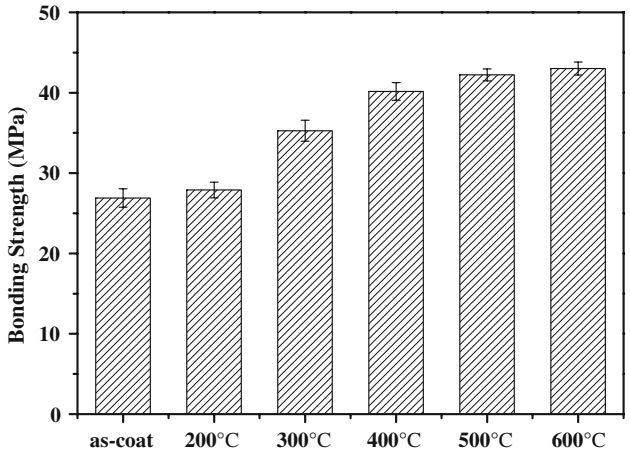

Fig. 4 Bonding strengths of HA layers deposited on Ti-40Zr substrates

fact, the strength of the HA coating layer improved with every increase in treatment temperature. This effect is likely due to the TiO_2 oxidized layer providing a better mechanical bond with the HA coating. In addition, in a related study, the bonding quality of plasma-sprayed HA coating on Ti alloy was reported to be slightly improved by the presence of a TiO_2 layer [21]. These results seem to indicate that the bonding strength of the coating layer is dependent on the substrate type, and in this study, the HA layer was found to bond more strongly to the oxidized layer than to the untreated Ti-40Zr substrate.

3.2.2 Corrosion resistance

Figure 5 shows the OCP results of the six different Ti-40Zr substrates in artificial saliva. As shown in Fig. 5, the OCP curves rose rapidly before reaching a stable value. The OCP curves of all samples significantly increased in proportion to their treatment temperatures. These results indicate that thermal oxidization treatment greatly increases OCP and therefore enhances corrosion resistance.

The changes in the corrosion potential for all samples over time are also shown in Fig. 5. Although all the specimens reached a stable potential, the treated specimens achieved stability more rapidly than the untreated Ti-40Zr substrate. For example, the sample treated at 600°C achieved a stable potential of approximately −0.07 V, while, in comparison, the untreated Ti-40Zr substrate reached a stable potential of −0.13 V. This result shows the effect of the formation of an adequate protective film through thermal treatment.

Figure 6 shows the potentiodynamic polarization results of the HA coated Ti-40Zr specimens in artificial saliva. Significant differences in potentiodynamic polarization curves were observed between the various treated surfaces. In particular, HA coated on thermal treated Ti-40Zr substrates showed lower passive current density and higher corrosion potential than untreated Ti substrates. Again, this result shows that thermal oxidization of Ti-40Zr can significantly improve corrosion resistance.

The potentiodynamic polarization measurements in Fig. 6 show that the polarization curve for specimen treated at 600°C had significantly higher ($P < 0.05$) corrosion potential (E_{corr}) value (87 ± 16 mV vs. SCE) than that of the untreated sample (−165 ± 23 mV vs. SCE). However, there were no significant differences in the E_{corr} values between samples treated at 200, 300, 400 and 500°C. At the same time, the corrosion current density (I_{corr}) values of the thermal oxidized specimens were generally lower than that of the untreated Ti-40Zr substrate, and all samples showed significant differences ($P < 0.05$). For example, the I_{corr} value of the sample treated at 600°C was 23.6 ± 3.2 nA/cm^2, and that of the untreated Ti-40Zr specimen was 175.4 ± 22.5 nA/cm^2. Thus, the potentiodynamic

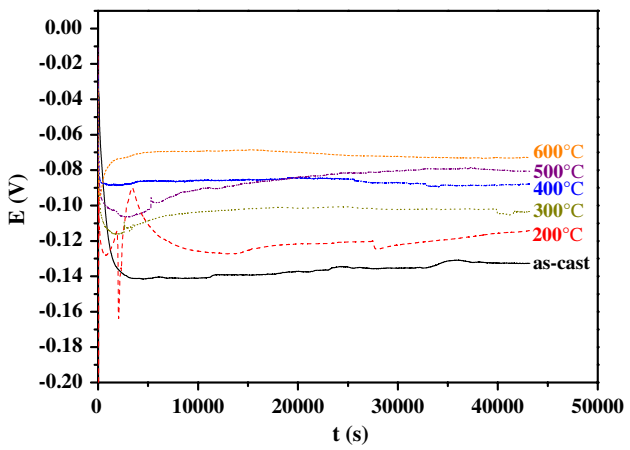

Fig. 5 OCP results of Ti-40Zr substrates in artificial saliva

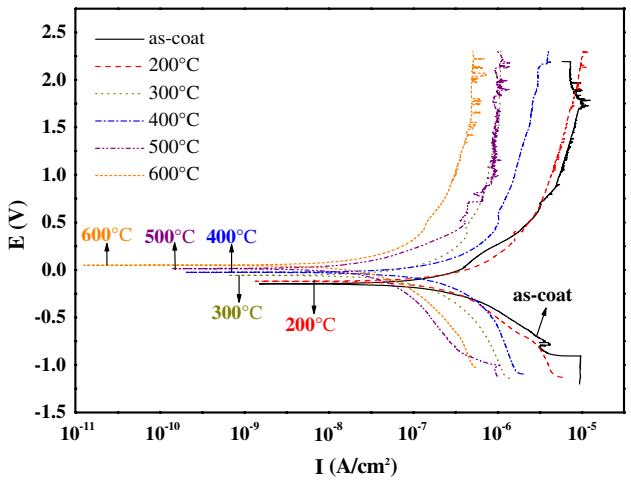

Fig. 6 Potentiodynamic polarization curves of HA coated Ti-40Zr specimens in artificial saliva

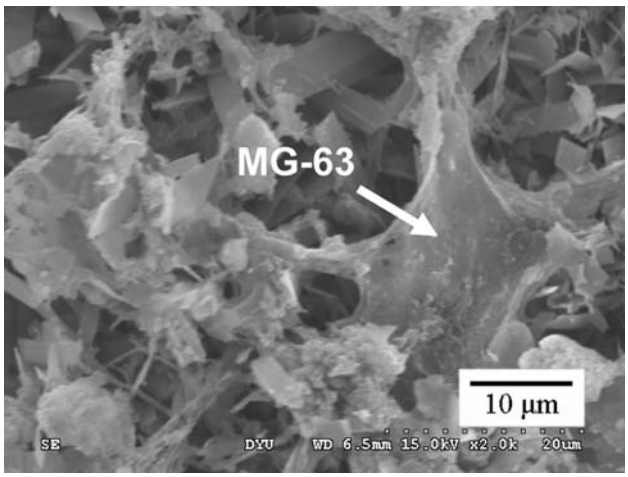

Fig. 7 SEM morphology of osteoblast-like cell MG-63 attached to HA coated Ti-40Zr substrate treated at 600°C

polarization test indicated that the thermal treated specimens had higher corrosion potential and lower passive current density than the untreated Ti-40Zr substrate, which confirms that the thermal oxidized layers provide better corrosion resistance than the untreated Ti-40Zr substrate.

3.2.3 Cell culture

Figure 7 shows SEM observation of the osteoblast-like cell MG-63 attached to the HA coated specimen which was treated at 600°C. The biocompatability of the HA layer coatings was evaluated by observing the proliferation and differentiation of osteoblast-like MG-63 cells. As shown here, the cells could adhere to and proliferate on the HA coating surface, indicating that the HA coatings have good biocompatibility, probably because the rough surface of HA coating can provide better cell adhesion.

4 Conclusions

This study clearly demonstrates the advantages of thermal treatment of Ti-40Zr substrates before coating. Thus, thermal treated samples showed better HA coating with improved bonding strength and corrosion resistance. In particular, treatment at higher temperatures increased this effect, with best results shown at 600°C. At this temperature oxidization was clearly shown to have taken place, with resultant beneficial effects. Overall, thermal oxidization at 600°C resulted in higher bond strength and better corrosion resistance than other temperatures. Finally, HA coatings have proliferated on all samples.

Acknowledgements The authors wish to gratefully acknowledge the National Sciences Council, Republic of China for supporting this research, project No. 97-2622-E-166-CC3.

References

1. Hao YL, Niinomi M, Kuroda D, Fukunaga K, Zhou YL, Yang R, et al. Aging response of the young's modulus and mechanical properties of Ti-29Nb-13Ta-4.6Zr for biomedical applications. Metab Mater Trans A. 2003;34A:1007.
2. Boehlert CJ, Cowen CJ, Jaeger CR, Niinomi M, Akahori T. Biomimetic and supramolecular systems. Mater Sci Eng C. 2005;25:263–75. doi:10.1016/j.msec.2004.12.011.
3. Lautenschlager EP, Monaghan P. Titanium and titanium alloys as dental materials. Int Dent J. 1993;43(3):245–53.
4. Ho WF, Chen WK, Wu SC, Hsu HC. Structure, mechanical properties, and grindability of dental Ti–Zr alloys. J Mater Sci Mater Med. 2008;19:3179–86. doi:10.1007/s10856-008-3454-x.
5. Hattori M, Hasegawa K, Yoshinari M, Kawada E, Oda Y, Okabe T. Casting accuracy of experimental Ti-Cu alloys. Dent Mater J. 2001;20(1):16–23.
6. Takahashi M, Kikuchi M, Takada Y, Okuno O. Mechanical properties and microstructures of dental cast Ti-Ag and Ti-Cu alloys. Dent Mater J. 2002;21(3):270–80.
7. Fathi MH, Mohammadi AD. Mater Sci Eng A. Preparation and characterization of sol-gel bioactive glass coating for improvement of biocompatibility of human body implant. 2008;474:128–33. doi:10.1016/j.msea.2007.05.041.
8. Kar A, Raja KS, Misra M. Electrodeposition of hydroxyapatite onto nanotubular TiO_2 for implant applications. Surf Coat Tech. 2006;201:3723–31. doi:10.1016/j.surfcoat.2006.09.008.
9. Hamada K, Kon M, Hanawa T, Yokoyama K, Miyamoto Y, Asaoka K. Hydrothermal modification of titanium surface in calcium solutions. Biomaterials. 2002;23:2265–72. doi:10.1016/S0142-9612(01)00361-1.
10. Hench LL. Bioceramics: from concept to clinic. J Am Ceram Soc. 1991;74:1487–510. doi:10.1111/j.1151-2916.1991.tb07132.x.
11. Mcpherson EJ, Dorr LD, Gruen TA, Saberi MT. Hydroxyapatite-coated proximal ingrowth femoral stems. A matched pair control study. Clin Orthop Relat Res. 1995;315:223–30.
12. Sun L, Berndt CC, Gross KA, Kucuk A. Material fundamentals and clinical performance of plasma-sprayed hydroxyapatite coatings a review. J Biomed Mater Res. 2001;58:570–92. doi:10.1002/jbm.1056.
13. Lopatin CM, Pizziconi V, Alford TL, Laursen T. Hydroxyapatite powders and thin films prepared by a sol-gel technique. Thin Solid Films. 1998;326:227–32. doi:10.1016/S0040-6090(98)00531-8.
14. Gottlander M, Johansson CB, Wennerberg A, Albrektsson T, Randin S, Ducheyne P. Bone tissue reactions to an electrophoretically applied calcium phosphate coating. Biomaterials. 1997;18:551–7. doi:10.1016/S0142-9612(96)00168-8.
15. Stamate MD. On the non-linear I–V characteristics of dc magnetron sputtered TiO2 thin films. Appl Surf Sci. 2003;205:353. doi:10.1016/S0169-4332(02)01130-3.
16. Casaletto MP, Ingo GM, Kaciulis S, Mattogno G. Surface studies of in vitro biocompatibility of titanium oxide coatings. Appl Surf Sci. 2001;172:167. doi:10.1016/S0169-4332(00)00844-8.
17. Leng YX, Huang N, Yang P, Chen JY, Sun H, Wang J, et al. Structure and properties of biomedical TiO_2 films synthesized by dual plasma deposition. Surf Coat Technol. 2002;156:295–300. doi:10.1016/S0257-8972(02)00092-0.
18. Hsu HC, Wu SC, Yang CH, Ho WF. ZrO_2/hydroxyapatite coating on titanium by electrolytic deposition. J Mater Sci Mater Med. 2008;20:615–9. doi:10.1007/s10856-008-3603-2.
19. Stoch A, Jastrzębski W, Długoń E, Lejda W, Trybalska B, Stoch GJ, et al. Sol–gel derived hydroxyapatite coatings on titanium and its alloy Ti6A14V. J Mol Struct. 2005;633:744–7. doi:10.1016/j.molstruc.2004.10.080.

20. Gbureck U, Masten A, Probst J, Thull R. Tribochemical structuring and coating of implant metal surfaces with titanium oxide and hydroxyapatite layers. Mater Sci Eng C. 2003;23:461–5. doi: 10.1016/S0928-4931(02)00322-3.

21. Kurzweg H, Heimann RB, Troczynski T, Wayman ML. Development of plasma-sprayed bioceramic coatings with bond coats based on titania and zirconia. Biomaterials. 1998;19:1507–11. doi:10.1016/S0142-9612(98)00067-2.