

The effect of heat treatment simulating porcelain firing processes on titanium corrosion resistance

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Purpose: Corrosion resistance of titanium used in metal-ceramic restorations in manufacturing is based on the presence of oxide layer on the metal surface. The procedures used during combining metallic material with porcelain may affect the changes in oxide layers structure, and thus anticorrosive properties of metallic material. The aim of the study was an evaluation of potential changes in the structure and selected corrosion properties of titanium after sandblasting and thermal treatment applicable to the processes of ceramics fusion. *Methods:* Milled titanium elements were subjected to a few variants of the processes typical of ceramics fusion and studied in terms of resistance to electrochemical corrosion. The study included the OCP changes over time, measurements of Icorr, Ecorr and Rp as well as potentiodynamic examinations. Surface microstructure and chemical composition were analyzed using SEM and EDS methods. *Results:* The results obtained allow us to conclude that the processes corresponding to ceramic oxidation and fusion on titanium in the variants used in the study do not cause deterioration of its anticorrosive properties, and partially enhance the resistance. This depends on the quality of oxide layers structure. *Conclusions:* Titanium elements treated by porcelain firing processes do not lose their corrosion resistance.

Key words: corrosion resistance, potentiodynamic polarization, porcelain firing, titanium-ceramic dental restorations

1. Introduction

Currently, despite the growing popularity of full-ceramic restorations, a significant number of prosthetic restorations is made using the ceramics fusion on metal method.

The technology of dental porcelain fusion on metal has gained a predominant position among manufacture of dentures like crowns and bridges, due to their toughness, esthetics and economical characteristics.

Metal substructure assures a very high mechanical strength of such crowns, while ceramic veneer guarantees, in most cases, a desirable esthetic effect. Titanium and its alloys occupy a significant position

among metallic materials for substructures [18]. Titanium properties, such as the highest corrosion resistance and compatibility, of all so-called base metal alloys, allow us to classify this metal as the most biocompatible of metallic materials.

In contact with physiological fluids, metallic materials may be subject to electrochemical pitting and crevice, as well as fretting, fatigue corrosion, and stress corrosion cracking. The presence of chloride ions in the environment, very high oxygenation of electrolyte solution, and its relatively high temperature (37 °C) are the significant factors in the phenomenon of both metal and alloy corrosion. Constantly changing conditions in oral cavity (e.g., changes in saliva pH, presence of food, microorganisms) are highly unfavorable. Titanium and its alloys

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are also exposed to corrosion [3], [9], [20]. Corrosion concerns not only metal elements of prostheses being in direct contact with saliva, but also occurs in the slot of metal substructure connection with ceramic veneer. Above all it concerns an internal surface of metal-ceramic crowns, since none of the prosthetic cements used for embedding crowns and bridges assures a suitable tightness of the connection. The electrolytic environment of oral cavity penetrates and stays in touch with metal surface (crown interior) causing corrosion processes.

Titanium, as a material used in metallic substructures, suffers from problems resulting from its allotropic crystalline lattice transformations (at a temperature of 882 °C), high affinity to oxygen and low thermal expansion. Low-melting ceramic masses of a firing temperature below 800 °C are used for titanium veneering [23]. This is a suitable range of temperatures, which prevents formation of too thick layers of titanium oxide, and thus is optimum for stable metal-ceramics connection occurrence [19].

The procedures of ceramics fusion on metal: surface oxidation, opaquer ceramics fusion, dentin and enamel ceramics fusion, glaze fusion, involve an oxidation of metallic surface and scale formation, which may affect corrosion properties, and thus biological properties of metallic material [8], [24].

Understanding corrosion behaviors of titanium in oral cavity environment constitutes a key issue in the clinical aspect and its biological tolerance. An effect of porcelain fusion on corrosion process occurrence in dental metal alloys is still not fully recognized issue.

The aim of the study

The aim of the study was an evaluation of an effect of thermal treatment applicable to dental ceramics fusion, on the state of surface, mainly corrosion resistance, of titanium prosthesis elements obtained in milling process.

2. Materials and methods

Material preparation

The study included titanium Grade 2 in the form of disc aimed at prostheses metal elements manufacturing. The samples for the research, in a form of drilled discs of a diameter of 14 mm and height of 7 mm, were designed in Netfabb basic CAD software and made using 5-axis YenaDC40 CNC dental

milling machine. The surface of the samples subjected to corrosion examinations was wet polished on a disc polisher with abrasive papers P600 to obtain flat structure similar to the structure of an internal surface of metal parts of the crown obtained after polishing with fine-grained stones with diamond coating.

After degreasing and clearing in water vapor stream, the samples were subject to thermal processing corresponding to ceramics fusion on metal in the Ivoclar Vivadent Programat EP3000 furnace for ceramics firing. The furnace was delivered with VP4 vacuum pump which reaches final vacuum at 30 mbar.

Heat treatment of samples simulating porcelain firing processes

Particular processes of thermal treatment corresponded to (in accordance with Noritake Super Porcelain Ti22 ceramics):

Oxidation:

- heating in the range from 500 °C to 800 °C with a rate of temperature growth of 50 °C/min, then
- at a temperature of 800 °C, holding in vacuum for 3 min.

All the samples were subjected to the oxidation process described above on the alloy surface.

Ceramics fusion on metal:

- variant I – 5 min heating at a temperature of 790 °C,
 - variant II – three heating processes at temperatures of 780 °C, 770 °C and 760 °C,
- with temperature growth rate from 40 to 50 °C/min.

The heating procedures corresponded to the temperatures of opaquer and dental ceramics fusion. Firing processes are precisely described in Table 1, with a division into stages and their approximated duration time. The time of each process was set by automation depending on humidity of the ceramics layer (and usually the size of the denture). Total time of the process is difficult to specify, because we need to include the time of drying, the time of heating under vacuum, and the time of cooling the specimens down after opening the furnace. The oven ends the program the second the heating chamber is fully open, however we need to wait until the oven signals cooling the chamber down to about 500 °C, which also takes time.

After cooling, such prepared samples were subject to electrochemical corrosion trials – the analysis included all variants of thermal treatment combined with control group sample not subjected to thermal treatment process.

Table 1. Firing parameters for Noritake Super Porcelain Ti22

	Dry-out time	Low temp.	Vacuum start	Heat rate	Release vacuum	Hold time	High temp.	Heating time – closed furnace
Oxidation	3 min	500 °C	500 °C	50 °C/min	790 °C	3 min	800 °C	~6 min
Opaque	5 min	500 °C	500 °C	50 °C/min	770 °C	–	780 °C	~5 min 36 s
Body/Enamel 1st & 2nd	7 min	500 °C	500 °C	40 °C/min	750 °C	–	770 °C	~6 min 30 s
Glaze	5 min	500 °C	–	50 °C/min	–	–	760 °C	~5 min 12 s

Experimental methods determining the corrosion resistance

Before corrosion tests the samples were degreased, then rinsed with ethyl alcohol and dried. Electrochemical examinations were conducted in glass electrolytic dish manufactured by Radiometer-Analytical, in which the sample studied was the working electrode (E_w), supporting electrode (E_c) was platinum electrode, and a reference electrode (E_{ref}) was calomel electrode in saturated KCl solution. The working surface of the sample was about 0.95 cm^2 . The measurements were made in 0.9% NaCl solution at a room temperature.

The NaCl solution (natriumchloratum 9 g, water for injections 1000 ml, NaOH, HCL q.s. – osmolarity 308 m, Osmol/l) was manufactured by infusion fluids factory in Kutno. Company responsible for fluid was Fresenius KABI.

The measurements using ATLAS 0531 set with AtlasCorr05 software enabling control of measurements and registration of results were made for each sample. The calculations were done using AtlasLab software enabling determination of corrosion process parameters.

The examinations included:

- measurement of free corrosion potential (E_{corr}) in an open circuit (OCP),

OCP – The open circuit electrode potential versus time measurement – method description

The goal of potential measurements is to measure the potential of the specimen without affecting, in any way, electrochemistry reactions on the specimen surface. The open circuit potential is a parameter which indicates the thermodynamical tendency of a material to electrochemical oxidation in a corrosive medium. After a period of immersion it stabilises around a stationary value. This potential may vary with time because changes in the nature of the surface of the electrode occur (oxidation, formation of the passive layer or immunity). The open circuit potential is used as a criterion for the corrosion behavior. A rise of poten-

tial in the positive direction suggests the formation of a passive protected film, and the steady potential indicates that protective layer is intact.

The Tafel straight extrapolation method was used to determine the value of corrosion current (I_{corr}) and polarization resistance (R_p).

The values of corrosion current density were obtained by an analysis of polarization line in the curvilinear area. The fact that anodic and cathodic corrosion reactions occur concurrently in the vicinity of the corrosion potential was considered, and in the analyzed cases both reactions occurred with the activation over potential.

The applied method of analysis involved adjustment of corrosion parameters such as (I_{corr}), (b_a), (b_c) in polarization curve equation to obtain maximally precise description of the data acquired from the measurements.

$$j = j_{corr} * (10^{((E - E_{corr})/b_a)} - 10^{((E_{corr} - E)/b_c)})$$

where:

I_{corr} – corrosion current density,

E_{corr} – corrosion potential,

b_a , b_c – anodic and cathodic coefficients of Tafel equation, respectively,

j – density of imposed external current.

The unknown values were (I_{corr}), (b_a) and (b_c).

Also, the polarization curves were registered using potentiodynamic method in conventional three-electrode system with calomel reference electrode ($E_0 = 0.236 \text{ V vs. NEW}$) and platinum supporting electrode. The values of conventional breakdown potential (E_{br}) understood as a measure of resistance to pitting corrosion were calculated from the potentiodynamic curves. E_{br} – potential for which the current density in the anodic range of polarization charts (in passive range) reached the value of $10 \mu\text{A}/\text{cm}^2$.

The surfaces of all examined samples before and after corrosion trials were analyzed using scanning electron microscope Hitachi SEM-4700 with X-ray microanalyzer of Thermo Scientific Ultra Dry. The study included both test scanning surface in contrast secondary electron (technique SEM-SE), as well as

the chemical analysis which was performed using X-ray spectroscopy of an energy dispersive (EDS). EDS method was used for qualitative analysis of chemical composition in selected micro-areas of the samples based on the presence or absence of the characteristic peaks in the spectrum. The value of accelerating voltage for all the samples was 25 keV.

Scanning Electron Microscopy (SEM) produces and scans a finely-focused beam of electrons across the specimen and measures signals resulting from the electron beam/specimen interaction. Two most common signals employed in SEM analysis include secondary electrons (SE) for imaging surface topography and backscattered electrons (BSE) for highlighting compositional differences. The SEM-SE produce very high-resolution images of a sample surface, revealing details less than 1 nm in size. The SEM-SE type was chosen due to the possibility of obtaining a characteristic three-dimensional appearance useful for understanding the surface structure of samples examined, especially after corrosion tests.

Energy-Dispersive X-Ray Spectroscopy (EDS) – method description

An energy-dispersive spectroscopy was used to separate the characteristic X-rays of different elements into an energy spectrum and to analyze this spectrum in order to determine the abundance of specific elements. EDS was used to find the chemical composition of materials (down to a spot size of a few microns), and to create element composition maps over a much broader raster area. Together, these capabilities provide fundamental compositional information for specimens examined. The obtained outputs from EDS analysis are presented in this study in the form of:

- *Spectrum*: a plot of the number of X-rays detected versus their energies. The elements present in the sample are identified by the characteristic X-rays.
- *Map*: an image showing how the concentration of one element varies over an area of a sample. In this example, the number of points indicates higher or lower concentrations of an element.

3. Results

EDS spectra and maps of distribution of selected chemical elements in the samples of titanium milled

and polished with papers of granularity of 600, depending on the kind of treatment are presented in Figs. 1–4. Figures 5–8 present the state of sample surface in all variants of manufacturing after corrosion tests. Morphology of the alloy was examined using SE detector. The obtained results of the changes in free potential over time for particular ways of surface preparation are presented in Fig. 9. The values of polarization resistance (R_p), potential (E_{corr}), density of corrosion current (I_{corr}), breakdown potential (E_{br}) for particular ways of alloy surface preparation determined using AtlasLab software are presented in Table 2. Potentiodynamic characteristics for polarization in the range from -1.0 V to 1.5 V with the rate of potential changes of 5 mV/sin semi-logarithmic arrangement are presented in Fig. 10.

Table 2

Kind of sample	j_{corr} [A/cm ²]	E_{corr} [mV]	R_{pol} [Ohm*cm ²]	E_{br} [mV]
Control sample	6.62E-08	-492	8.44E+05	430
Sample after oxidation	1.80E-07	-214	1.55E+04	676
Sample after oxidation and single firing	5.22E-07	-97	2.71E+04	701
Sample after oxidation and triple firing	9.25E-08	-194	2.96E+05	1003

4. Discussion

A comparison of the results of EDS analysis (Figs. 1–4) in selected micro-areas of milled and polished titanium surface that were not subject to thermal treatment, and micro-areas that were subject to both the oxidation processes and corresponding to fusion processes, allow us to determine the changes of state of alloy surface. After thermal treatment processes, the chemical composition of surface layers of the samples was not subject to changes (not taking into account high-temperature oxidation processes). A very low contribution of impurities was noted, and they would have been a result of surface modification – these components were observed on EDS spectra in the form of peaks of considerably lower intensity. The maps of surface distribution of the elements for the samples after oxidation and after the processes simulating the fusion demonstrated an increasingly more uniform distribution of oxygen covering samples surface with subsequently applied thermal treatments.

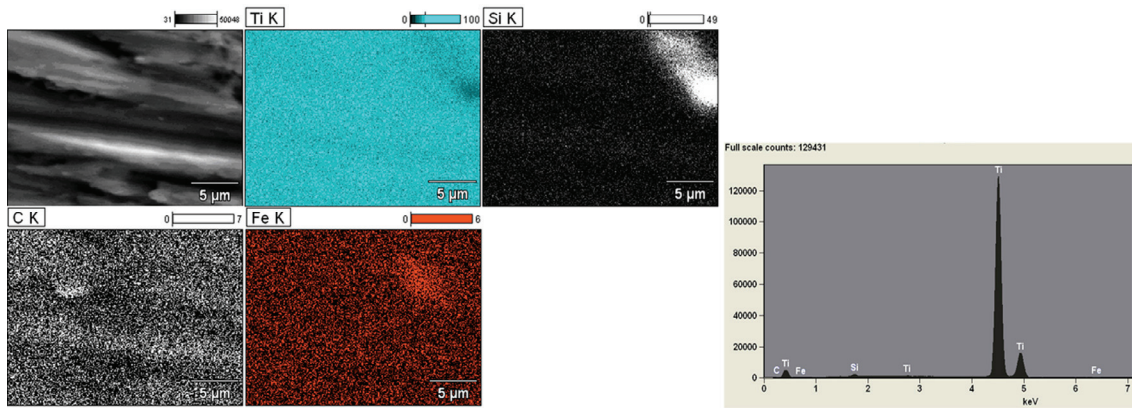


Fig. 1. SEM-SE micrograph showing morphology of profile-milled sample (control sample); EDS map of Ti, Si, C, Fe surface distribution (left) and averaging EDS results from area presented above (right)

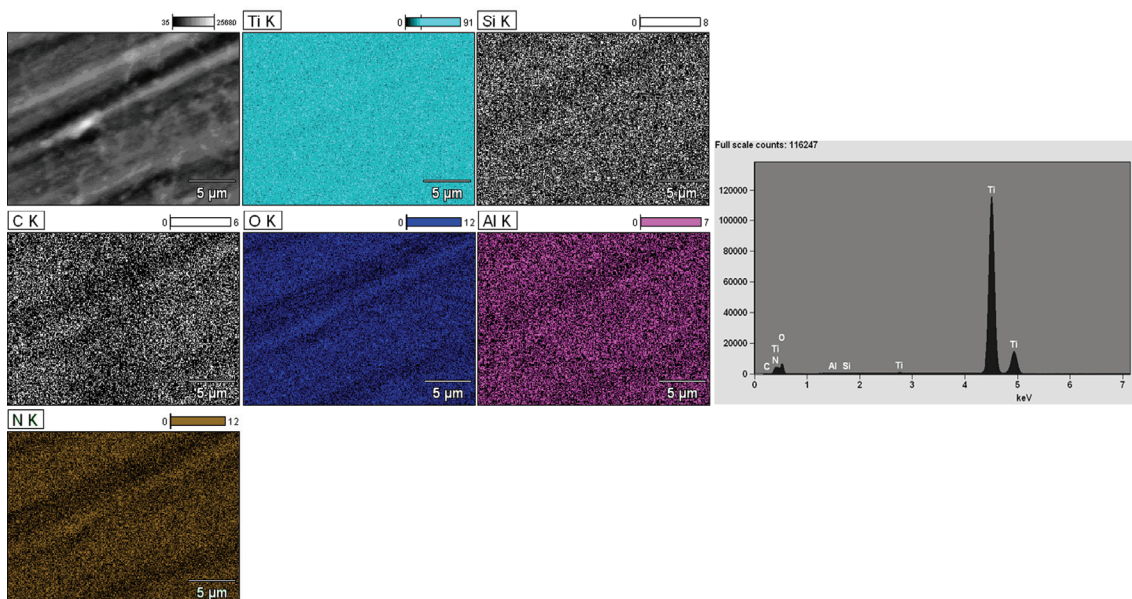


Fig. 2. SEM-SE micrograph showing morphology of profile-milled sample after oxidation; EDS map of Ti, Si, C, O, Al, N surface distribution (left) and averaging EDS results from area presented above (right)

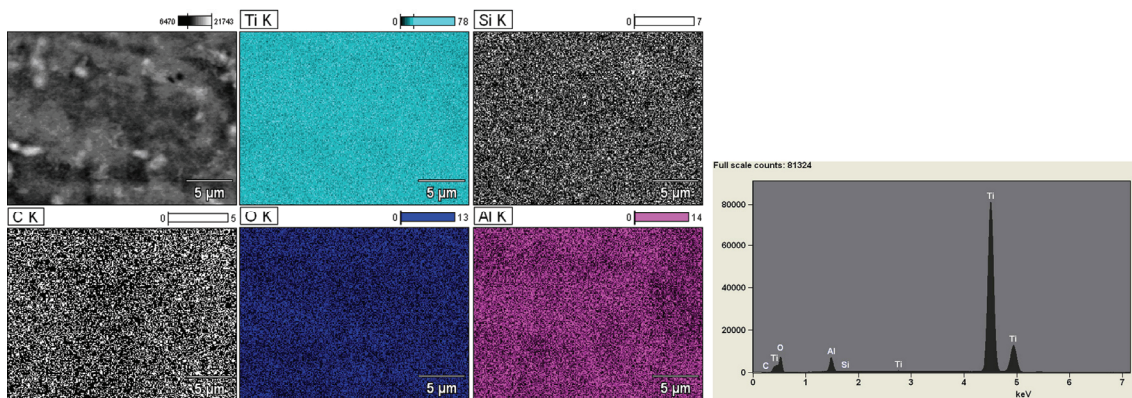


Fig. 3. SEM-SE micrograph showing morphology of profile-milled sample after oxidation and single firing; EDS map of Ti, Si, C, O, Al surface distribution (left) and averaging EDS results from area presented above (right)

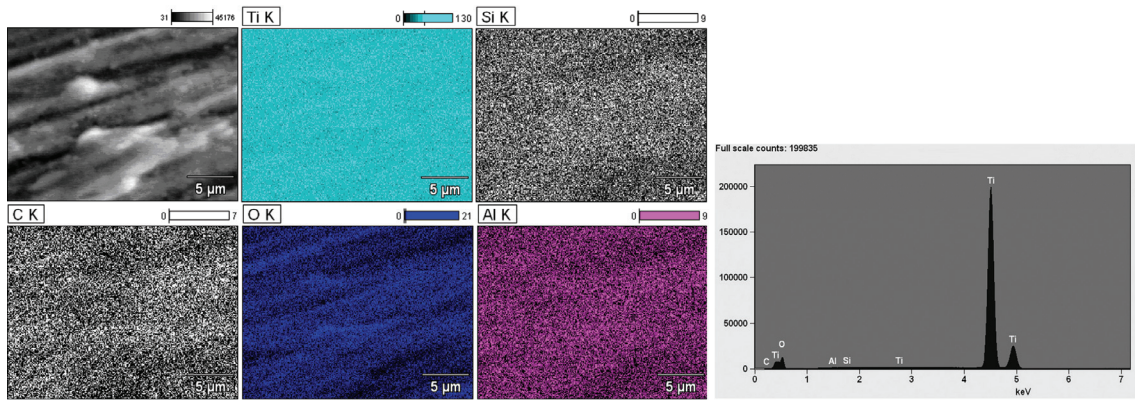


Fig. 4. SEM-SE micrograph showing morphology of profile-milled sample after oxidation and triple firing; EDS map of Ti, Si, C, O, Al surface distribution (left) and averaging EDS results from area presented above (right)

Figures 5–8 present the state of samples surface after complete corrosion tests. Single surface damage without distinct corrosion traces was observed for the reference sample (Fig. 5). Oxidized sample (Fig. 6) did not exhibit any symptoms of corrosion damage. The areas covered with cracked oxide layer, i.e., the sites predisposed to an initiation of corrosion processes, were observed on the surface of the sample oxidized and subject to single fusion (Fig. 7). It should be believed that just these defects of sample surface are responsible for its reduced corrosion resistance compared to other samples. No corrosion damage was either observed on the surface of the sample oxidized and subject to three-time fusion (Fig. 8). It was covered with a uniform oxide layer.

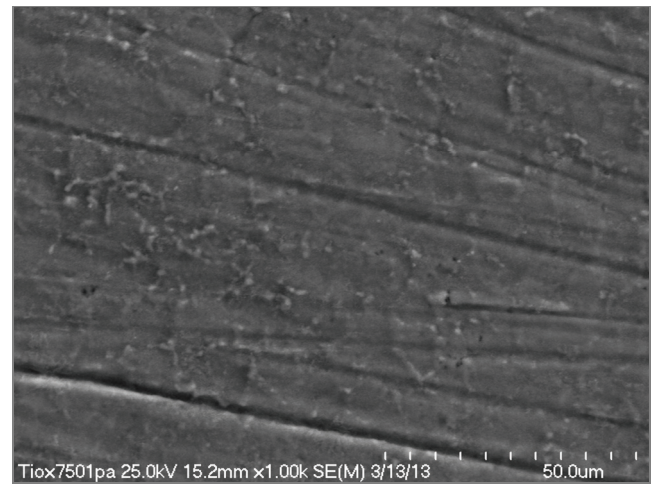


Fig. 6. SEM-SE surface state of profile-milled and oxidized sample after potentiodynamic tests

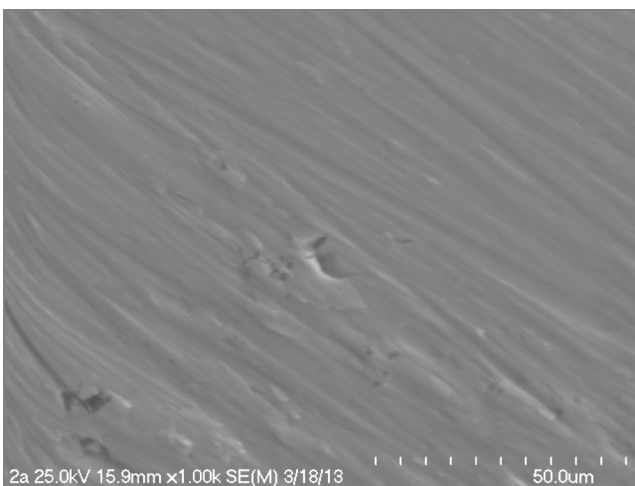


Fig. 5. SEM-SE surface state of profile-milled sample (control sample) after potentiodynamic tests



Fig. 7. SEM-SE surface state of profile-milled sample after oxidation and single firing and after potentiodynamic tests

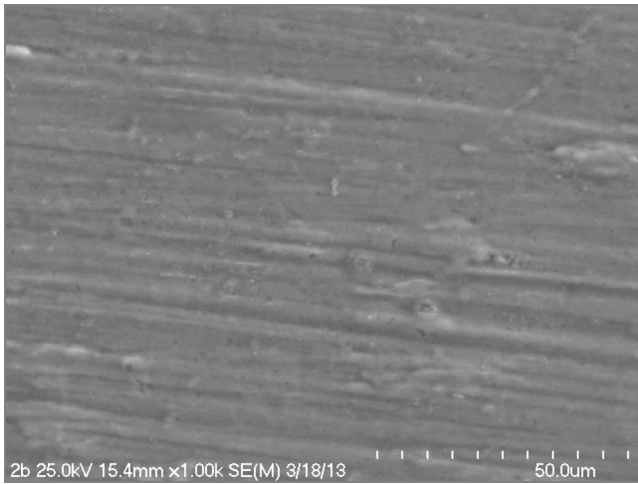


Fig. 8. SEM-SE surface state of profile-milled sample after oxidation and triple firing and after potentiodynamic tests

All OCP curves (Fig. 9), except the curve for the sample oxidized and subject to single fusion, demonstrated an increasing tendency, which means an increase in corrosion resistance progressing in time function (an increase in auto-passive layers properties). The highest dynamics in potential value growth was demonstrated for the oxidized sample subject to three-time fusion. Corrosion parameters (corrosion current and potential, and polarization resistance) (Table 2) did not demonstrate any decrease in corrosion resistance of alloy surface after the processes of oxidization and fusion, except the curve for the sample oxidized and subject to single fusion, since for the oxidized titanium sample as well as oxidized and subject to three-time fusion, an increase in polarization resistance was noted, the values of corrosion current density were subject to a decrease, and corrosion potential shifted towards more positive values.

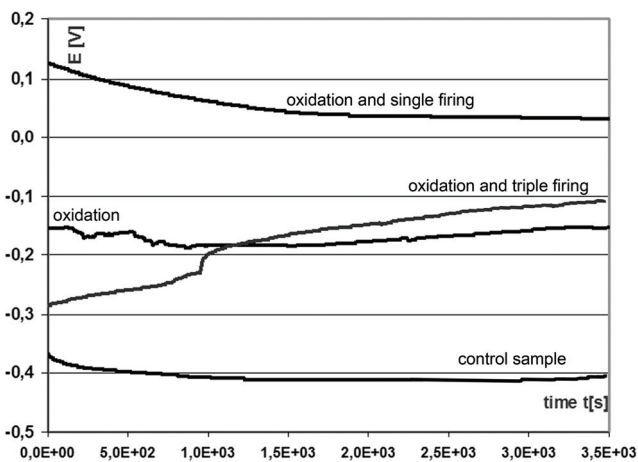


Fig. 9. OCP versus time curves of all kinds of samples in 0.9% NaCl solution

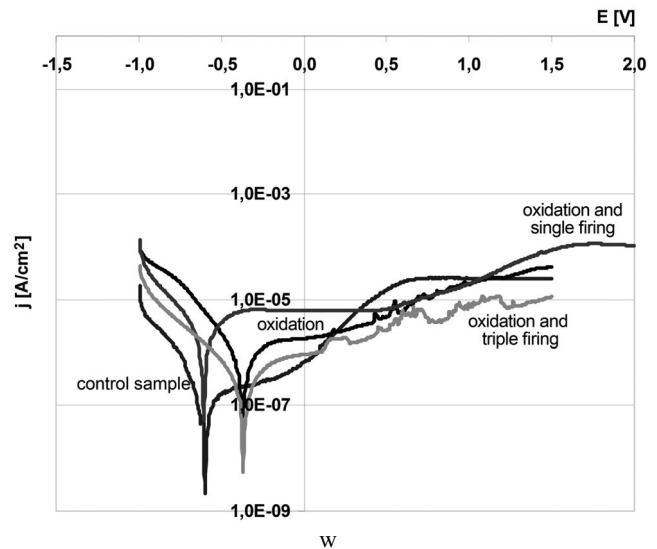


Fig. 10. Potentiodynamic polarization curves of all kinds of samples in 0.9% NaCl solution

Potentiodynamic curves for oxidization and fusion processes were shifted towards positive values with respect to the reference sample and also presented lower values of currents density in anodic ranges compared to the initial sample. All the curves in anodic range demonstrated a considerably wider passive range compared to the initial sample, which proves an increased resistance to pitting corrosion. The shapes of all curves are typical of localized corrosion with a breakdown of passivity caused by the presence of Cl^{-1} ions in corrosive environment. The breakdown potential is the highest for sample after oxidation and triple firing ($E_{br} = 1003$ mV in comparison with $E_{br} = 430$ mV for control sample).

There are only sparse reports in the literature concerning an evaluation of dental ceramics fusion effect on corrosion resistance of titanium-based metallic materials in dentistry. The studies concerning titanium thermal processing in prosthetic applications are mainly focused on evaluation of surface morphology and selected mechanical properties. Jamesh et al. [7] evaluated the properties of titanium surface before and after thermal oxidization process (TO) at a temperature of 650 °C for 48 h. The morphology of Ti TO surface demonstrated the presence of oxide layer on the whole surface without any damage. Oxide layers were evaluated as relatively uneven. The mechanism of Ti TO was also presented in the studies of Kumara [10], [11]. The results of XRD analysis for Ti TO demonstrated the presence of rutile and internal oxidization zone in Ti. The same structure was also reported in other publications [6], [16], [22]. Siva Kriszna et al. [22] reported TiO formation at temperatures lower than 700 °C,

and rutile above 800 °C, as dominant phases of titanium oxidization. Guleryuz and Cimenoglu [6] informed about the presence of anatase for the samples oxidized at 600 °C for 24 and 48 h, while rutile was the predominant phase only in the case of oxidization at 650 °C/48 h. Ti oxidization considerably enhanced the hardness, both due to the presence of hard oxide, and also the zone of internal oxidization. Nearly three-fold hardness increase was noted after TO at 650 °C/48 h. It was observed that mechanical properties of Ti TO depend to a high degree on the conditions of TO process, which limit the kind of oxide layers formed on a surface, thickness, potential porosity and state of stresses present in the layer [4], [11], [15], [17], [22].

The reports concerning corrosion properties of titanium and its alloys were presented by Jamesh et al. [7], who also examined corrosion behavior of titanium in 0.1 and 4 M HCl and HNO₃ before and after the process of thermal oxidization at a temperature of 650 °C for 48 h. Insignificant changes were observed in the course of OCP curves in time function for the samples non-oxidized and oxidized in HCl. In turn, Yu et al. [25] observed a sudden decrease in OCP value for alloys Ti-50Zr and Ti-45Nb, which was due to a decreased thickness of naturally formed passive layer followed by a uniform dissolution and in consequence activation of both alloys surface at 5 M HCl/37 °C. The shift of OCP curve in anodic direction was observed in the study of Jamesh after corrosion examinations in HNO₃ for both concentrations (0.1 and 4 M). Oxidizing character of HNO₃ favored passivation and facilitated passive layers thickness. The shifts of potentials towards anodic direction were higher for the samples in an initial state compared to those after oxidization. Similar results were noted by Robin [21] for Ti-4Al-4V alloy in 1 M HNO₃ solution.

Further research in the study [7] demonstrated that the curves of TO polarization for titanium, compared to the samples in an initial state, are shifted towards lower current values in both solutions HCl and HNO₃. Thermally oxidized titanium was characterized by an enhanced corrosion resistance compared to the samples in an initial state, both in HCl and HNO₃. An improved corrosion resistance, according to the authors, is an effect of surface covering by thicker oxide layers (~20 μm), constituting an effective barrier physically separating metal surface from corrosion environment. It was also observed in the studies of Firstov and other researchers [4], [5], [22] that in the case of titanium samples cooled with furnace, the oxide layers after oxidization process are character-

ized by lower porosity, which is directly reflected in higher corrosion resistance. The results of the studies of Kumar and other researchers, like the study of Jamesh [7], point to a significantly higher corrosion resistance of thermally oxidized titanium in various corrosive environments [6], [10]–[14]. Guleryuz and Cimenoglu [6] demonstrated in the fast corrosion tests in 5 M HCl that Ti-6Al-4V after thermal oxidization in air at a temperature of 600 °C/ 60 h presented a considerably higher corrosion resistance compared to the initial state. The authors did not observe any losses in oxidized alloy mass, even after 36 h plunging in corrosion solution, and they relate this to the formation of thick and solid oxide layer on alloy samples surface. Bloyce et al. [2] using the potentiodynamic method compared corrosion resistance in 3.5% NaCl of titanium samples subject to plasma nitriding (PN), thermal oxidization and chemical passivation in palladium salts and then thermally oxidized (PTO), and the samples in an initial state. Both TO and PTO samples demonstrated a shift of corrosion potential in a positive direction compared to PN and control samples. Fast corrosion tests in boiling 20% HCl demonstrated 13-fold and 27-fold resistance increase for TO and PTO samples, respectively, compared to PN samples. The study of Ashrafizadeh [1] examined a corrosion resistance of titanium alloy Ti-6Al-4V after different variants of thermal oxidization: at 500 °C, 600 °C, 700 °C and 800 °C with heating at a rate of 5 °C/min. Typical potentiodynamic polarization curves for control (PK) and thermally oxidized titanium alloy in 0.9% NaCl pointed to a difference in corrosion behavior of the oxidized samples depending on oxidization variant. The rate of corrosion decreased with an increase in oxidization temperature from 500 °C to 600 °C and 700 °C that was related to the formation of rutile layer on alloy surface, which is characterized by good anticorrosion properties, and its increasing thickness with an increase in oxidization temperature. In the case of TO at a temperature of 800 °C, the surface of the samples demonstrated a decrease in corrosion resistance which, as demonstrated in SEM examinations, was caused by the occurrence of cracks and porosity of already too thick an oxide layer and formation of galvanic corrosion. The highest corrosion resistance was obtained after TO at 600 °C. For these oxidization conditions, the critical potential ($E_{br} = 1.5$ V) was 0.5 V higher compared to TO samples at other temperatures. The layer of titanium oxide covering the surface of TO alloy at 600 °C was even, free from cracks, characterized by good adhesion to the substrate. Thermal oxidization at 600 °C for 1 h, with heating rate of 5 °C/min and cooling

with furnace, was considered as optimum for an improvement in corrosion resistance of the titanium alloy examined.

The conclusions from the papers cited are consistent with the results obtained in this study – thermal oxidation in selected ranges of temperatures enhanced titanium corrosion resistance, and it was dependent on the quality of oxide layer structure, free of defects layers ensured an increased electrochemical corrosion resistance, surface defects of oxide layer observed for the sample oxidized and subject to single thermal processing corresponding to fusion resulted in deterioration of anticorrosion properties in comparison with other thermally treated samples.

An increase in titanium corrosion resistance obtained for other variants of thermal processing modeling oxidation and ceramics fusion allows us to expect improved biological properties in clinical conditions.

5. Conclusions

The processes corresponding to oxidization and ceramics fusion on titanium do not cause deterioration of its anticorrosion properties, and partially enhance the resistance.

The best corrosion resistance, in particular resistance against the pitting corrosion, was achieved for sample after oxidation and triple firing with the highest value of breakdown potential equal to 1003 mV.

Metal elements of crowns and bridges not covered with porcelain, and especially crowns interior, should not be subject to mechanical processing (polishing), which may decrease their corrosion resistance.

References

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References

[1] ASHRAFIZADEH A., ASHRAFIZADEH F., *Structural features and corrosion analysis of thermally oxidized titanium*, J. Alloy Compd., 2009, Vol. 480, 849–852.

[2] BLOYCE A., QI P.Y., DONG H., BELL T., *Surface Modification of Titanium Alloys for Combined Improvements in Corrosion and Wear Resistance*, Surf. Coat. Technol., 1998, Vol. 107, 125–132.

[3] BÜRGERS R., HAHNEL S., REICHERT T.E., ROSENTRITT M., BEHR M., GERLACH T., HANDEL G., GOSAU M., *Adhesion of Candida albicans to various dental implant surfaces and the influence of salivary pellicle protein*, Acta Biomater., 2010, Vol. 6, 2307.

[4] EBRAHIMI A.R., ZAREI F., KHOSROSHAHI R.A., *Effect of Thermal Oxidation Process on Fatigue Behavior of Ti-4Al-2V Alloy*, Surf. Coat. Technol., 2008, Vol. 203, 199–203.

[5] FIRSTOV G.S., VITCHEV R.G., KUMAR H., BLANPAIN B., VAN HUMBEECK J., *Surface Oxidation of NiTi Shape Memory Alloy*, Biomaterials, 2002, Vol. 23, 4863–4871.

[6] GULERYUZ H., CIMENOGLU H., *Effect of Thermal Oxidation on Corrosion and Corrosion-Wear Behaviour of a Ti-6Al-4V Alloy*, Biomaterials, 2004, Vol. 25, 3325–3333.

[7] JAMESH M., KUMAR S., SANKARA NARAYANAN T.S.N., *Effect of Thermal Oxidation on Corrosion Resistance of Commercially Pure Titanium in Acid Medium*, J. Mater. Eng. Perform., 201, Vol. 21(6), 900–906.

[8] JOHNSON T., VAN NOORT R., STOKES C.W., *Surface analysis of porcelain fused to metal systems*, Dent. Mater., 2006, Vol. 22, 330–337.

[9] KRZĄKAŁA A., SŁUŻAŁSKA K., DERCZ G., MACIEJ A., KAZEK A., SZADE J., WINIARSKI A., DUDEK M., MICHALSKA J., TYLKO G., OSYCZKA A.M., SIMKA W., *Characterisation of bioactive films on Ti-6Al-4V alloy*, Electrochimica Acta, 2013, Vol. 104, 425.

[10] KUMAR S., SANKARA NARAYANAN T.S.N., GANESH SUNDARA RAMAN R.S., SESHADRI S.K., *Thermal Oxidation of CP-Ti: Evaluation of Characteristics and Corrosion Resistance as a Function of Treatment Time*, Mater. Sci. Eng. C, 2009, Vol. 29, 1942–1949.

[11] KUMAR S., SANKARA NARAYANAN T.S.N., GANESH SUNDARA RAMAN S., SESHADRI S.K., *Thermal Oxidation of CP Ti – An Electrochemical and Structural Characterization*, Mater. Charact., 2010, Vol. 61, 589–597.

[12] KUMAR S., SANKARA NARAYANAN T.S.N., GANESH SUNDARA RAMAN S., SESHADRI S.K., *Thermal Oxidation of Ti6Al4V Alloy: Microstructural and Electrochemical Characterization*, Mater. Chem. Phys., 2010, Vol. 119, 337–346.

[13] KUMAR S., SANKARA NARAYANAN T.S.N., GANESH SUNDARA RAMAN S., SESHADRI S.K., *Fretting Corrosion Behaviour of Thermally Oxidized CP-Ti in Ringer's Solution*, Corros. Sci., 2010, Vol. 52, 711–721.

[14] KUMAR S., SANKARA NARAYANAN T.S.N., GANESH SUNDARA RAMAN S., SESHADRI S.K., *Surface Modification of CP-Ti to Improve the Fretting Corrosion Resistance: Thermal Oxidation vs. Anodizing*, Mater. Sci. Eng. C, 2010, Vol. 30, 921–927.

[15] LEINENBACH C., EIFLER D., *Influence of Oxidation Treatment on Fatigue and Fatigue-Induced Damage of Commercially Pure Titanium*, Acta Biomater., 2009, Vol. 5, 2810–2819.

[16] LOPEZ M.F., JIMENEZ J.A., GUTIERREZ A., *Corrosion Study of Surface-Modified Vanadium-Free Titanium Alloys*, Electrochim. Acta, 2003, Vol. 48, 1395–1401.

[17] NAKAJIMA K., TERAOKA K.I., MIATA T., *The Effect of Microstructure on Fatigue Crack Propagation of a + b Titanium Alloys: In-Situ Observation of Short Fatigue Crack Growth*, Mater. Sci. Eng. A, 1998, Vol. 243, 176–181.

[18] OKABE T., HERO H., *The use of titanium in dentistry*, Cells. Mater., 1995, Vol. 5, 211–230.

[19] PANG I.-CH., GILBERT J.L., CHAI J., LAUTENSCHLAGER E.P., *Bonding characteristics of low-fusing porcelain bonded to pure titanium and palladium-copper alloy*, J. Prosthet. Dent., 1995, Vol. 73, 17–25.

- [20] PUCKETT S.D., TAYLOR E., RAIMONDO T., WEBSTER T.J., *The relationship between the nanostructure of titanium surfaces and bacterial attachment*, *Biomaterials*, 2010, Vol. 31, 706.
- [21] ROBIN A., ROSA J.L., SANDIM H.R.Z., *Corrosion Behavior of Ti-4Al-4V Alloy in Nitric, Phosphoric and Sulphuric Acid Solutions at Room Temperature*, *J. Appl. Electrochem.*, 2001, Vol. 31, 455–460.
- [22] SIVA R.K., D., BRAMA Y.L., SUN Y., *Thick Rutile Layer on Titanium for Tribological Applications*, *Tribol. Int.*, 2007, Vol. 40, 329–334.
- [23] SUROWSKA B., BIENIAŚ J., WALCZAK M., SANGWAL K., STOCH A., *Microstructure and mechanical properties of ceramic coatings on Ti and Ti-based alloy*, *Appl. Surf. Sci.*, 2004, Vol. 238, 288–294.
- [24] TUNCDEMIR A.R., KARAHAN I., POLAT S., MALKOC M.A., DALKIZ M., *The effect of repeated porcelain firings on corrosion resistance of different dental alloys*, *J. Adv. Prosthodont.*, 2013, Vol. 5, 44–50.
- [25] YU S.Y., BRODRICK C.W., RYAN M.P., SCULLY J.R., *Effects of Nb and Zr Alloying Additions on the Activation Behavior of Ti in Hydrochloric Acid*, *J. Electrochem. Soc.*, 1999, Vol. 146, 4429–4438.