THE EFFECT OF NITROGEN-ION IMPLANTATION ON THE CORROSION RESISTANCE OF TITANIUM IN COMPARISON WITH OXYGEN- AND ARGON-ION IMPLANTATIONS

VPLIV DUŠIKOVE IONSKE IMPLANTACIJE NA KOROZIJSKO ODPORNOST TITANA V PRIMERJAVI S KISIKOVO IN ARGONSKO IONSKO IMPLANTACIJO

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Commercially pure (CP) titanium was surface modified with nitrogen-, argon- and oxygen-ion implantations in order to investigate the material's corrosion resistance in a simulated body fluid. Five doses were chosen for the ions, ranging from $5 \cdot 10^{15}$ cm^{-2} to $2.5 \cdot 10^{17}$ cm^{-2}. In-vitro open-cyclic potential-time measurements and cyclic polarization studies were carried out to evaluate the corrosion resistance of the modified surface in comparison to an unmodified surface. Specimens implanted at $4 \cdot 10^{16}$ cm^{-2} and $7 \cdot 10^{16}$ cm^{-2} showed the optimum corrosion resistance, higher doses showed a detrimental effect on the corrosion resistance. Argon- and oxygen-ion implantation at these doses did not show any improved corrosion resistance, indicating the beneficial role of nitrogen on the corrosion resistance of titanium in the simulated body-fluid environment. Grazing-incidence X-ray diffraction (GIXD) was employed on the implanted specimens to determine the phases formed with the increasing doses. X-ray photoelectron spectroscopy (XPS) studies on the passive film of the implanted samples and on the unimplanted samples were analyzed in order to understand the role of nitrogen in improving the corrosion resistance. The results of the present investigation indicated that nitrogen-ion implantation can be used as a viable method for improving the corrosion resistance of titanium. The nature of the surface and the reason for the variation and the improvement in the corrosion resistance are discussed in detail.

Key words: ion implantation, orthopedic implants, corrosion, titanium, nitrogen, oxygen, argon

Površinska modifikacija čistega titana je nastala z dušikovo, argonsko in kisikovo ionsko implantacijo z namenom določitve korozijske obstojnosti titanovih površin v simulirani telesni tekočini. Za ionsko implantacijo je uporabljeno pet različnih doz ionov v območju od $5 \cdot 10^{15}$ cm^{-2} do $2.5 \cdot 10^{17}$ cm^{-2}. Korozijska obstojnost modificirane površine v primerjavi s pogoji brez implantacije je ovrednotena s cikličnimi potencialnimi časovnimi meritvami in študijem ciklične polarizacije. Optimalno korozijsko obstojnost so pokazali vzorci, ki so bili implantirani z dozo $4 \cdot 10^{16}$ cm^{-2} in $7 \cdot 10^{16}$ cm^{-2}. Preostale ionske doze so poslabšale korozijsko obstojnost implantiranih vzorcev. Pri teh dozah argonska in kisikova ionska implantacija ni izboljšala korozijske odpornosti vzorcev, ki je bila zaznana ob koristnem vplivu dušika na korozijsko obstojnost titana v simulirani telesni tekočini. Pri večanju ionskih doz so nastale fazne spremembe, ki so bile identificirane z rentgensko difrakcijo implantiranih vzorcev. Vloga dušika pri izboljšanju korozijske odpornosti je analizirana s študijem rentgenske spektroskopije fotoelektronov na pasivni plasti pri pogojih implantacije in brez nje. Rezultati predstavljene raziskave kažejo, da je dušikovo ionsko implantacijo mogoče uporabiti kot zanesljivo metodo za izboljšanje korozijske obstojnosti titana. Podrobno je predstavljena lastnost površine in vzrok za spremembo in izboljšanje korozijske odpornosti.

Ključne besede: ionska implantacija, ortopedski implantáti, korozija, titan, dušik, kisik, argon

1 INTRODUCTION

The inherent mechanical properties of metallic materials have made them the material of choice for orthopedic implants. Three alloys – stainless steels, cobalt-chromium alloys and titanium and its alloys – are the materials normally used for this type of application. The favorable local-tissue response and the excellent corrosion resistance of titanium and its alloys have promoted their widespread use at the expense of the other two types of metallic materials. Owing to its enhanced fatigue strength the titanium alloy Ti6Al4V was considered as an interesting alternative to the previously used stainless-steel and cobalt-chromium alloys [1]. However, over the long term the presence of vanadium in this alloy may cause problems, even though the vanadium present in the Ti6Al4V alloy is very stable and the release of vanadium ions under normal conditions is always lower than the toxic level. The toxicity of vanadium is well known, and it can be aggravated when an implant is fractured and the material subsequently undergoes fretting [2]. This phenomenon may cause local irritation of the tissues surrounding the implants, or over the long term the metallic ions released by the implants may sensitize the patient.

In order to avoid the potential risks several solutions have been proposed. One solution is to continue to use CP titanium as an alternative to this alloy. However, titanium is not inert when it is incorporated into the human body. Titanium releases metallic ions, which

subsequently form corrosion products in the fluids [3,4]. Moreover, with an articular prosthesis like a hip or a knee joint, fretting and wear take place, which can result in more titanium ions being released and a degradation of the ultra-high-molecular-weight polyethylene attached to the joint. This phenomenon is more significant in the case of titanium than with stainless steels and cobalt-chromium alloys [5].

Considerable attention had been paid in the recent past to the surface treatment of these materials in order to reduce the problems. For example, ion implantation has been used to improve the tribological behaviour of these materials [6]. However, less attention has been paid to evaluating the rate of ion release and the corrosion resistance of the modified surfaces.

Yu et al [7] found that nitrogen-ion implantation of the Ti6Al4V alloy reduced the passive current density in a bio-brine solution. Nitrogen-ion implantation with the same alloy at different doses also influenced the corrosion resistance in the simulated body fluid [8,9]. The aim of our investigation was to optimize the conditions of nitrogen-ion implantation for commercially pure titanium and to correlate the implantation parameters with the corrosion resistance. Argon- and oxygen-ion implantations were carried out to compare the corrosion parameters with nitrogen-ion implantation and to understand whether the increased corrosion associated with the nitrogen-ion implantation is a chemical effect produced by the nitrogen or a microstructure change produced by the ion implantation. A surface analysis using GIXD was carried out to further understand the role of nitrogen in the corrosion resistance of titanium in the simulated body fluid.

2 METHODS AND MATERIALS

Commercially pure titanium samples of 8.5 mm diameter (supplied by Midhani, India) were ground with 1000-grit SiC paper and polished with 6 μm and 1 μm diamond pastes. The polished samples were then ultrasonically cleaned with acetone and rinsed with deionized water.

2.1 Ion implantation

Nitrogen-, oxygen- and argon-ion implantations were carried out using a 150 kV accelerator at energies of (70, 80 and 140) keV, respectively. The reason for choosing the different energies was to obtain similar concentration profiles for the implanted ions. Modeling software called TRIM® was used to obtain the concentration profile for each ion as shown in **Figure 1**. For the nitrogen-ion implantation five different doses were chosen in the range from $5·10^{15}$ cm^{-2} to $2.5·10^{17}$ cm^{-2}. For the oxygen- and argon-ion implantation three doses were chosen from this range. A summary of the energy and the doses for each ion is given in **Table 1**.

Table 1: Summary of nitrogen-, argon- and oxygen-ion implantation for different doses
Tabela 1: Dušikova, argonska in kisikova ionska implantacija pri različnih dozah

Ion	Nitrogen (70 keV) (cm^{-2})	Argon (140 keV) (cm^{-2})	Oxygen (80 keV) (cm^{-2})
Material-Titanium	$5·10^{15}$, $1·10^{16}$, $4·10^{16}$, $7·10^{16}$, $1·10^{17}$, $2.5·10^{17}$	$5·10^{15}$, $7·10^{16}$, $2.5·10^{17}$	$5·10^{15}$, $7·10^{16}$, $2.5·10^{17}$

2.2 Corrosion measurements

Ringer's solution (9.0 g/l NaCl, 0.43 g/l KCl, 0.24 g/l CaCl$_2$ and 0.2 g/l NaHCO$_3$) was used as the electrolyte and maintained at pH 7.4 and 37.4 ±1 °C to simulate body-fluid conditions. Two electrochemical techniques were used to evaluate the corrosion resistance of the implanted surface in comparison with the untreated surface. In the OCP-time measurements the specimen's
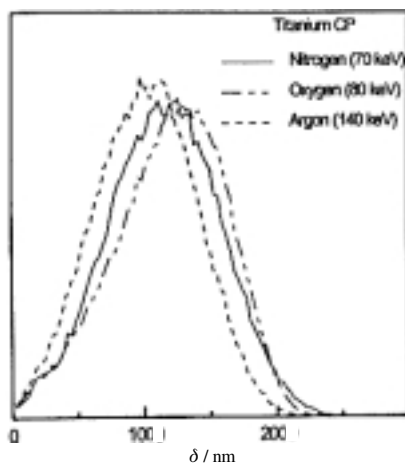

Figure 1: Calculated depth profile δ of N$^+$-, Ar$^+$- and O$^+$-implanted CP titanium
Slika 1: Izračunan globinski profil δ N$^+$, Ar$^+$ in O$^+$ na implantiranem titanovem vzorcu CP
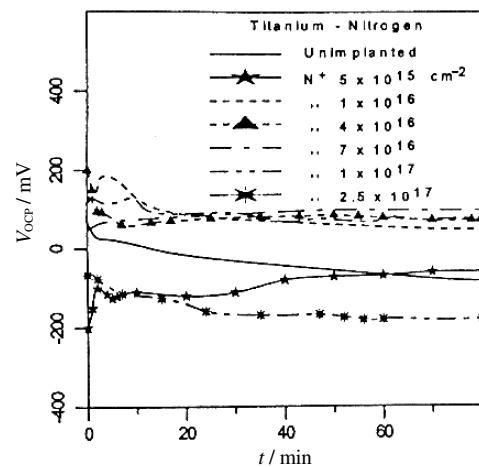

Figure 2: OCP-time measurements of nitrogen-ion-implanted titanium
Slika 2: OCP-časovne meritve titana, implantiranega z ioni dušika

potential was monitored as a function of time, starting from the sample's immersion into the electrolyte. A saturated calomel electrode was used as the reference electrode. For the cyclic polarization test platinum foil was used as the counter electrode. A scan rate of 1 mV/s was applied to the specimens starting from –750 mV to +2000 mV and then reversed in order to obtain the cyclic polarization curve. Grazing-incidence X-ray diffraction studies were carried out on the nitrogen-ion-implanted specimens with different doses to understand the phase changes and compound formation after the implantation process. An incidence angel of 1° was used to allow a maximum penetration depth of 0.3 μm for the X-rays into the Ti substrate.

3 RESULTS AND DISCUSSION

3.1 Nitrogen-ion implantation

3.1.1 Electrochemical studies

The OCP of the specimens measured as a function of time for nitrogen-ion-implanted samples and the unimplanted samples are presented in **Figure 2**. The OCP of the unimplanted specimens was at the noble potential to begin with; however, after 60 minutes it was

Figure 3: Potentiodynamic cyclic polarization curves for nitrogen-ion-implanted CP titanium in comparison with an unimplanted specimen
Slika 3: Potencialno-dinamične ciklične polarizacijske krivulje na vzorcu titana CP, implantiranega z ioni dušika in primerjava z vzorcem brez implantacije

shifted to the active potential (+50 mV to –83 mV). At a very low implantation dose ($5 \cdot 10^{15}$ cm^{-2}) the OCP was initially observed to be at an active potential compared to the unimplanted specimen; however, the OCP moved to a nobler potential with time, when compared to the unimplanted specimen. The OCP was found to shift towards a nobler potential after increasing the doses up to $7 \cdot 10^{16}$ cm^{-2}, and beyond this the OCP started to decrease. The OCP fell drastically to a more negative potential than that of the unimplanted specimen when implanted with a high dose of nitrogen ($2.5 \cdot 10^{17}$ cm^{-2}). The moderate doses of $1 \cdot 10^{16}$ cm^{-2} to $1 \cdot 10^{17}$ cm^{-2} not only showed the nobler potential but also a rapid attainment of the steady state was observed. The enhancement of the potential and the attainment of a stable potential in a short time were attributed to the protective surface layers formed during the implantation. Ashworth et al [10] reported a similar shift of the OCP in the noble direction for implanted specimens and attributed it to the thickening of the native oxide layer formed during the implantation. The shift of the OCP towards the active direction for the nitrogen-ion-implanted specimens at doses above $1 \cdot 10^{17}$ cm^{-2} can be attributed to the sputtering of the oxide layer formed during implantation.

The nitrogen addition may not have a significant role in the OCP of the implanted specimen. Titanium is a passive metal and it undergoes spontaneous passivity when it is placed in an aqueous solution. The change in the OCP would mainly arise from either a thickening of the air-formed passive film or a change in the surface roughness with doses, and/or a combination of both effects.

Figure 3a and **b** are the cyclic polarization curves for the specimens with varying doses of nitrogen-ion implantation. **Table 2** gives the details of the OCP and the passive current density for all the tested conditions. The implantation at lower doses ($5 \cdot 10^{15}$ cm^{-2} and $1 \cdot 10^{16}$ cm^{-2}) showed a lower passive current density and the trend continued up to the specimen implanted at $7 \cdot 10^{16}$ cm^{-2}. The specimen implanted at $7 \cdot 10^{16}$ cm^{-2} showed a minimum passive current density, and beyond this the passive current density started to increase. The dose of $2.5 \cdot 10^{12}$ cm^{-2} showed a higher passive current density along with an anodic peak at 0–400 mV in the cyclic polarization curve. The increased passive current density at these doses indicated that the modified surface is prone to corrosion in the simulated body-fluid conditions. The raid increase in the current density at around 1.2 V for the unimplanted and all the implanted conditions, except the dose of $2.5 \cdot 10^{17}$ cm^{-2}, arises from the oxygen evolution [11]. The samples implanted at $2.5 \cdot 10^{17}$ cm^{-2} did not show a large increase in their current density in this region, indicating the absence of oxygen evolution. The electrical conductivity of the passive film of Ti in the acidic environment is low, and the increase in the anodic potentials leads to a high
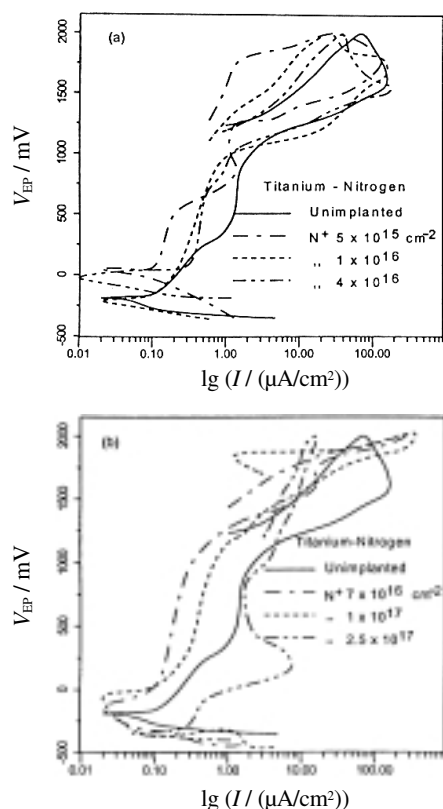
electrical field across the passive layer. Under these circumstances ion transport occurs and film growth continues to a thickness of hundreds of nanometers [12]. Though the titanium becomes anodized in the acidic pH, it will not happen in the higher pHs. This was confirmed in the present investigation. The reduction in the oxygen evolution for the specimen implanted at $2.5 \cdot 10^{17}$ cm^{-2} could be attributed to the low electrical conductivity and the growth of the passive film.

Table 2: Corrosion parameters of nitrogen-, argon- and oxygen-ion-implanted CP titanium specimens
Tabela 2: Korozijski parametri na titanskih CP-vzorcih, implantiranih z ioni dušika, argona in kisika

Specimens	Open Circuit Potential, V_{OPC} / mV (After 80 minutes)			Passive Current Density, i_{pass} /(μA/cm^2) at 500 mV		
	N$^+$	Ar$^+$	O$^+$	N$^+$	Ar$^+$	O$^+$
Unimplanted	-83	-83	-83	1.2	1.2	1.2
$5 \cdot 10^{15}$	-46	-23	+19	0.25	0.4	0.34
$1 \cdot 10^{16}$	+35	-	-	0.33	-	-
$4 \cdot 10^{16}$	+75	-	-	0.44	-	-
$7 \cdot 10^{16}$	+110	-129	-39	0.14	0.8	0.52
$1 \cdot 10^{17}$	+75	-	-	0.31	-	-
$2.5 \cdot 10^{17}$	-150	-145	-41	2.0	0.9	0.8

3.1.2 GIXD studies

GIXD studies were carried out for the sample that was nitrogen-ion implanted at $7 \cdot 10^{16}$ cm^{-2} and $2.5 \cdot 10^{17}$ cm^{-2} in a comparison with an unimplanted specimen in order to explain the dependence of the corrosion resistance on nitrogen fluencies. The diffraction pattern of the specimens is shown in **Figure 4**. The diffraction patterns were scanned in the 2Θ range of 30–55°. The unimplanted specimen showed four peaks, which correspond to the Ti (hcp) peaks. The specimen implanted with a dose of $7 \cdot 10^{16}$ cm^{-2} showed a similar pattern to that of the unimplanted specimen, but with a small peak at a 2Θ of 36.85°, which corresponds to TiN (111). On the other hand, the specimen implanted with a dose of $2.5 \cdot 10^{17}$ ions/cm^2 showed two additional peaks, which were indexed to TiN (111) and TiN (200). It was reported that [13] nitrides start to appear at a dose of $5 \cdot 10^{16}$ cm^{-2} (50 keV), the size and the number of precipitates increasing with the increase in the dose. Generally, a nitrogen addition will transform the hcp-Ti to bcc-Ti$_2$N and finally to fcc-Ti$_2$N and fcc-TiN phases [14]. Also, the lattice parameter may give a rough idea of composition, though care must be taken to account for other possible variations, particularly internal stress. For the atomic ratio of N/Ti = 1 the lattice parameter will be 0.424 17 nm and the lattice parameter value decreases with a decrease in the N/Ti ratio [15]. In the present case, the TiN (111) peak showed a lattice parameter value of 0.423 78 nm, which represents N/Ti $\approx$ 0.8, from the diagram presented in reference [15]. This indicated the initial stages of nitride formation in the sample implanted at a dose of $7 \cdot 10^{16}$ cm^{-2}. At still higher doses ($2.5 \cdot 10^{17}$ cm^{-2}) the
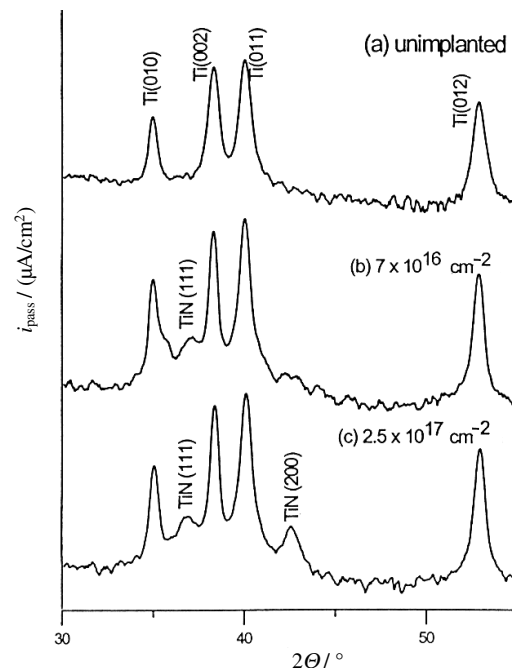

Figure 4: GIXD studies of unimplanted and nitrogen-ion-implanted specimens.
Slika 4: Študij rentgenske difrakcije na vzorcih, implantiranih z dušikovimi ioni

TiN(200) peak showed a lattice parameter of 0.424 11 nm with respect to the N/Ti ratio approaching unity.

3.1.3 The role of nitrogen in the corrosion resistance of titanium

The nitrogen-ion-implanted titanium showed marked changes in its corrosion resistance with the variation in the doses. The doses between $4 \cdot 10^{16}$ and $7 \cdot 10^{16}$ ions/cm^2 were found to be the optimum, with higher doses having a detrimental effect. The improvement in the passivity in the simulated body-fluid conditions may be due to the following reason: The availability of a large amount of nitrogen at the surface will make the surface inactive by resisting the interaction with the reactive O^{2-} and Cl$^-$ with titanium. Nitrogen present in the implanted layers in the solid solution forms oxynitrides during the cyclic polarization and enhances the corrosion resistance. Our XPS results showed the formation of oxynitrides in the passive film of the implanted specimen. At higher doses, the titanium forms its nitrides, which introduces metallurgical inhomogeneities to the surface. These nitrides tend to detach from the metallic matrix and form a galvanic couple with the metal matrix. As a result, the nitride precipitate will remain as a cathode and the other metal surface will undergo active dissolution, and hence an increased current density was observed.

3.2 Argon-ion implantation

Figure 5a shows the OCP-time measurement for the argon-ion-implanted titanium specimens. The implanta-

tion carried out at low doses ($5 \cdot 10^{15}$ cm^{-2}) showed a sharp decrease in the OCP at the initial stage and attained a steady state at around –20 mV, which is a nobler shift compared to the unimplanted specimen. However, the specimens implanted at $7 \cdot 10^{16}$ cm^{-2} and $2.5 \cdot 10^{17}$ cm^{-2} showed shifts in the OCP, which were far more negative than the unimplanted condition. Though the OCP of the specimen implanted at $7 \cdot 10^{16}$ cm^{-2} was lower than the unimplanted specimen, it achieved the steady state much earlier. However, the specimen implanted at $2.5 \cdot 10^{17}$ cm^{-2} showed the lowest OCP values (–120mV) with some fluctuation, and it could not achieve the steady state during a measurement up to 60 min. The shift of the OCP to a more negative potential suggests that argon-ion implantation enhances the activity of the metal surface.

The potentiodynamic cyclic polarization behaviors of Ar-ion-implanted titanium specimens are shown in **Figure 5b**. The specimen implanted at $5 \cdot 10^{15}$ cm^{-2} showed a reduction in the passive current density compared to the unimplanted condition. However, compared with the nitrogen-ion implantation of the same dose, the reduction is not significant. The doses exhibiting the smallest current density ($7 \cdot 10^{16}$ cm^{-2}) in the nitrogen-ion implantation did not show a significant reduction in their passive current density for argon-ion
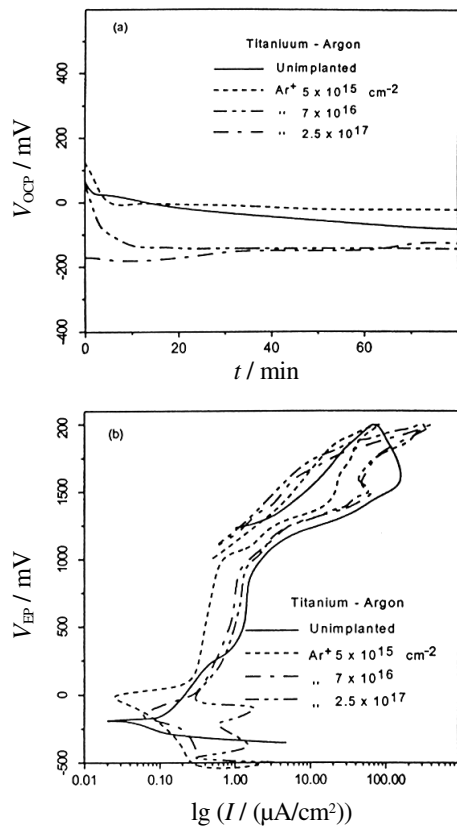

Figure 5: (a) OCP-time measurements (b) cyclic polarization curves for argon-ion-implanted titanium
Slika 5: (a) OCP-časovne meritve (b) cikličnih polarizacijskih krivulj na vzorcu titana, implantiranega z ioni argona
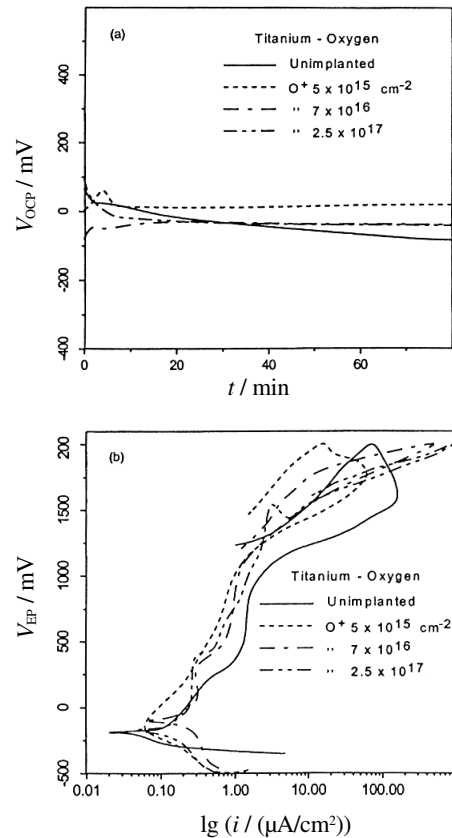

Figure 6: (a) OCP-time measurements (b) cyclic polarization curves for oxygen-ion-implanted titanium
Slika 6: (a) OCP-časovne meritve (b) cikličnih polarizacijskih krivulj na vzorcu titana implantiranega z ioni kisika

implantation. At high doses of argon-ion implantation ($2.5 \cdot 10^{17}$ cm^{-2}) the current density was still higher, suggesting the dissolution of the metals. The specimen showed a hump at –300 mV to –50 mV, which in the cathodic region indicates a high degree of cathodic reaction on the surface that is in the air-formed oxide film.

3.3 Oxygen-ion implantation

Figure 6a shows the OCP-time measurements of oxygen-ion-implanted titanium specimens at three different doses compared to the unimplanted specimen. All the implanted specimens showed a shift in the OCP towards a nobler direction and attained a steady state in a short time. The specimen implanted at $5 \cdot 10^{15}$ cm^{-2} reached a potential of +20 mV in 80 min. The other two doses showed a value of –20 mV. The noble shift for the all the implanted specimens is attributed to the stable surface layers produced by the oxygen-ion implantation. In the case of N- and Ar-ion implantations, the high dose ($2.5 \cdot 10^{17}$ cm^{-2}) specimens showed lower OCP values than the unimplanted specimen. The noble value obtained in the O-ion implantation may be attributed to the formation of oxides in the implantation layer, which resist the dissolution.

Cyclic polarization showed a similar trend to OCP time measurements (**Figure 6b**). All the implanted specimens showed a lower passive current density than the unimplanted specimen. The specimens implanted at $2.5 \cdot 10^{17}$ cm^{-2} did not show any hump in the cathodic region and/or in the initial stages of anodic oxidation, indicating that there is dissolution in this region. Like the Ar-ion implantation it also exhibited a peak at +1.2V, which is responsible for the oxygen evolution.

In summary, Ar- and O-ion implantations showed a marginal improvement for low doses of Ar-ion implantation and doses ranging from $5 \cdot 10^{15}$ cm^{-2} to $2.5 \cdot 10^{17}$ cm^{-2} for the O-ion implantation. However, the improvements observed in these implantations are much lower when compared to the N-ion implantation. The specimen implanted at a dose of $2.5 \cdot 10^{17}$ cm^{-2} is not detrimental for the Ar- and O-ion implantations, unlike the N-ion implantation. The variation in the corrosion parameters of the implanted specimens clearly indicated the improvement in the corrosion resistance as a result of N-ion implantation is purely a chemical effect produced by the nitrogen.

4 CONCLUSION

Nitrogen-ion implantation on commercially pure (CP) titanium showed an improvement in the electrochemical behaviour of the passive film. Doses between $4 \cdot 10^{16}$ cm^{-2} and $7 \cdot 10^{16}$ cm^{-2} are recommended for orthopedic applications. Higher doses showed a detrimental effect due to the formation of nitrides. Argon- and oxygen-ion implantations did not improve the corrosion resistance significantly when compared to the nitrogen-ion implantation.

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