Surface properties and mechanism of corrosion resistance enhancement in a high temperature nitrogen ion implanted medical grade Ti

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The surface characteristics and mechanism of corrosion resistance enhancement in a high temperature nitrogen ion implanted medical grade Ti was investigated. The implantations were carried out in a constant energy (80 keV) and dose (2.1 × 10^{18} Ion cm^{-2}) at room temperature (~300 K, without heating the substrate) and at different elevated temperatures (473 K, 673 K and 873 K by external heating of the substrate). For implantation temperature optimization, the nitride phase formation on the implanted samples was characterized using grazing incidence X-ray diffraction (GI-XRD) method and also the electrochemical polarization tests in the Ringer’s solution as a simulated body fluid were carried out. A significantly enhanced corrosion resistance was achieved for the titanium sample implanted at 473 K between different implantation temperatures, which was attributed to the higher protective performance of the nitride layer over Ti, resulted from the accelerated formation of uniform and dense nitride phases on its surface. The corroded surface of the samples was observed by a field emission scanning electron microscope (FE-SEM). Several delaminations and detachments in the nitride layer were observed over the room temperature implanted sample, however the 473 K implanted sample was relatively intact. The deteriorated corrosion resistance of the 673 K and 873 K samples was attributed to the non-uniformity of the surface and phase transition from α to β-Ti, respectively.

For the 473 K implanted sample as a selected implantation temperature, the enhanced corrosion resistance mechanism was investigated more accurately. The surface layer of 473 K implanted sample was studied by a Multi-Beam Focused Ion Beam-Scanning Electron Microscope (FIB-SEM) and was compared with an unimplanted and a 300 K implanted sample. The cross section of 473 K implanted sample was studied using FIB method to study the distribution of nitrogen atoms by EDS mapping technique. The depth profiles of the nitrogen atoms in the implanted samples were also obtained from EDS analysis. Surface feature and roughness of samples were studied by atomic force microscopy (AFM). According to the AFM results, the surface of 473 K implanted sample with uniformly distributed nano-scaled islands, showed a higher roughness value compared to the 300 K implanted one and was predicted to have more compatibility with body tissues. Electrochemical behavior of unimplanted, 300 K and 473 K implanted samples was studied using impedance spectroscopy methods in the Ringer’s solution as a simulated body fluid. The mechanism of the corrosion resistance improvement at high temperature implanted sample was developed according to the impedance spectroscopy results.

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1. Introduction

Titanium (Ti) and its alloys owing to their biocompatibility, ability to withstand attacks from body fluids, staying inert in the human body and staying strong and flexible during usage are considered as one of the most useful materials in medical applications [1]. Applying an oxide or nitride layer over Ti is one of the most efficient methods to enhance its corrosion resistance and erosion resistance [2]. Titanium nitride, having a hardness equivalent to the sapphire and carborundum (9.0 on the Mohs scale) [3], has been frequently used as a coating on metals to improve their surface properties. Titanium nitride is chemically stable at room temperature and its oxidation occurs above 1073 K [4]. Exceptional hardness, high electrical conductance, low coefficient of friction, high wear resistance and high melting point are some of its outstanding properties [5,6]. Titanium nitride as a non-toxic coating has an appropriate compatibility with human body which has made it a good candidate for coating in medical implants (e.g. joint connectors) [7].

Physical vapor deposition (e.g. reactive sputtering using radio frequency) [8,9], chemical vapor deposition [10,11], plasma nitriding [12, 13] and ion implantation [14,15] are some of the most frequently used methods for fabrication of titanium nitride thin films. Among these methods, the ion implantation is strongly preferred due to several advantages. The implanted layer has an excellent adhesion, the concentration and depth distribution of ions are easily controllable and solid solubility limits can be exceeded. Furthermore, the implantation of
nitrogen ions on Ti surface leads to an improved passivity and corrosion resistance. This is due to the fact that the formation of TiN and Ti₂N phases suppresses the migration of metal (Ti) ions and stabilizes the growth of TiO₂ layer on the surface [16].

To date the effect of various parameters such as nitrogen ion dose, implantation time and implantation energy on the surface properties of Ti substrate has been studied [17–21]. According to the literature, there is still a lack of comprehensive investigation about the mechanism of enhanced corrosion resistance and surface characteristics of high temperature implanted samples. Through ion implantation, the ions penetrating the substrate create a huge amount of displacements in the target atoms. Both of the ions and dislodged atoms can continue displacing and cause further damage. The energy spreads over many moving particles and eventually the energy per particle becomes too small and the cascade phenomenon stops. Therefore, after an ion implantation process, a crystalline surface transforms into a highly disordered structure. Hence, a subsequent activation-annealing process is required for recovering the substrate crystalline state; nevertheless, a great portion of defects will remain unaffected even after extensive heat treatments. On the contrary, by heating the target using a heating system during implantation, the competing process of self-annealing can occur to repair some or all of the damages as they are generated. Indeed, elevated temperature ion implantation is applied as a method for maintaining the crystalline structure after ion implantation [22]. In addition, the implantation of ions at high temperatures activates the diffusion mechanisms conducted by radiation-accelerated diffusion accompanied with precipitation of the implanted ions on dislocations [22]. Furthermore, the formation of a uniform and strength nitride layer increases the corrosion resistance of the high temperature implanted samples. A limited number of studies have been carried out on the effect of high-temperature ion implantation on the surface properties of the alloys and almost all of them have confirmed that, for a given dose of implantation, the relative defect concentration decreases with increasing the implantation temperature due to the enhanced ion diffusion and improvement of implantation efficiency [23,24].

In this study, the effect of different applied temperatures during ion implantation process on the surface properties and corrosion behavior of medical grade Ti was studied. Furthermore, the best temperature for the implantation was optimized for medical grade Ti and the mechanism in which the corrosion resistance increases was developed.

2. Experimental

2.1. Nitrogen ion implantation

The medical grade Ti was used as ion implantation substrate. Prior to the ion implantation process, the cylindrical samples (2 cm in diameter) were mechanically polished on silicon carbide abrasive papers (up to 4000 grit) followed by a final polishing step with a colloidal silica suspension (particle size of 50 nm) and ultrasonically cleaning in acetone. The ion implantations were carried out in a metal vapor vacuum arc (MEVVA) ion implanter with sample processing chamber fabricated from 316 stainless steel and internal diameter of 480 mm. The power supply of the implanter facility is powered from the 220 V mains by means of a 0–220 V, 20 A variable autotransformer working at voltages up to 100 kV above ground. All ion implantations started at constant vacuum condition of ~3.4 × 10⁻³ Pa. After the introduction of the nitrogen gas into the implantation chamber, the pressure was increased up to ~1.4 × 10⁻² Pa. The nitrogen ion dose of 2.1 × 10¹⁸ ion cm⁻² with an average energy of 80 keV was used for 30 min. For implantation at elevated temperature, the Ti substrate was heated up to the 473 K, 673 K and 873 K. In order to maintain the temperature constant during the implantation, the temperature of the substrate at the bottom side was continuously monitored with a K type thermocouple. For the sample implanted at room temperature, no external heating was applied. Various Ti samples were implanted at room temperature and higher temperatures to make sure the results are enough accurate and reliable.

2.2. Ion implantation temperature optimization

Phase characterization of the nitrogen ion implanted surfaces was carried out using a grazing incidence X-ray diffractometer (GI-XRD, Philips X’pert MPD, Netherlands) equipped with a Cu Kα radiation source working at 40 kV and 40 mA in a glancing geometry (incidence angle fixed at 1°). Primary corrosion behavior investigations were carried out using potentiodynamic polarization tests. All electrochemical experiments were performed in a three-electrode glass cell at room temperature using Autolab (PGSTAT-101, Netherlands) potentiostat/galvanostat analyzer. A saturated calomel electrode (SCE; Ag/AgCl + 0.197 V vs. SHE) and a platinum foil were used as the reference and counter electrodes, respectively. The electrochemical tests were conducted in the Ringer’s solution (0.1% potassium chloride, 0.7% sodium chloride, 0.1% calcium chloride, 0.1% sodium bicarbonate and 99% water) as a simulated body fluid. Each sample was immersed in the solution for 40 min in order to achieve the stable open-circuit potential (OCP). During the polarization test, the anodic and cathodic polarization curves were recorded by conducting scans at a rate of 1 mV s⁻¹ starting from 0.5 V to 1.0 V (vs. SCE). The surface of the samples after the corrosion tests were studied by a field emission scanning electron microscope (FE-SEM; Tescan, Czech Republic) and were compared with the SEM images before corrosion.

2.3. Mechanism of enhanced corrosion resistance in high temperature implantation

Surface features of 300 K and 473 K implanted samples were observed by a MultiBeam Focused Ion Beam-Scanning Electron Microscope (FIB-SEM, JEOL JIB–4501, Japan) after implantation. Furthermore, the cross section of the implanted samples was channeled using FIB and the distribution of the nitrogen atoms was observed using EDS mapping technique. The depth profiles of the implanted samples were also obtained from EDS analysis. The effect of ion implantation on the surface roughness and morphology of the samples was studied using an atomic force microscope (AFM, Nanoscope III, Multimode, Bruker, USA) with a maximum resolution of 20 Å (X-Y resolution). Electrochemical impedance spectroscopy (EIS) methods were carried out for a precise corrosion behavior characterization. The EIS experiments were also performed at the same condition of potentiodynamic polarization tests. An excitation signal sinusoidal potential of 10 mV through a frequency range from 10 kHz down to 100 MHz was used for EIS tests. The impedance diagrams were recorded at the steady OCP and corresponding results were analyzed by ZView 3.3 software (Scribner Associates Inc.).

3. Results and discussions

3.1. Ion implantation temperature optimization

The GI-XRD patterns of the samples are represented in Fig. 1 and different phases have been indexed on the patterns. The diffraction peaks in the GI-XRD pattern of the unimplanted sample are attributed to the hexagonal close-packed (HCP) Ti. After nitrogen ion implantation at 300 K, some new peaks have appeared which can be ascribed to the formation of the face centered cubic (FCC) nitride phases (such as TiN and Ti₃N). Schmidt et al. [25] showed that the implantation of nitrogen ions on the Ti–6Al–4V alloy stabilizes the α-Ti phase and when the solid solubility is surpassed, forms compounds with varying compositions and stoichiometries. The precipitates of sub-stoichiometric titanium nitride phases form a continuous and highly nitrogen-enriched layer over the Ti substrate. There are two dominant processes expected to occur during the implantation of nitrogen ions on Ti [26]. One is the two-stage
transformation of Ti–TiN–Ti2N, in which the conversion of surface layer of Ti to TiN happens by reordering of the stacking sequences from ABAB, in the HCP structure to the ABCABC in the FCC structure of TiN. During the first stage, the nitrogen ions arbitrarily occupy the octahedral interstitial sites. The next step is the transformation of TiN to Ti2N in which the nitrogen atoms rearrange inside the octahedral sites. The second prevailing process is the direct transformation of Ti to TiN. In this process the HCP structure of the Ti transforms to the tetragonal structure of the Ti2N in which, the nitrogen atoms stay in distorted octahedral interstitials. According to the GI-XRD patterns, it is obvious that in 473 K implanted sample, the nitride peaks are more intense and some new Ti2N peaks appeared. This observation is attributed to the enhanced diffusion of nitrogen ions into the Ti surface during implantation at high temperature. TiN is the most favorable phase in low temperature implantation while at high temperature, both TiN and Ti2N phases are likely to form. This phenomenon can be explained by different activation energies in the formation processes of TiN and Ti2N [27,28]. The GI-XRD of 673 K implanted sample is almost similar to the 473 K implanted one; however, it shows higher intensity of Ti2N phase, which is a favorable phase at higher temperatures. At 873 K, Ti specimen shows the presence of β phase in addition to the α phase in the surface. The existence of the β phase at this sample reveals that the temperature of Ti substrate under ion bombardment has exceeded the beta transformation temperature which is between 700 °C and 800 °C. The formation of β-Ti with a lamellar structure increases the surface roughness, which creates the preferred regions for corrosion initiation [29].

Regarding Fig. 1, it is obvious that the Bragg peaks of GI-XRD pattern of high temperature implanted sample are shifted to the lower values, which denotes the fact that the lattice parameters of this sample have been increased compared to the low temperature implanted sample [30]. Additionally, the higher intensity of nitride phases in the GI-XRD pattern of high temperature implanted sample might be attributed to the embedding of more nitrogen ions within the Ti structure. Indeed, at higher temperature implantation process, both of the ballistic and diffusion modes for entrance of nitrogen to the Ti structure become activated. This phenomenon leads to the accommodation of more nitrogen ions within the Ti lattice and the higher concentration of nitrogen ions in the lattice of Ti favors more precipitation of nitride phases.

Investigation of the nitride phase formation during ion implantation process has a particular importance from the thermodynamic point of view. However, thermodynamic measurement of the Ti2N phase formation by reactions like Ti + TiN = Ti2N is a difficult issue. That is because, the thermodynamic data about the nitride phase formation at different temperatures are limited. For instance, for the case of Ti2N phase, just the molar enthalpy of formation at 298 K \( \Delta H^f(298 \text{ K})(\text{Ti}2\text{N}) = -95 \text{ kcal/mol} \) is available [31]. The molar entropy of different phases which are shown with general M2N chemical formula (M is considered as a metal) is about \( S^f(298 \text{ K})(\text{M}_2\text{N}) = -18.7 \text{ kcal/mol} \). Assuming these values for 300 K (which is near to 298 K), the molar Gibbs free energy for Ti2N formation at this temperature will be as following: 

\[
\Delta G^f(298 \text{ K})(\text{Ti}_2\text{N}) = \Delta H^f(298 \text{ K})(\text{Ti}_2\text{N}) - T \times \Delta S^f(298 \text{ K})(\text{Ti}_2\text{N}) = -95 \text{ kcal/mol} \].

Consequently, the molar Gibbs free energy for Ti + TiN = Ti2N reaction at 300 K can be calculated as: 

\[
\Delta G^f = \Delta G^f(298 \text{ K})(\text{Ti}_2\text{N}) - [\Delta G^f(298 \text{ K})(\text{TiN}) + \Delta G^f(298 \text{ K})(\text{Ti})] = -15.6 \text{ kcal/mol} \].

According to the thermodynamic, it can be concluded that the formation of Ti2N phase at 300 K and 473 K is possible but as the Gibbs free energy of the high temperature implanted sample is more negative compared to the low temperature implanted one, the possibility of Ti2N phase formation will be higher. The GI-XRD results (Fig. 1) also confirm this fact with higher intensity of Ti2N phase in high temperature implanted sample.

In order to compare and optimize the corrosion resistance of Ti samples implanted at different temperatures, potentiodynamic polarization tests were carried out. Fig. 2a shows the Tafel plots of different samples. The corrosion potential and current density \( i_{corr} \) changes versus implantation temperature obtained from Tafel plots are also demonstrated in Fig. 5b. According to Fig. 5b, although all of the implanted samples show higher amounts of corrosion potentials compared to the unimplanted Ti, there is a peak in 473 K implanted sample (0.3 V). The corrosion current density significantly decreases by implantation

![GI-XRD patterns](image-url)
after corrosion test, clearly indicates titanium nitride layer over the high temperature implanted sample. Furthermore, the thick and uniform titanium oxide and titanium nitride phases there is a drastic decrease in the corrosion resistance. The Tafel curves of the implanted samples also show a passivation behavior, which implies the formation of an oxide layer over the samples (Fig. 5a). Therefore, the bombardment of high-energy ions can create more damages on the surface and subsequently more sensitive regions to the corrosion attack (Fig. 3g). These factors collectively lead to the lower corrosion resistance in the 673 K implanted sample.

In the SEM image of 673 K implanted sample a different surface feature to the decreased corrosion resistance of Ti [33,34]. Such imperfections are more prone to appear in the non-uniformly implanted samples as low temperature implanted one (at 300 K) and implanted samples at higher temperatures with high-energy rough regions and cracks on the surface. The SEM micrographs of samples before and after corrosion tests are compared in Fig. 3. The Fig. 3a represents the surface of Ti substrate without implantation. Several detached corrosion products from the surface of unimplanted Ti are observed in Fig. 3b. Through the ion implantation process, the intense ion bombardment creates several defects over the nitride layer such as cracks and holes in the interface of grown nitride regions. These vulnerable sites act as narrow channels, which transfer the corrosive solution to the Ti substrate. Subsequently the micro-galvanic cells form between the nitride layer and Ti substrate.

Since the nitride layer is nobler than Ti substrate against the electrochemical attacks, the nitride layer acts as cathode and the Ti substrate as anode. Too small anode area compared to the cathode area leads to a drastic galvanic corrosion phenomenon in the Ti substrate. A corrosive anion, like chloride enters through the tiny channels in to the Ti–titanium nitride interface. The anodic corrosion expands in a wide area in the interface between coating and substrate and creates several deep crevices on the Ti. This phenomenon finally leads to the separation of some fragments of nitride layer. Delamination and detachment of nitride layer significantly occurred on the low temperature implanted sample (Fig. 3d). The micro-galvanic corrosion is almost dominated in the TiN compound but occurs slightly in the Ti_2N phase [35]. Regarding the XRD results (Fig. 1), the Ti_2N phase is prevailing in the 473 K implanted sample and as a result, the galvanic attack has been extremely limited in this sample. Furthermore, the thick and uniform titanium oxide and titanium nitride layer over the high temperature implanted sample (Fig. 3e) significantly protect it in the Ringer’s solution. The undamaged surface of 473 K implanted sample in Fig. 3f SEM image of 473 K sample after corrosion test, clearly confirms this concept (Fig. 3f). As the implantation temperature increases to the 673 K, the precipitation of nitride phases on the surface increases which can increase the surface roughness and high energy zones (Fig. 3g). Furthermore, annealing the surface under and an applied high temperature decreases its strength. At a lower strength, the bombardment of high-energy ions can create more damages on the surface and subsequently more sensitive regions to the corrosion attack (Fig. 3g). These factors collectively lead to the lower corrosion resistance in the 673 K implanted sample.

In the SEM image of 873 K implanted sample a different surface feature attributed to the phase transition is observed (Fig. 3i). This lamellar structure is related to the β-Ti phase which, can be created at the temperatures higher than 973 °C [29]. Although the applied temperature to this sample was set to the 873 K, but it can be interpreted that the high energy ion bombardments also contribute to the further temperature increase, which leads to the phase transition. In 873 K implanted sample, with a bimodal structure consisted of both α (HCP) and β (BCC) phases, owing to the formation of a galvanic cell between two phases there is a drastic decrease in the corrosion resistance. The Tafel curves of the implanted samples also show a passivation behavior, which implies the formation of an oxide layer over the samples (Fig. 5a).

According to the potentiodynamic polarization results, the 473 K implanted sample, demonstrates the highest corrosion resistance in the Ringer’s solution compared to the other samples. Therefore, the behavior of this sample was studied in terms of corrosion resistance enhancement mechanism in an optimum high temperature ion implanted sample. The analysis was also compared with the unimplanted and 300 K implanted samples.

Fig. 3. SEM images of: unimplanted sample (a) before and (b) after corrosion, implanted sample at 300 K (c) before and (d) after corrosion, implanted sample at 473 K (e) before and (f) after corrosion, implanted sample at 673 K (g) before and (h) after corrosion and implanted sample at 873 K (i) before and (j) after corrosion.
3.2. Mechanism of enhanced corrosion resistance in high temperature implantation

Fig. 4 represents the FIB-SEM images of the surface and cross section of the implanted samples at 300 K and 473 K immediately after implantation. Fig. 4a demonstrates the nanostructured surface of the 300 K (low temperature) implanted sample and Fig. 4b shows the 473 K (high temperature) implanted sample. In both of the surfaces, several tiny and white nanoparticles are observed. The particles existing on the surface of high temperature implanted sample are bigger than that of low temperature implanted one and well distributed over the surface. This phenomenon might be a consequence of high temperature applied during implantation process which favors more precipitation and growth of nitride compounds on the surface either by increasing the absorption of nitride ions to the surface or by diffusion of nitrogen atoms from depth to the surface. In order to study the cross section of the samples in terms of distribution of the nitrogen atoms through implantation layer, a tiny region on the surface was channeled using FIB (Fig. 4c) and then was observed by SEM. Fig. 4d and e shows the cross sectional view of the implanted samples at low and high temperatures, respectively. A special morphology can be distinguished in the SEM images about several nanometers underneath the surface for both of the samples. A red arrow in Fig. 4d has marked the start point of this morphology; a region consisting of several small circle regions. This feature might be attributed to the higher hardness of this region compared to the upper parts, which have more resistance against ion beam milling during channeling by FIB. This fact means that more nitride phases are located in this region underneath the surface, which is the case for ion implanted samples. In order to prove this concept, EDS mapping was employed to illustrate the distribution of the nitrogen atoms in this regions. Fig. 4f and g presents the EDS maps of the Ti and N of the low temperature samples, respectively and Fig. 4h and i demonstrates the distribution of EDS maps of high temperature implanted sample. The start point of highly concentrated N regions in the maps is in a good accordance with the start point of circle morphologies in the SEM images (Fig. 4d and e). The highly reached area of N atoms has been started very closer to the surface compared to the low temperature implanted sample. The distribution of the N atoms is also far more uniform than the low temperature implanted one.

The depth profiles of the implanted samples near the surface are also obtained by EDS analysis within a 1.5 μm long span from surface to the

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Fig. 4. (a) FIB-SEM image of low temperature (300 K) implanted sample, (b) FIB-SEM image of high temperature (473 K) implanted sample, (c) FIB-SEM image of a typical channeled part on the surface of low temperature implanted sample, (d) FIB-SEM image from the cross section of low temperature implanted sample, (e) FIB-SEM image from the cross section of high temperature implanted sample, (f and g) EDS mapping of nitrogen and titanium atoms, respectively, corresponding to the Fig. 2d and (h and i) EDS mapping of nitrogen and titanium atoms, respectively, corresponding to the Fig. 2e.
The thickness of implanted layer is about 800 nm for low temperature implanted sample and around 1.2 μm for high temperature implanted one. There is a peak in both of the samples for the presence of nitrogen atoms near the surface in the layer down to the depth of about 100 nm and 220 nm for high and low temperature implanted samples, respectively. The depth profile of the sample implanted at 473 K, demonstrates a wide distribution of the nitrogen atoms through implanted layer and there is no significantly sharp peak in its profile compared to the low temperature implanted sample and is near to the surface. This observation can be interpreted as a direct result of temperature during ion implantation, which activates the diffusion processes, and the nitrogen atoms move towards the surface and also towards the depth. Thus, the experimental results clearly show that the ion implantation treatment at higher temperature can effectively regulate the gradient of nitrogen concentration in the implanted layer. It thus follows that this treatment could improve the mechanical properties of the surface in terms of hardness and consequently the biocompatibility of Ti.

The influence of surface roughness on the cellular response of the body implants has been investigated limitedly [36–38]. However, it was found that the surface roughness of the implant affects the growth of bone cells [39]. Several in vivo studies have proved that, increasing of effective surface area of implants enhances their contact with bone cells [40–43]. Li et al. [44] studied the effect of surface roughness of hydroxyapatite on ROS 17/2.8 cell response, in terms of cell attachment and proliferation. The rough surface demonstrated an enhanced cell attachment and proliferation, which was attributed to the more availability of the medium and serum proteins through the grooves underneath the attached cells. Considering the scale of the surface features, the surface roughness of implants is divided into macro, micro, and nano-sized topologies [45,46]. The nano-sized topography containing irregularities less than 100 nm are believed to mimic better the nano-architecture of the natural tissues [47].

In this study, the effect of nitrogen ion implantation on the surface topology of Ti was studied using an atomic force microscope (AFM) (Fig. 6). The 3D-AFM images of samples implanted at 300 K and 473 K (Fig. 6b and c respectively) demonstrate different surface topologies. The high temperature implanted sample reveals a surface consisted of several small islands, uniformly distributed over the surface (Fig. 6c). However, the low temperature implanted sample represents a partly irregular surface consisted of some islands within a smooth area (Fig. 6b). Thus, it is observed that applying a high temperature during ion implantation process alters the growth dynamics of nitride layer by increasing the lattice parameter of Ti and enhancing its ion adsorption capacity. Consequently, the ion bombardment leads to an effective adsorption of ions and then precipitation and growth of new nitride phases on the preferred areas. The newly grown elevated points prevent ion collision to the low-lying surface regions, which cause the well-known “shadow” phenomenon on these areas. The elastic collisions of the incident ions cause erosion in the sharper sites of the surface and the detached particles drop to the shadow places. Eventually a uniform nitride coating consisted of relatively blunted-tip islands, which are homogeneously distributed on the surface, is formed. The aforementioned process occurs partly for the case of low temperature implanted sample because of its lower ion adsorption capability. Therefore, non-uniform distributions of nitride islands are formed on the surface of this sample. The existence of small islands over the surface of implanted samples, determines the amount of their roughness. The root mean square roughness (RMS) and mean roughness (Ra) values of the samples obtained from 3D-AFM images are given in Table 1. The RMS and Ra values are calculated as 59.005 nm and 45.54 nm for high temperature implanted sample respectively, which are much higher than that of low temperature implanted sample (Table 1). As previously mentioned, the nano-scaled roughness gives rise to the best adapting possibility for the implants in the body’s environment. Additionally, the higher surface roughness (at the nanoscale) leads to the higher contact capability between implants and tissue cells. Regarding the nanoscale range of the roughness values of implanted samples, it is concluded that, the high temperature implanted sample with a higher roughness can perform better in the body’s environment.

The EIS results of samples in the Ringer’s solution are represented in Fig. 7. The impedance characteristics of samples allow determining the physicochemical properties of the sample-corrosion medium interface by means of fitting them with equivalent electrical circuits. Fig. 7a illustrates the Nyquist plots of samples. As it is well known, the size of the Nyquist semicircle determines the amount of electrochemical impedance and the larger value of impedance, suggests a higher corrosion resistance. The high temperature implanted sample with the largest Nyquist diagram, demonstrates the highest corrosion resistance in the Ringer’s solution. The Nyquist diagrams demonstrate one depressed semicircle, which is a result of merging two separate semicircles (two corrosion processes). This fact is observed more obviously in the Bode plots as two time constant diagrams (Fig. 7b and c). The specific shape of the Bode phase angle plots signifies the passivation phenomenon in the samples (Fig. 7b). The high temperature implanted sample shows the highest phase angle degree of 91° and 86° in high and low frequency
ranges, respectively. Additionally, this sample stays passive over a wide range of frequencies (0.08–164 Hz), compared to low temperature implanted sample. The phase angle and its frequency range are smaller for the case of low temperature implanted sample, but keeps its passive state. The Bode–module plots show a descending trend with two slope changes, denoting the activation of two distinct corrosion phenomena at high and low frequencies (Fig. 7c). The highest impedance value (3.3 MΩ cm²) is related to the high temperature implanted sample referring to its enhanced corrosion resistance against the penetration of attractive active species such as chloride ions. The impedance in the low frequency range represents an inductive behavior, which originates from the penetration of corrosive solution into the TiN layer-Ti substrate interface via surface holes. The high frequency region shows an ohmic (capacitance) behavior and a phase shift of about five occurs. The phase shift starts increasing and then decreases in the medium frequency range, which is an indication of the double layer capacity formation between the substrate and the solution. Accordingly, the surface of implanted samples can be divided into the two sub-interfaces: corrosive solution-TiN and corrosive solution-Ti substrate. This type of impedance data is best modeled using an equivalent circuit shown in Fig. 7d. The equivalent circuit is comprised of the solution resistance (Rₛ), the dielectric property of the TiN layer at high frequencies, consisted of a constant phase element (CPE₁) and resistance of nitride layer (R₁) and the elements related to the TiN-Ti substrate interface at low frequency range, which are CPE₂ and the polarization charge transfer resistance (R₂). The CPE parameter is usually used instead of a capacitance to account for the non-ideal capacitance response due to the almost complete absence of pure capacitance in the real electrochemical process. The increase in the CPE values, denotes the decrease in the thickness of the protective layer and subsequently the decrease in the corrosion resistance of the surface [48,49]. Table 2 summarizes the EIS parameters obtained from the fitting of EIS results to the equivalent circuit shown in Fig. 7d. According to the Table 2, the high temperature implanted sample has a lower CPE₁ value (7.5 × 10⁻⁶ F cm⁻²) compared to the low temperature implanted one (5.2 × 10⁻⁵ F cm⁻²) indicating the formation of a thicker protective layer over it. The higher R₁ value in the high temperature implanted sample (41,750 Ω cm²) shows the enhanced protective role of its nitride coating compared to the low temperature implanted one. The CPE₂ is also lower (5.9 × 10⁻⁶ F cm⁻²) for the case of high temperature implanted sample. There is a higher corrosion resistance in the interface between TiN layer and Ti substrate in the high temperature implanted sample with a higher R₂ value (39,824 Ω cm²) which can be attributed to the stabilization of a passive titanium oxide
film in this region. Areas et al. [17] observed that implantation of pure Ti at 25 keV, with an implantation dose of 3 × 10¹⁷ Ti cm⁻², has improved its corrosion behavior in HBSS solution. They attributed this improvement to the formation of a homogeneous distribution of small precipitates of TiN and Ti₃N, which screens underlying Ti atoms, thus avoiding their migration and stabilizing the growth of a passive oxide film. It is well known that a great corrosion resistance of Ti is due to a protective and self-adherent oxide film of a thickness of 2–6 nm formed on its surface, which is mainly composed of titanium dioxide (TiO₂) [32, 50]. The formation of a uniform oxide layer during corrosion process of Ti in water-based solutions, which inhibits the dissolution of Ti, is according to the following reaction:

\[
\text{Ti} + 2\text{H}_2\text{O} + \text{TiO}_2 + 4\text{H}^+ + 4\text{e}^- \tag{1}
\]

The Ti₂O₃ may also be formed [25] but is unstable and rapidly transforms to the TiO₂ when it comes in contact with water:

\[
\text{Ti}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow 2\text{TiO}_2 + 2\text{H}^+ + 2\text{e}^- \tag{2}
\]

Thus, the superior corrosion resistance of high temperature implanted sample is not only attributed to the thicker nitride layer, but also to the formation of an effective TiO₂ layer in the Ti–TiN interface.

4. Conclusion

In this study, the effect of different nitrogen ion implantation temperatures on the corrosion resistance of the medical grade Ti was investigated. The GI-XRD results showed the formation of TiN and Ti₃N nitride phases over the samples. The optimum temperature for high temperature implantation was found to be 473 K based on electrochemical polarization results. The micro-galvanic corrosion was extremely high in the high temperature implanted sample through a highly uniform protective layer consisted of TiN and Ti₃N phases and a passive layer. The SEM image of low temperature implanted sample exhibited delamination and separation of nitride particles as a result of micro-galvanic corrosion on the sample. The studies on the cross-section of the high temperature implanted sample showed a better distribution of nitrogen atoms in the implantation layer. An increase in the surface roughness of high temperature implanted material was observed in 3D-AM images. The mechanism of corrosion resistance enhancement was developed according to the EIS studies and surface characterizations. Based on the EIS results, it was concluded that the enhanced corrosion resistance of the implanted samples is attributed to the nitride layer along with an underlying oxide film.

References


