Mechanical properties and corrosion behavior of the nitriding surface layer of Ti–6Al–7Nb using large pulsed electron beam (LPEB)

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Abstract

Large pulsed electron beam (LPEB) irradiation was used as a single surface finishing process for Ti–Al–Nb. Nitrogen plasma gas and cathodic apparatus have been adopted to induce nitriding effect of Ti–6Al–7Nb during the electron beam irradiation. The atomic concentration of nitrogen atoms at the re-solidified layer could be achieved up to ~18% by LPEB nitriding. Nano-hardness in the re-solidified layer was improved by ~75% following the irradiation process, as a result of a phase transformation and the formation of TiN. The re-solidified layer induced by LPEB nitriding, consisted of TiN, TiO2, and TiO2N, indicated significantly modified corrosion resistance showing a nobler corrosion potential, decreased corrosion current density, and improved charge transfer resistance. The increasing fraction of TiN at the re-solidified layer, induced by LPEB nitriding, was suggested as being responsible for remarkable improvement of mechanical properties and corrosion resistance, embedding uniformly noble and stable characteristics at the top surface. The corrosion-resistant surface layer with superior mechanical properties on Ti–6Al–7Nb has been successfully demonstrated by LPEB nitriding technique.

Keywords: Titanium, Nitriding, Large pulsed electron beam, Corrosion, Hardening

1. Introduction

In recent decades, titanium and titanium alloys have been studied extensively because of their high weight-to-strength ratio, good corrosion resistance, and biocompatible behavior [1,2]. According to previous research, a naturally formed thin oxide layer (TiO2) protects the basic material from corrosion by acting as a passive film [3]. Especially, Ti–6Al–4V (Grade 5) alloy has been used most commonly for orthopedic implants because the combination of α and β phase structures makes an appropriate surface hardness and elastic modulus [4]. Due to the galvanic couple between the α and β phases, however, it has been demonstrated that the corrosion resistance is decreased versus single-phase titanium alloys [5,6]. Additionally, the β-stabilizer, vanadium (V), of Ti–6Al–4V, can form a cytotoxic agent (V2O5) in bodily fluids [7,8]. For these reasons, since the 1980s, other α+β phase and β-phase titanium alloys have been actively developed. One of the best possible substitutes for Grade 5 is Ti–6Al–7Nb alloy (Protasul-100), for which the corrosion resistance has been reported to be greatly superior and the β-stabilizer, niobium (Nb), has been suggested to be non-toxic in bodily fluids, unlike V [9,10].

Nevertheless, Ti–6Al–7Nb has some fundamental problems due to its readily corrupted thin oxide layer (1–4 nm) with a poor galvanic couple. As a result, additional corrosion-resistant coatings are necessary, such as anodization and electrochemical deposition [11–14]. The anodization method is the most frequently used surface treatment of titanium and its alloys, and it has been reported that anodization of titanium alloys led improved corrosion resistance with a nobler TiO2 [11,14,15]. The deposition of Ca–P improves the corrosion resistance and biocompatibility [16]. However, as Song [17] and Gu et al. [18] referred, mechanical properties of corrosion-resistant films have been one of the most important concerns on electrochemically stable surface layer. As corrosion resistance of metallic materials is related to chemical stability of oxide layers and materials themselves, mechanical properties of surface films are generally regarded independently [18]. In this context, there is a clear and strong need to develop surface treatment that can induce corrosion-resistant surface layer with superior mechanical properties. Recently, nitriding has received wide attention because a nitrogen-implanted surface has been found to be chemically inert and thermally stable [19,20]. Remarkably, many studies have supported that titanium nitride (TiN), used as a hard ceramic coating material, has nobler corrosion resistance with
Nitriding methods to date can be classified into three different coating techniques: gas nitriding, plasma nitriding, and laser gas nitriding (LGN). Gas nitriding, a chemical vapor deposition (CVD) method, implants nitrogen ions using the catalytic decomposition of ammonia gas (NH₃) [24,25]. Although it is a cost effective method, it has been reported that it should be avoided for biomaterials because of the toxicity of NH₃ [26]. Plasma nitriding, such as plasma-assisted ion implantation, direct current (DC) magnetron sputtering, and focused ion beam implantation, has been used extensively industrially [27,28]. However, some disadvantages have been reported that the coating film can readily become delaminated from the substrate due to its brittleness, and surface defects, such as micro-cracks, pores, and cavities, are hardly removed [29]. Finally, laser gas nitriding is a direct energy method that uses a laser beam for the melted substrate to react with nitrogen (N₂) gas. Although, this method enables relatively rapid processing at atmospheric pressure, LGN also causes coating cracks and it is inefficient for complex shapes and large areas [30,31]. To summarize the nitriding techniques, fabricating a uniformly stable TiN layer without defects and inhibition of delamination are important to increase corrosion resistance.

Large pulsed electron beam (LPEB) treatment has been introduced and modified as an innovative finishing process for surface treatment and polishing in a single step [32]. Surface finishing using electron beam irradiation has been widely adopted for magnesium- and iron-based alloys [33–35]. According to previous research with LPEB irradiation on Ti–6Al–7Nb, it was found that corrosion resistance and nano-hardness were improved by LPEB treatment [36]. However, nitrogen implantation was obviously small on the re-solidified. Thus, the possibility of titanium nitriding using LPEB has not yet been reported.

In the present study, we attempted to develop a crack-less nitriding process by combining a nitrogen ion implantation system using LPEB and a cathodic process to improve the corrosion characteristics and nano-hardness of Ti–6Al–7Nb. LPEB irradiation was performed using argon (Ar) and N₂ plasma gas and the results of nitriding effects were evaluated in terms of surface morphology, microstructure, nano-hardness, wear resistance, and corrosion resistance.

2. Experimental

2.1. Preparation of samples

A 25-mm diameter and 5-mm-thick Ti–6Al–7Nb (supplied by Changsheng Titanium Co., Ltd.) samples were prepared by cutting extruded bar of the alloy. The samples were ground and polished from 180– to a 1200-grit finish (Allied High Tech Products). After LPEB irradiations, the samples were cut in two cross-sectional parts using a wire electric discharge machine (SL400GG, Sodick). Then they were mounted and polished up to 4000-grit SiC papers and 1-μm diameter diamond suspension (#90-33015, Applied High Tech Products). Finally, they were etched with Kroll’s reagent (H₂O:HF:HNO₃ = 10:3:6 v/v%) to reveal grain structures at LPEB-irradiated regions.

2.2. Large pulsed electron beam and cathodic apparatus

The LPEB (PF32B, Sodick), shown in Fig. 1, consisted of four main parts: solenoid, electron acceleration system, plasma source, and a two-dimensional (2D) translation stage in a vacuum chamber [32]. A standard set-up for LPEB irradiation generally uses argon (Ar) gas as a plasma source. For this study, the plasma source was changed from Ar to nitrogen (N₂) for LPEB nitriding process, which represents the LPEB irradiation using N₂ plasma gas. Furthermore, a negative DC bias cathodic apparatus was attached to the general experimental set-up to attract N₂ plasma from environment to the substrates. The Ti–6Al–7Nb sample was connected to a copper electrode to apply a negative DC bias as summarized in Fig. 1. The irradiation frequency of LPEB was 0.1 Hz with 2 μs of pulse duration and 10 s of dwell time. Although the total processing time is related with the number of irradiation pulses, it is relatively rapid process that the processing time is mostly less than 5 min per sample including vacuuming time due to the short pulse duration and large beam size with 60 mm in diameter. The detailed parameters of LPEB irradiation are summarized in Table 1.

2.3. Microstructures characterizations

Before and after LPEB irradiations, the microstructural changes of Ti–6Al–7Nb samples were evaluated in terms of each combination of parameters via field emission scanning electron microscopy (SEM). The microstructural analyses on the surface and cross-section after LPEB irradiations were performed using a FEI Nano 230 Nova NanoSEM equipped with energy dispersive X-ray spectrometer (EDS).

Surface roughness (Rₛ) variations were observed following LPEB irradiations using three-dimensional white-interferometer (NV-3000, NanoSystem). The measurements were carried out five times

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acceleration voltage</td>
<td>30 kV</td>
</tr>
<tr>
<td>Energy density</td>
<td>10 J/cm²</td>
</tr>
<tr>
<td>Plasma gas pressure (Ar and N₂)</td>
<td>0.05 Pa</td>
</tr>
<tr>
<td>Pulse duration</td>
<td>2 μs</td>
</tr>
<tr>
<td>Irradiation frequency</td>
<td>0.1 Hz</td>
</tr>
<tr>
<td>Negative DC bias</td>
<td>0 to – 1000 V</td>
</tr>
<tr>
<td>Number of pulses</td>
<td>0 to 200 pulses</td>
</tr>
</tbody>
</table>
at different regions on the same sample and \( R_a \) was averaged.

2.4. Phase analyses and chemical characterizations

The EDS analyses of elements, including C, N, O, and Ti, on the top surface were carried out with a 20-kV acceleration voltage. Chemical compositions and states of LPEB-irradiated layer were analyzed by X-ray photoelectron spectroscopy (XPS) with a 90° takeoff angle and 0.45 eV energy step size. A spectroscopy of the elemental compositions were recorded by ESCALAB 250XI (Thermo Fisher Scientific) using Al-K\( \alpha \) radiation. Because the top surface of Ti–6Al–7Nb was possibly oxidized by exposure to atmospheric conditions after LPEB irradiations, nitriding effects of LPEB irradiations could not be exactly evaluated at the top surface. Therefore, not only the binding energies of the top surface but also those of 10-nm deep regions were detected by ion etching.

2.5. Mechanical properties characterization

Nanoindentation tests (NHT2, Anton Paar) were performed by a continuous stiffness measurement technique. A three-sided pyramidal Berkovich tip was used as an indentation tool. Nanoindentation was assessed at the top surface after LPEB irradiations to specify the nano-hardness along depth by increasing indentation load from 10 mN to 500 mN. A step increasing load was set to 10 mN and the maximum load at each step was sustained during 10 s to obtain steady-state nano-hardness.

2.6. Electrochemical measurements

A standard three-electrode electrochemical cell was designed and manufactured using polytetrafluoroethylene (PTFE, \( (C_2F_4)_n \)). A 1 cm\(^2\) circular hole at the PTFE cell facilitated to expose only LPEB-irradiated surface to an electrolyte and normalized evaluation of electrochemical performances. A coiled platinum counter electrode and a saturated calomel reference electrode (SCE, \( E_0 = 0.24 \) V vs. saturated hydrogen electrode) were used for potentiodynamic polarization tests, electrochemical impedance measurements, and chronocoulometry (CA) analyses. For all types of electrochemical measurements, 1 wt% sodium chloride (NaCl) aqueous solution was adopted as the electrolyte. The electrochemical tests were performed with multi-channel electrochemical instrument (IVIUMnSTAT, IVIUM Technologies) controlled by IVIUMsoft software.

Prior to testing, the substrate surfaces were exposed to the electrolyte for approximately 30 min to attain a steady-state open-circuit potential (OCP). Following stabilization, potentiodynamic polarization tests were carried out with a scan rate of 1 mV/s over a range of \(-500\) to \(+1000\) mV/SCE with respect to the OCP. The results of three independent polarization tests were obtained for samples treated by the same LPEB parameters, and the representative polarization curves were plotted. Polarization electrochemical parameters, including corrosion potential (\( E_{corr} \)), corrosion current density (\( i_{corr} \)), and cathodic and anodic Tafel slopes (\( \beta_c \) and \( \beta_a \)) were averaged from the three independent tests.

The electrochemical impedance spectroscopy (EIS) was obtained in the frequency range from 2500 Hz to 0.03 Hz with a 10 mV vs. OCP level of alternating current (AC) amplitude. The EIS data were investigated through Nyquist plots, Bode plots, and hypothetical impedance parameters specified from two-time-constant equivalent-circuit model.

The CA analyses were conducted to subsidiary compare the rate of corrosion progressed in a 1 wt% NaCl solution before and after LPEB irradiations with various irradiating conditions. A constant potential, \(+100\) mV/SCE, was applied to adopt the potential at surely active region of polarization. The tests were conducted using high-resolution electrochemical instrument (EZstat-Pro, NuVant Systems Inc.) with current density resolution of 3 nA/cm\(^2\). The data were transiently recorded every 100 ms during 30 min.

Fig. 2. Scanning electron microscopy (SEM) images on Ti–6Al–7Nb surfaces (a) before and after 10 pulses of LPEB irradiations with (b) 0 V-biased in Ar plasma gas, (c) 0 V-biased in N\(_2\) plasma gas, and (d) –100 V-biased in N\(_2\) plasma gas.
Fig. 3. (a, b, c, d) White-interference micrographs on the surface of Ti–6Al–7Nb after LPEB irradiations, and (e) a SEM image and EDS result near the crater-generated region corresponding to (d).

Fig. 4. Cross-sectional SEM images of LPEB-treated Ti–6Al–7Nb samples with (a) Ar plasma gas and a single pulse, (b) N2 plasma gas and a single pulse, (c) Ar plasma gas and 10 pulses, and (d) N2 plasma gas and 10 pulses.
3. Results and discussions

3.1. Surface morphology and phase analyses

Fig. 2 shows the SEM images and corresponding roughness at the surface following LPEB irradiation using Ar and N₂ plasma gas. The surface roughness (Rₐ) was reduced significantly following LPEB irradiation with both Ar and N₂ plasma gas. The lowest value of Rₐ was obtained from 10 pulses of LPEB irradiations without a negative DC bias; Rₐ was reduced from ~540 nm to ~90 nm on the LPEB irradiated surface both with Ar and N₂ plasma gas comparing to the bare surface. This may be attributable to surface dissolution by LPEB, which could melt the polishing mark and generate a phase transformation on the surface [37]. However, when applying a negative DC bias for the nitriding process, Rₐ on the surface was slightly larger than that on the surface with no DC bias because numerous crater-like defects were generated following LPEB irradiation as specified by white-interference micrographs in Fig. 3a-3d. Especially, with a negative DC bias larger than −100 V, the defects were formed frequently and their sizes were larger. The partial evaporation of non-metallic inclusions, such as manganese sulfide (MnS) and metal carbide, is well known to be the major reason for crater generation during the LPEB irradiation process [38]. However, in the case of Ti–6Al–7Nb, there are almost no non-metallic inclusions, suggesting that the mechanism of crater generation differ from iron-based alloys. Thus, SEM images and corresponding EDS analyses were performed to reveal the crater generation mechanism during the LPEB nitriding process (Fig. 3e). The EDS results indicated that small particles consisted of iron at the center of the craters. Thus, it can be concluded that the increasing density of craters with increasing negative DC bias resulted mainly from sputtering effects on the surface by generating a glow discharge of plasma ions remaining in the vacuum chamber. Thus, it is preferred that the DC bias level should not exceed −100 V, because this is relatively low compared with the threshold voltage.

Fig. 4 shows cross-sectional SEM images of Ti–6Al–7Nb alloys following LPEB irradiation with Ar and N₂ plasma gas. With a single pulse of LPEB irradiation, the depth of the re-solidified layer was 4.66 μm with Ar plasma gas; this decreased to 2.61 μm using N₂ plasma gas during LPEB irradiation. The depth of the re-solidified layer increased with more pulses; however, it did not vary markedly above 10 pulses. The depth of the re-solidified layer induced by LPEB irradiation was deeper with Ar (Fig. 4a and 4c) than N₂ plasma gas (Fig. 4b and 4d). This could be a result of a change in beam energy density transferred to the surface of the substrates. The beam energy induced from the electron gun is partially absorbed by plasma gas ionizing atoms. The ionization energy of each plasma source used in LPEB irradiation is expressed as:

\[ \text{Ar} + (1.520.6 \text{kJ/mol}) \rightarrow \text{Ar}^+ + e^- \]  
\[ \frac{1}{2} \text{N}_2 + (1.874.5 \text{kJ/mol}) \rightarrow \text{N}^+ + e^- \]

As shown in Eqs. (1) and (2), Ar plasma is induced simply, only consuming the ionized enthalpy of 1520.6 kJ/mol in a single ionization step. In contrast, N₂ plasma is generated in multiple steps to make the same number of electrons by consuming a total enthalpy of 1874.5 kJ/mol to break the powerful triple bond of the nitrogen molecule (472.5 kJ/mol) and to ionize (1402 kJ/mol). Thus, energy absorbed on the surface of substrates is relatively smaller with N₂ plasma gas, leading to a thinner depth of the re-solidified layer than with Ar.

3.2. Chemical component

In the case of nitriding processes, the fraction of nitrogen plays a major role in evaluating performance [31]. The EDS results which indicate variations in atomic concentrations following LPEB irradiation are summarized in Tables 2 and 3, in terms of the negative DC bias and number of pulses, respectively. Corresponding variations in nitrogen concentration are shown in Fig. 5. Compared with bare Ti–6Al–7Nb, the atomic concentration of nitrogen was increased slightly after LPEB irradiation with Ar plasma gas (Fig. 5a). This could be a result of the flushing gas, which was used to clean up the vacuum chamber between pulses [36]. Because nitrogen was used as the flushing gas during LPEB irradiation, some of the gas remained in the chamber, forming a small fraction of TiN at the re-solidified layer. By changing the plasma source for LPEB from Ar to N₂, it was possible to achieve a much higher fraction of nitrogen in the re-solidified layer. LPEB nitriding without a negative DC bias increased the nitrogen fraction, to 17.08 at.%, at the top surface. Moreover, the nitrogen fraction was increased further by applying a negative DC bias to the substrate. It was increased to over 18 at.% with a negative DC bias ranging from 0 to −1000 V. The optimized number of pulses in terms of nitrogen fraction was well matched to that of the re-solidified depth. The atomic concentration at the re-solidified layer was almost unaffected by increasing the number of pulses above 10 (Fig. 5b). The effect of negative DC bias was clear; the nitrogen fraction was increased with −100 V of bias compared with 0 V. However, no significant change in nitrogen fraction was observed with various DC biases above −100 V; all

<table>
<thead>
<tr>
<th>Type of plasma gas</th>
<th>Negative DC bias (V)</th>
<th>Pulses (shots)</th>
<th>Atomic concentration (at.%)</th>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Ti</td>
</tr>
<tr>
<td>N₂</td>
<td>−100</td>
<td>10</td>
<td>3.51 18.27 3.26 63.68</td>
</tr>
<tr>
<td>N₂</td>
<td>−100</td>
<td>20</td>
<td>5.31 17.80 3.84 61.53</td>
</tr>
<tr>
<td>N₂</td>
<td>−100</td>
<td>30</td>
<td>5.95 18.12 3.85 61.84</td>
</tr>
<tr>
<td>N₂</td>
<td>−100</td>
<td>50</td>
<td>4.87 17.96 3.21 63.46</td>
</tr>
<tr>
<td>N₂</td>
<td>−100</td>
<td>100</td>
<td>5.63 18.36 3.27 64.03</td>
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<tr>
<td>N₂</td>
<td>−100</td>
<td>200</td>
<td>7.07 17.43 3.93 63.02</td>
</tr>
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</table>

Table 2

Energy dispersive X-ray spectroscopy results of Ti–6Al–7Nb following LPEB irradiation with 10 pulses in terms of negative DC bias.

<table>
<thead>
<tr>
<th>Type of plasma gas</th>
<th>Negative DC bias (V)</th>
<th>Atomic concentration (at.%)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C  N  O  Ti</td>
</tr>
<tr>
<td>Untreated</td>
<td>0</td>
<td>9.86 3.23 13.92 55.77</td>
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<tr>
<td>Ar</td>
<td>0</td>
<td>5.42 5.87 8.69 63.48</td>
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<tr>
<td>N₂</td>
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<td>3.81 17.08 3.84 64.75</td>
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<tr>
<td>N₂</td>
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<td>3.51 18.27 3.26 63.68</td>
</tr>
<tr>
<td>N₂</td>
<td>−500</td>
<td>5.35 18.45 4.17 60.70</td>
</tr>
<tr>
<td>N₂</td>
<td>−1000</td>
<td>5.00 18.88 3.09 62.90</td>
</tr>
</tbody>
</table>

Table 3

Energy dispersive X-ray spectroscopy results of Ti–6Al–7Nb after LPEB irradiation as a function of the number of pulses.
substrates were similar, ~18.5 at.%. Thair et al. [39] showed that TiN was not formed if the nitrogen concentration was lower than ~6 at.%; otherwise, TiN was formed uniformly at the surface if nitrogen concentration was ~20 at.%. Thus, we may conclude that an effective nitriding process was achieved using LPEB irradiation with N₂ plasma gas and a negative DC bias. Also, −100 V of DC bias was the optimal condition because larger biases did not modify the nitrogen concentration significantly and induced the small crater-like defects shown in Fig. 3c and 3d.

In addition to EDS analyses, XPS results specified the formation of TiN in the re-solidified layer after LPEB nitriding. The XPS results are presented in Fig. 6. The spectral data were obtained at the top surface and 10 nm-deep regions with 0, −100, −500, and −1000 V bias in N₂ gas. It is clear that TiN and TiOₓNᵧ were formed successfully on Ti₆Al₇Nb after LPEB nitriding. In Fig. 6a, the binding energy of the Ti-2p₃/2 peak or shoulder was shifted from the 458–460 eV range to 453–456 eV. Also, the Ti-2p₁/2 peak was moved from the 464–465 eV range to 459–461 eV, with a higher overall intensity of the spectrum. These XPS results showed similarities with other nitriding researches [40–42]. It has been documented that TiN and TiOₓNᵧ corresponding to the Ti-2p₃/2 peak appeared at the ~454.5 [40] and the Ti-2p₁/2 peak indicating TiN was measured at ~460.85 eV [42]. Thus, the shift of the Ti-2p spectrum suggested that TiN was formed inside the re-solidified
layer, and a compound layer, composed mainly of TiO$_x$, was formed at the top surface. Additionally, the spectrum of N-1s in Fig. 6b showed the extent of TiO$_x$N$_y$ at the top surface and TiN at 10 nm below the top surface [43]. These results were well agreed also with the spectrum of Ti-2p and O-1s, as shown in Fig. 6a and 6c. To conclude, LPEB nitriding could facilitate nitrogen implantation in the re-solidified layers and the formation of TiO$_x$N$_y$ layers on the nitrided layers.

3.3. Mechanical properties

TiN is known to have much higher hardness than conventional titanium alloys, such as Ti–6Al–4V and Ti–6Al–7Nb. Moreover, surface hardening effect of LPEB irradiations has been firmly established in previous researches [44]. Thus, comparisons of nano-hardness profiles among bare and LPEB-treated Ti–6Al–7Nb with Ar and N$_2$ plasma gas are appropriate to specify the surface hardening and extent of the nitrogen diffusion into the substrates [23]. Fig. 7 shows variations in nano-hardness as a function of the depth profile after LPEB irradiation with Ar and N$_2$ plasma gas. The nano-hardness near the top surface was increased slightly following LPEB irradiation with Ar plasma gas. At the top surface, it was modified by ~15%, and the depth of modification was observed to be

![Fig. 7. Variations in nano-hardness at re-solidified layer as a function of depth.](image)

![Fig. 8. White-interference micrographs of wear tracks after a ball-on-disc wear test on Ti–6Al–7Nb surfaces (a) before and after LPEB irradiation with (b) 0 V-biased in Ar gas, (c) 0 V-biased in N$_2$ gas, (d) –100 V-biased in N$_2$ gas, and corresponding (e) friction coefficients, (f) widths and depths of wear tracks measured at (a)–(d).](image)
of Ti–6Al–7Nb could be effectively modified by LPEB irradiation forming TiN at the re-solidified layer. The modification on mechanical properties at the re-solidified layers was also well reflected in ball-on-disc wear tests. Fig. 8 shows white-interference micrographs, friction coefficients, and widths and depths of wear tracks after the wear tests. Although the friction coefficients were similar for the bare and LPEB-treated samples regardless of LPEB parameters (Fig. 8e), configurations of wear tracks were significantly different. The lowest worn depth of ~8 µm and width of ~600 µm were obtained from the LPEB-nitrided Ti–6Al–7Nb biased with –100 V among the four samples. The greater wear resistance of re-solidified layer following LPEB irradiations could be associated with its higher surface hardness; the decreasing tendency of wear track width and depth followed the increasing tendency of nano-hardness depending on LPEB parameters.

3.4. Corrosion performance

From the phase, microstructural, and nano-hardness analyses, it was clear that 10 irradiation pulses and a –100 V DC bias were the optimal conditions because the fraction of nitrogen did not vary with increasing number of pulses to more than 10 or a DC bias voltage larger than –100 V. Thus, the corrosion characteristics were evaluated with a sample irradiated through 10 LPEB pulses and a –100 V DC bias. Fig. 9 shows representative potentiodynamic polarization curves of the untreated and LPEB-treated Ti–6Al–7Nb alloys and corresponding variations of corrosion potentials and corrosion current densities in a 1 wt% NaCl aqueous solution at room temperature. The electrochemical parameters estimated from the Tafel extrapolation, including corrosion potential, corrosion current density, and Tafel slopes, are summarized in Table 4. The corrosion potential became nobler following LPEB irradiation; it increased from –404.7 mV/SCE on the bare surface to –303.5 mV/SCE on the LPEB-nitrided surface with Ar plasma gas. The corrosion potential on the LPEB-nitrided surface with N2 plasma gas was nobler than that on the LPEB-treated surface with Ar plasma gas. Moreover, it was possible to achieve a positive level of corrosion potential following LPEB nitriding on Ti–6Al–7Nb using a bias of –100 V. Thus, we can summarize that the corrosion resistance was increased by LPEB irradiation and further increased by LPEB nitriding from the nobler corrosion potential, as summarized in Fig. 9b. In addition to the corrosion potential, the changes in corrosion current densities also indicated an improvement in the corrosion resistance following LPEB irradiation with Ar and N2 plasma gas. Comparing to the bare surface (194.9 nA/cm²), much lower corrosion current density was obtained on LPEB-nitrided surface with Ar plasma gas, N2 plasma gas, and negative DC bias of –100 V (<50 nA/cm²). The corrosion rate corresponding to corrosion current density has been studied previously. The relationship between corrosion current density and corrosion rate can be expressed, as follows, using Faraday’s law [46]:

\[
v = \frac{M}{2F\rho} i_{\text{corr}}
\]

(3)

where \(M\) is the molar mass for Ti–6Al–7Nb, \(i_{\text{corr}}\) is the corrosion current density of the sample, \(\rho\) is the density of the sample, and \(F\) is the Faraday constant. The current density and corrosion rate were calculated using the Tafel slopes and corrosion potentials corresponding to corrosion currents.

Table 4

<table>
<thead>
<tr>
<th>Type of plasma gas</th>
<th>Negative DC bias (V)</th>
<th>(E_{\text{corr}}) (mV/SCE)</th>
<th>(i_{\text{corr}}) (nA/cm²)</th>
<th>(\beta_a) (mV/dec)</th>
<th>(\beta_c) (mV/dec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>0</td>
<td>–404.7 ± 5.58</td>
<td>194.9 ± 5.04</td>
<td>971 ± 20.6</td>
<td>–372 ± 10.5</td>
</tr>
<tr>
<td>Ar</td>
<td>0</td>
<td>–303.5 ± 5.25</td>
<td>49.9 ± 4.60</td>
<td>1254 ± 22.9</td>
<td>–602 ± 22.9</td>
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<tr>
<td>N2</td>
<td>0</td>
<td>–243.0 ± 9.45</td>
<td>45.4 ± 2.41</td>
<td>1450 ± 40.0</td>
<td>–440 ± 22.0</td>
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<tr>
<td>N2</td>
<td>–100</td>
<td>43.2 ± 8.00</td>
<td>51.6 ± 5.01</td>
<td>943 ± 11.0</td>
<td>–790 ± 16.0</td>
</tr>
</tbody>
</table>
current density, \( z \) denotes the electron number, \( F \) is the Faraday constant, and \( \rho \) is the density. It is clear that corrosion rate, which is the corrosion propagation speed once it occurs, is linearly proportional to the corrosion current density. Consequently, it can be concluded that the corrosion rate is decreased significantly by LPEB irradiation on Ti-6Al-7Nb both with Ar and N\(_2\) plasma gas.

This modification of corrosion resistance following LPEB irradiation and LPEB nitriding is strongly related to the formation of a stable and passive re-solidified layer. As shown in the polarization curves (Fig. 9a), a slight active-passive transition region at \(-100\) mV/SCE was observed on the bare surface of Ti-6Al-7Nb. However, spontaneously passive characteristics in the anodic environment were obtained on LPEB-treated samples with both Ar and N\(_2\) plasma gas. It is also known that oxide layers formed at the surface, consisting mainly of TiO\(_2\), are responsible for the high corrosion resistance of titanium-based alloys [47]. A typical titanium oxide layer that forms at the surface of titanium alloys is generally weak and thin; however, more stable and firmly established oxide layers can be achieved following LPEB irradiation.

The corrosion-inhibiting effects of these passivation, oxide, and re-solidified layers can be characterized by the charge transfer resistance. The charge transfer resistance, obtained from the EIS spectra, can be analyzed simply using Nyquist plots, Bode plots, and corresponding equivalent circuit modeling. Fig. 10a–c shows Nyquist plots and Bode plots of Ti-6Al-7Nb before and after LPEB irradiation with/without DC bias. It is clear that LPEB irradiation with both Ar and N\(_2\) plasma gas enhanced the impedance of the surface by forming a stable and passive re-solidified layer combined with oxygen. All of the LPEB-treated surfaces of Ti-6Al-7Nb indicated a larger radius on Nyquist plots compared with that on the bare surface. The largest radius of the semi-circle on Nyquist plots was obtained with the sample treated by LPEB with N\(_2\) plasma gas and \(-100\) V of DC bias. Comparing the samples treated by LPEB with Ar plasma gas and N\(_2\) plasma gas, a higher impedance at high frequencies was observed at the surface of the sample treated with Ar plasma gas; however, this was reversed at low frequencies, so that the impedance measured at frequencies lower than \(10\) Hz was larger on the LPEB-treated sample with N\(_2\) plasma gas than Ar plasma gas (Fig. 10b).

For further discussions on the corrosion characteristics at the surface of Ti-6Al-7Nb before and after LPEB irradiation, equivalent electrical circuit models corresponding to the corrosion

### Table 5

<table>
<thead>
<tr>
<th>Type of plasma gas</th>
<th>Negative DC bias (V)</th>
<th>( R_s (\Omega \text{ cm}^2) )</th>
<th>( \text{CPE}_\sigma (\mu \text{F/cm}^2) )</th>
<th>( n_\sigma )</th>
<th>( R_p (\Omega \text{ cm}^2) )</th>
<th>( \text{CPE}_\alpha (\mu \text{F/cm}^2) )</th>
<th>( n_\alpha )</th>
<th>( R_{ct} (\Omega \text{ cm}^2) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>0</td>
<td>0.1611</td>
<td>8.228</td>
<td>0.9296</td>
<td>0.1683</td>
<td>6.963</td>
<td>0.9078</td>
<td>34.40</td>
</tr>
<tr>
<td>Ar</td>
<td>0</td>
<td>0.1626</td>
<td>2.890</td>
<td>0.8984</td>
<td>0.5455</td>
<td>1.020</td>
<td>0.9837</td>
<td>2013</td>
</tr>
<tr>
<td>N(_2)</td>
<td>0</td>
<td>0.1610</td>
<td>0.3827</td>
<td>0.8096</td>
<td>0.3792</td>
<td>0.3790</td>
<td>0.9887</td>
<td>5327</td>
</tr>
<tr>
<td>N(_2)(-100)</td>
<td>-100</td>
<td>0.1657</td>
<td>0.8379</td>
<td>0.8849</td>
<td>0.5559</td>
<td>0.2449</td>
<td>0.9515</td>
<td>6194</td>
</tr>
</tbody>
</table>

Fig. 10. (a) Nyquist plots and (b, c) Bode plots of Ti-6Al-7Nb before and after LPEB irradiations, and the equivalent circuit model corresponding to (d) bare and (e) LPEB-treated surfaces.
mechanisms of LPEB-treated Ti–6Al–7Nb are proposed, as illustrated in Fig. 10d and e. The corresponding electrical parameters interpreted and fitted from EIS data are summarized in Table 5. The equivalent circuit models consist of the solution resistance (R_s), the constant phase elements indicating capacitance of passive oxide films (CPE_{2}), the reaction resistance considering the semiconducting properties of defects in the passive film (R_{ct}), the charge transfer resistance of substrates (R_{ct}), and the double layer capacitance (CPE_{dl}). The analysis results using the proposed two-time constant equivalent circuit model matched well with the variations in corrosion resistance indicated by the polarization curves and EIS spectra. The R_{ct} for bare Ti–6Al–7Nb was 34.4 kΩ/cm², which was much lower than that of the LPEB-treated samples. In contrast, LPEB irradiation with Ar plasma gas could lead to the formation of a stable re-solidified layer on the surface. Thus, the corresponding R_{ct} at the re-solidified layer was hugely increased to 2013 kΩ/cm² with Ar gas, and further increased to 5327 kΩ/cm² with N₂ gas. The highest value of R_{ct}, 6194 kΩ/cm², was obtained from the LPEB-nitrided Ti–6Al–7Nb sample with −100 V bias. Although LPEB irradiations with Ar gas modifies R_{ct} by generating electrochemically stable re-solidified layer, further modification of R_{ct} through LPEB nitriding could be a result of the increasing fraction of TiN formed on the re-solidified layer by changing the plasma gas from argon to nitrogen. A higher TiN fraction was achieved by using N₂ plasma gas versus Ar plasma gas. Rossi et al. [48] revealed that the chemical stability of TiN itself leads to the highly corrosion-resistant characteristic of TiN, as assessed by an analysis of corrosion performance in extremely aggressive electrolytes. Thus, the most modified corrosion resistance analyzed from the polarization curves and EIS spectra could be supported by the modified R_{ct} on LPEB-nitrided samples with or without DC bias.

In order to clearly specify the effect of corrosion-resistant re-solidified layer induced by LPEB nitriding on corrosion reactions, CA curves were analyzed potentiostatically at a certain anodic potential, +100 mV/SCE. Fig. 11 shows the CA curves on Ti–6Al–7Nb samples before and after LPEB irradiations. The current densities measured from samples were increased dramatically in a few seconds immediately after the anodic potential applied. This increase of current density is mainly due to the dissolution of a passive oxide film [49]. After the momentary increase of current density, the curves soon decreased continuously till the oxide film to be fully dissolved. Finally the current density could be saturated at a certain level indicating continuous corrosion reaction of the bare Ti–6Al–7Nb and re-solidified layer. As shown in Fig. 11, the highest level of current density was obtained on the bare surface indicating the most reactive characteristic to corrosion, and it was not saturated till 30 min testing. The current densities obtained from LPEB-treated samples were significantly lower than that from the bare surface. The LPEB-treated sample with Ar plasma gas indicated 40 nA/cm² of current density at the first, and it was saturated at −10 nA/cm² after 30 min. The LPEB-nitrided samples both with and without DC bias showed the lowest current density; it was initially increased up to −30 nA/cm², and then saturated at nearly zero after −200 s indicating no corrosion reactions. Thus CA analyses confirmed that the re-solidified layer induced by LPEB nitriding has superior corrosion resistance.

Fig. 11. Chronoamperometry of Ti–6Al–7Nb before and after LPEB irradiations.

4. Conclusions

The LPEB nitriding process, describing LPEB irradiation using N₂ plasma gas and cathodic apparatus to apply a negative DC bias, has been introduced as a unique, effective, and crack-free nitriding method for Ti–6Al–7Nb alloys. Most importantly, increasing fraction of TiN on re-solidified layers following LPEB nitriding facilitated to fabricate the surface layer with high corrosion resistance and mechanical properties. Although only small fraction (~6 at.%) of nitrogen was implanted by conventional LPEB irradiations with Ar gas, the LPEB nitriding increased the fraction of implanted nitrogen at the re-solidified layer up to ~18 at.% with −100 V of bias. A hardened surface by distorting the lattice structure due to interstitially implanted nitrogen atoms, forming TiN in the re-solidified layer, led improved nano-hardness and wear resistance. Furthermore, the corrosion resistance of Ti–6Al–7Nb was modified by constructing a passive and stable re-solidified layer consisted of TiN, TiO₂, and TiO₂Nₓ. The chronoamperometry measurements revealed that no reactions occur at the LPEB-nitrided surface as their current densities were saturated at nearly zero after dissolution of oxide layers. Hence, the LPEB nitriding could offer promising prospects for industrial applications as a single-step finishing process which could simultaneously modify mechanical properties and corrosion resistance.

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