Effects of Cryo-Treatment on Corrosion Behavior and Mechanical Properties of Laser-Welded Commercial Pure Titanium

Yanping Zhu1,2, Changyi Li1 and Lianyun Zhang1,*

1School of Stomatology, Tianjin Medical University, Tianjin 300070, P. R. China
2Department of Prosthodontics, Tianjin Stomatological Hospital, Tianjin 300041, P. R. China

The objective of this study was to investigate the effects of cryo-treatment on the microstructure, corrosion behavior, and mechanical properties of Ti before and after laser welding. The microstructure was studied by optical microscopy. It was found that the grain size for Ti became smaller after cryo-treatment. Cryo-treatment could also refine and stabilize the crystal lattice structure and distribute precipitate particles throughout the material in the welded metal. Potentiodynamic polarization measurements were employed to investigate the corrosion behavior in an artificial saliva solution. Electrochemical results showed that the laser-welded Ti after cryo-treatment exhibited the most obvious passivation behavior of all the specimens. The mechanical properties of Ti, cryo-treated Ti (C-Ti), laser-welded Ti (W-Ti), and cryo-treated, laser-welded Ti (CW-Ti) were characterized by tensile tests. It was found that the tensile strength and elongation could be improved for Ti and laser-welded Ti by cryo-treatment without impairing its corrosion resistance.  [doi:10.2320/matertrans.M2013373]

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1. Introduction

In recent years, much effort has been devoted to developing dental prostheses with higher security and durability. Titanium and titanium alloys have been widely used in dental devices owing to their low density, excellent corrosion resistance, and unique biocompatibility; however, the dimensional contraction of Ti induced by casting below the high melting point can lead to the deformation of castings. In order to reduce and remedy this dimensional contraction, laser welding is employed to connect Ti metals.

Laser welding is a promising technique with smaller heat affected zone (HAZ), reduced distortion of metals, and lower damage to acrylic resin or porcelain. Recent studies indicate that the strength of laser welding samples can be close to the original material when optimal parameters (power, pulse, and spot diameter) were selected; however, there are still some problems such as lower elongation and corrosion resistance. Due to melting and re-solidification, the welded metal microstructure is changed. Meanwhile, due to recrystallization and grain growth in the HAZ caused by thermal cycles, the work hardening of the base metal will be almost lost. Hence, the microstructure of materials will be altered, further influencing their corrosion behavior mechanically. Watanabe et al. found that the tensile strength and elongation were close to the original material when the appropriate parameters were selected. Orsi et al. reported that the corrosion current density (Icorr) of titanium welded joints were higher than that of the original material, indicating that the corrosion resistance was reduced. Methods such as heat treatment or cryogenic treatment may help to resolve above-mentioned problems.

Cryo-treatment technology is expected to compensate for the disadvantages of traditional dental materials due to its lower required investment, simple equipment, easy operation, and significant economic benefits. Cryo-treatment immerses the samples in a cold medium (such as liquid nitrogen) according to a certain processing curve until achieving a certain temperature. The material’s performance will be improved by inducing microstructural changes and stress redistribution. Zhu et al. used cryo-treatment to improve the mechanical properties of oral cast alloys. The results showed that the yield strength and hardness of the cobalt–chromium alloy were improved without causing significant linear deformation. However, to the best of the author’s knowledge, no study has been conducted to reveal the effect of cryo-treatment on laser-welded titanium joints to improve their overall performance.

Accordingly the purpose of the present study is to evaluate the effect of cryo-treatment on the corrosion behavior and mechanical properties of commercially pure titanium after laser welding using the electrochemical potentiodynamic polarization technique and tensile testing.

2. Materials and Methods

2.1 Sample preparation for electrochemical tests

Commercially pure titanium (ASTM grade II, 99.995% purity, from Beijing Mountain Technical Development Center for Non-Ferrous Metals) was used. The Ti specimens were machined to 10 mm × 10 mm × 0.5 mm. A welded Ti sample was made from two machined specimens. The specimen has the same dimensions (10 mm × 10 mm × 0.5 mm) and was butt welded together using a laser welder. Laser parameters and welding conditions are listed as follows. Both longitudinal sides of metals were laser welded using a laser welder (Comlaser 4, Dentaurum, Germany) in an argon atmosphere. The laser welding parameters (output of 500 W, pulse duration of 10 ms, spot diameter of 1 mm) were preset to have a penetration depth of approximately 0.5 mm. The spot laser welding was performed from one end to the other end in such a way that the previous 50% welded spot overlapped with the current welding spot. Ti sheets before and after laser welding were further cryo-treated in liquid nitrogen. Typically, the samples were first suspended just above the surface of the liquid nitrogen bath.

*Corresponding author, E-mail: lianyun.zhang@126.com

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for 0.5 h and then dipped into the liquid nitrogen for 24 h. Finally, they were removed from the liquid nitrogen and kept just above the bath for 0.5 h. The aim of suspending the samples above the surface of the liquid nitrogen bath before and after cryo-treatment was to avoid drastic temperature changes from room temperature to 77 K and vice versa. The samples were assumed to be cooled or warmed gradually. Electrochemical corrosion behavior was evaluated for all the cryo-treated samples. Electrochemical tests of each prepared couple were undertaken in an artificial saliva solution at 310 K (See Table 1). All reagents were analytical grade (from Tianjin Lianxing Company). A saturated calomel electrode (SCE) reference electrode and a platinum counter electrode were used for the corrosion test. The welded sample used as a working electrode was sealed by resin, leaving the welded area exposed in the solution. The area of the welded area was determined using the image analysis. Firstly, magnified graphs were taken showing the welded area. This welded area was then traced out and analyzed using the Scion Image Analysis software. Hence, the welded area can be obtained. An electrochemical workstation (ZF-100, Shanghai Chenhua Equipment Co. Ltd., China) was used to perform the open-circuit potential and potentiodynamic tests. Before the measurement, potential dynamic polarizations were started from open-circuit potential in order to remove the oxidation film formed in air. The amplitude of the potential dynamic scanning potential ranged from $-2$ to $2$ V. The scanning rate was $0.001$ V s$^{-1}$. In the polarization curves, the potential where the active dissolution of the alloy occurs is referred to as the corrosion potential ($E_{\text{corr}}$). The corresponding current density of the intersection point of the two tangential lines of cathodic polarization and anodic polarization is called the corrosion current density ($I_{\text{corr}}$).

2.2 Sample preparation for mechanical tests

A schematic diagram and digital photograph of the Ti sample used for the tensile test are shown in Figs. 1(a) and 1(b), respectively. The welding samples for this test were made by butt welding two identical pieces, which were obtained by cutting a piece shown in Fig. 1 vertically through the middle (See the welding process in Fig. 1(c)). The laser parameters and welding conditions are identical to those listed in Section 2.1. After laser welding, the samples were scanned by Computed Tomography (Y. COUGAR SMT, YXLON International GmbH, Germany). The images of the welded Ti sample in Fig. 2 show negligible weld defects and cracks before and after cryo-treatment.

The tensile test was conducted using a universal testing machine (Model 3367, Instron Crop., USA) at a cross-head speed of $2$ mm min$^{-1}$ and a gauge length of $10$ mm. Fracture load (N) and elongation (%) were recorded, and mean values and standard deviations of three measurements ($n = 3$) were calculated.

2.3 Surface analysis

For optical microscopy, samples were mechanically polished and then etched (solution: 3 mL of 45 mass% hydrofluoric acid and 6 mL nitric acid in 100 mL deionized water) at room temperature for 10 s. They were then examined using an optical microscope (Axiovert 200MAT, Zeiss, Germany). After the tensile test, the Ti, cryo-treated Ti (C-Ti), laser-welded Ti (W-Ti), and cryo-treated, laser-welded Ti (CW-Ti) were characterized by scanning electron microscopy (SEM, XL-30 Philips, Netherlands).

3. Results and Discussion

It is well known that the biocompatibility of Ti alloys is generally related to specific properties of materials. The microstructure, corrosion behavior, and mechanical properties of Ti must all be considered when using Ti in dental alloys.

3.1 Composition and structure

Optical microstructures of (a) Ti, (b) C-Ti, (c) W-Ti, and (d) CW-Ti are shown in Fig. 3. The original Ti was made of fairly equiaxed and homogeneous grains. The sizes of
equiaxed grains for Ti are in the range of 45–52 µm, and their sizes decrease to 23–43 µm after cryo-treatment (Figs. 3(a) and 3(b)). Due to the effects of the laser welding heat input, martensitic transformation occurred. Firstly, the α phase transformed to the β phase above 1156 K during the welding process. Then, the high temperature BCC β phase transformed to the low temperature HCP α martensite phase during the cooling procedure. The martensite structure can be found in the weld metal (WM), and chemical composition inhomogeneity appeared. The joints were devoid of visible contamination. Meanwhile, it was also observed that cryogenic treatment refined and stabilized the crystal lattice and distributed precipitate particles throughout the weld metal, resulting a stronger and hence more durable material.

3.2 Electrochemical corrosion behavior

The potentiodynamic polarization results of Ti, cryo-treated Ti (C-Ti), laser-welded Ti (W-Ti), and cryo-treated, laser-welded Ti (CW-Ti) in artificial saliva solution at 310 K are shown in Fig. 4. There is no distinct difference in the cathodic polarization curves of these samples, indicating that the same cathodic reaction occurred on their surface but with different rates, which may correspond to the dissolved oxygen reduction reaction as follows:

\[ \text{O}_2 + 4e^- + 2\text{H}_2\text{O} \rightarrow 4\text{OH}^- \]  \hspace{1cm} (1)

Further scanning in the anodic direction causes the current to rise rapidly. After reaching the corrosion potential \( (E_{\text{corr}}) \), it starts to exhibit anodic polarization behavior. The current densities of Ti, C-Ti, and W-Ti continuously increase up to the passivation potential of \( E_p \) indicating a typical behavior of activation-dissolution. After that point \( (E_b) \), the current increases slowly with potential. The potential \( E_b \) is a breakdown potential that indicates destruction of a passivated film. This is associated with the electroformation of a TiO\(_2\) passivation layer according to reaction (2):

\[ \text{Ti} + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4\text{H}^+ + 4e^- \]  \hspace{1cm} (2)

The electrodeposition of TiO\(_2\) on the surface blocks the dissolution active sites. When the surface was entirely covered with a TiO\(_2\) film, the current density remained independent or increased slowly with potential, which marked the onset of passivation. The region between \( E_p \) and \( E_b \) is referred to as the transpassive region and \( \Delta E \) is a difference between \( E_p \) and \( E_b \). Further scanning of potential in the anodic direction partially removed the passivation film at the surface because of the highly reducing initial potentials. This indicated a typical behavior of activation-dissolution
The current density reached a maximum of 45.75 µA cm$^{-2}$, which is referred to as the critical current density ($I_{cc}$). The potential at this current density is defined as the pseudopassivation potential ($E_{pp}$).

For better visualization of the polarization behavior of Ti, C-Ti, W-Ti, and CW-Ti in saliva media, the corrosion parameters, including $E_{corr}$, $I_{corr}$, $E_p$, $E_b$, $E_{pp}$, and $\Delta E = E_b - E_p$ were obtained using standard techniques from the potentiodynamic polarization plots (See Table 2). The $I_{corr}$ of C-Ti (0.536 µA) and W-Ti (0.570 µA) were both lower than that of Ti (0.917 µA), which indicates that the corrosion resistance of Ti can be enhanced by cryo-treatment. Additionally, laser welding did not negatively affect the corrosion resistance of Ti. The same polarization phenomenon was also observed in CW-Ti. However, the passivation range, $\Delta E$, of CW-Ti was approximately 1.365 V, which is over twice as high as that of the other three samples. This passivation behavior is associated with the presence of defects, such as micro-pores, which promote a fast increase in current density. For the CW-Ti specimen, the high value of $\Delta E$ reveals much more stable passivation. This implies that the pitting corrosion tendency of laser-welded Ti can be reduced by cryo-treatment, which further confirms that the cryo-treatment on the laser-welded Ti can improve the corrosion resistance to some extent. When the material is used in a dental prosthesis, the behavior in the low-potential region is more important. CW-Ti shows the lowest $E_{corr}$, the highest $I_{corr}$, and the highest passivation current at approximately $-0.5$ V. These results indicate that cryo-treatment decreases corrosion resistance at intermediate conditions. Hence, it can be concluded that the cryo-treatment can improve the corrosion resistance at high-potential conditions but will degrade it at low-potential conditions.

### 3.3 Mechanical properties

The tensile test results of Ti, C-Ti, W-Ti, and CW-Ti are shown in Fig. 5. The data was statistically analyzed by One-way analysis of variance (ANOVA) and followed by Turkey’s HSD test at a 95% significance level. Statistical p-value was set to $p < 0.05$. Figures 6 and 7 show the ultimate tensile strength ($\sigma_{UTS}$) and elongation ($\Delta l/l$) of the four specimen types. Standard deviations are also shown by.

### Table 2: Corrosion parameters of the potentiodynamic polarization for Ti, C-Ti, W-Ti, and CW-Ti in artificial saliva solution at 310 K.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>$E_{corr}$/V vs. SCE</th>
<th>$I_{corr}$/µA cm$^{-2}$</th>
<th>$E_p$/V vs. SCE</th>
<th>$E_b$/V vs. SCE</th>
<th>$\Delta E$/V</th>
<th>$E_{pp}$/V vs. SCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>-0.681</td>
<td>0.917</td>
<td>-0.499</td>
<td>0.046</td>
<td>0.545</td>
<td>0.812</td>
</tr>
<tr>
<td>C-Ti</td>
<td>-0.796</td>
<td>0.536</td>
<td>-0.565</td>
<td>0.043</td>
<td>0.608</td>
<td>0.816</td>
</tr>
<tr>
<td>W-Ti</td>
<td>-0.976</td>
<td>0.570</td>
<td>-0.582</td>
<td>0.047</td>
<td>0.629</td>
<td>0.816</td>
</tr>
<tr>
<td>CW-Ti</td>
<td>-1.191</td>
<td>1.935</td>
<td>-0.910</td>
<td>0.455</td>
<td>1.365</td>
<td>1.623</td>
</tr>
</tbody>
</table>

$E_{corr}$: corrosion potential, $I_{corr}$: corrosion current density, $E_p$: passivation potential, $E_b$: breakdown potential, $\Delta E = E_b - E_p$, $E_{pp}$: pseudopassivation potential.
thin bars at the top edge of the block bars. Each group was estimated from 3 data points. The values of UTS and elongation are shown in Table 3. The UTS and elongation of C-Ti were slightly higher than those of Ti. This indicates that the cryo-treatment is able to improve the tensile strength and ductility. The UTS increased from 336 to 406 MPa, and elongation increased from 6 to 15% when comparing W-Ti and CW-Ti. Although the values of UTS and elongation for W-Ti and CW-Ti are lower than those of Ti and C-Ti, the effect of cryo-treatment in the welded Ti is more significant than in pure Ti. For welded Ti, the UTS and elongation increased by 20 and 150% after cryo-treatment, respectively. In contrast, the UTS and elongation increased only by 6 and 2% for pure Ti, respectively. It is known that the original Ti metal has higher strength and ductility without significant defects. Therefore, it seems unlikely that cryo-treatment would bring further improvement to its mechanical properties. However, for welded Ti, the welding zone will be

Table 3 The values of ultimate tensile strength ($\sigma_{UTS}$) and elongation for Ti, C-Ti, W-Ti, and CW-Ti.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>$\sigma_{UTS}$/MPa</th>
<th>Elongation, $\Delta l/l$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>419 ± 10</td>
<td>38 ± 3</td>
</tr>
<tr>
<td>C-Ti</td>
<td>445 ± 7</td>
<td>38 ± 6</td>
</tr>
<tr>
<td>W-Ti</td>
<td>336 ± 28</td>
<td>6 ± 1</td>
</tr>
<tr>
<td>CW-Ti</td>
<td>406 ± 13</td>
<td>15 ± 5</td>
</tr>
</tbody>
</table>

Fig. 6 Means and standard deviations of UTS of four groups (Ti, C-Ti, W-Ti, and CW-Ti), $p < 0.05$ indicates a statistically significant difference in each group.

Fig. 7 Means and standard deviations of the elongation of four groups (Ti, C-Ti, W-Ti, and CW-Ti), $p < 0.05$ indicates a statistically significant difference in each group.

Fig. 8 Secondary electron images by scanning electron microscopy of the fracture surface of the specimens after tensile test; (a) Ti, (b) C-Ti, (c) W-Ti, and (d) CW-Ti.
influenced by the welding heat and will inevitably produce various defects. After cryo-treatment, the residual stress and defects could be significantly reduced, suggesting expected improvements in the tensile strength and elongation.

Figure 8 shows the SEM fractographs of the Ti, C-Ti, W-Ti and CW-Ti. It can be seen from Figs. 8(a) and 8(b) that ductile dimples were the dominant features for Ti and C-Ti. For pure Ti, small craters were observed in the areas between the large dimples (primary dimples). The primary dimples were shallow and coarsely populated. After cryo-treatment, the Ti’s dimples appeared deeper and the amount of small craters decreases, as shown in Fig. 8(b). Hemispherical or equiaxial dimples may form because of the influence of uniform plastic strain in the direction of the applied stress.27) Primary dimpling is responsible for plastic deformation. In Fig. 8(c), the fracture mode of the W-Ti sample is brittle intercrystalline fracture. These fracture micrographs indicate that the pure Ti had ductility, but the Ti after laser welding fractured in the weld metal area without plastic deformation. When the laser-welded Ti was further cryo-treated, the fracture mode in Fig. 8(d) was a mixed mode, with fine dimple fractures accompanied by cleavage. Therefore, the cryo-treatment led to an increase in the ductility and improved the mechanical properties, which is in good agreement with the results of Fig. 6.

According to Kalia’s study,28) all of the individual constituents that make up an alloy are placed into their most stable state. These constituents then are aligned optimally with surroundings. Molecular bonds are strengthened by cryo-treatment. Particle alignment and grain refinement combine to relieve internal stresses, which can contribute to part failure. This results in a material that is optimized for durability. The extremely low temperature during cryogenic processing also slows movement at the atomic level and increases the internal molecular bonding energy, promoting a pure structural balance throughout the material. As a result a material is obtained with an extremely uniform, repeatable balance throughout the material. As a result a material is obtained with an extremely uniform, repeatable balance throughout the material. As a result a material is obtained with an extremely uniform, repeatable balance throughout the material. As a result a material is obtained with an extremely uniform, repeatable balance throughout the material. As a result a material is obtained with an extremely uniform, repeatable balance throughout the material. As a result a material is obtained with an extremely uniform, repeatable balance throughout the material. As a result a material is obtained with an extremely uniform, repeatable balance throughout the material. As a result a material is obtained with an extremely uniform, repeatable balance throughout the material. As a result a material is obtained with an extremely uniform, repeatable balance throughout the material.