Microstructural examination and corrosion behavior of selective laser melted and conventionally manufactured Ti6Al4V for dental applications

Hafiz Muhammad Hamza, Kashif Mairaj Deen, Waseem Haider

A B S T R A C T

The selective laser melting of Ti6Al4V would induce definite changes in the microstructure that may affect its corrosion properties. Microstructural examination showed the formation of relatively thin beta (β) lamella in selective laser melted (SLM) Ti6Al4V compared to wrought Ti6Al4V. X-ray diffraction analysis (XRD) analysis confirmed the presence of alpha and beta phases in both SLM and wrought Ti6Al4V. However, the higher concentration of the β phase in SLM Ti6Al4V compared to wrought Ti6Al4V was evident in the microstructure. As candidate dental implant materials, the corrosion behavior of both SLM and wrought Ti6Al4V was assessed in artificial saliva (AS) and deionized water (DI) containing various species i.e. fluoride (F), calcium chloride (CaCl2) and lactic acid (LA). Electrochemical impedance spectroscopy and potentiodynamic polarization analysis was carried out to estimate the corrosion behavior of SLM and wrought Ti6Al4V at room temperature. SLM Ti6Al4V offered better corrosion resistance than wrought Ti6Al4V in all solutions at pH > 6. However, wrought Ti6Al4V comparatively presented high corrosion resistance in AS + LA, DI + CaCl2 and DI + LA solutions (pH < 6). The lower dissolution rate of SLM Ti6Al4V (at pH > 6) was attributed to larger β content in the microstructure compared to wrought Ti6Al4V.

1. Introduction

Known as 3D printing, additive manufacturing (AM) of metals is popular in the manufacturing of medical devices and implants for the biomedical applications [1]. Selective laser melting is a common method of additive manufacturing in which metal powder is selectively melted and the part is built layer by layer [2]. Traditional manufacturing of metallic alloys has limited its use to manufacture complex geometries. However, the selective laser melting process is capable of making complex geometries like the shape of the bone, dental, skull and customized implants [3–5].

For biomedical applications, good mechanical and corrosion properties are dependent - on the right choice of materials. Titanium and its alloys are the most popular implant materials due to their good mechanical properties and capability to withstand in an aggressive biological environment when exposed to body fluids and human tissues [6,7]. Commercially pure titanium (CP-Ti) is a popular material for biomedical implants due to its excellent corrosion resistance [8,9]. However, the mechanical performance of the CP-Ti can be enhanced by the addition of various alloying elements such as aluminum and vanadium [10,11]. It has also been found that the Ti6Al4V alloy exhibit higher or comparable corrosion resistance than CP-Ti. The relatively improved corrosion resistance of Ti6Al4V is possibly attributed to the surface oxide film that is composed of oxides of alloying elements such as vanadium and aluminum [12–14]. On the other hand, it has also been reported that these alloying elements in the Ti6Al4V implant may release into the surrounding tissues of the body and may pose serious health concerns [11]. To overcome these challenges, the addition of non-harmful alloying elements i.e. Mo, Ta, and Zr in Ti alloys has been studied. These alloying additions stabilize the beta phase in the microstructure and are considered least harmful to the human body. However, these alloys have received less attention due to their higher density, which most likely restricts their use in the development of biomedical implants [10].

Intrinsic to the manufacturing process, the microstructural changes have been observed in the selective laser melted (SLM) Ti6Al4V alloy [15,16]. Variations in the microstructure of SLM materials are due to layer by layer deposition and high cooling rates during melting and solidification processes [17,18]. Due to the microstructural variations induced by the manufacturing process parameters, the corrosion behavior of SLM Ti6Al4V is also affected and may be different than the wrought Ti6Al4V [19]. Particularly, for dental applications, Ti6Al4V presented higher corrosion resistance in human saliva [20–22]. However, some allergic reactions in the patients associated with the titanium implants have been reported in the literature [23]. One of the major factors causing allergies was the dissolution of ionic species from titanium implants when these materials interact with the saliva, sodium fluoride, calcium chloride and lactic acid [24–26]. Fluoride based
products are used for the protection and maintenance of dental implants in the form of sodium fluoride (NaF) [19,25,27]. Daniel et al. [25] studied the behavior of fluoride ions in artificial saliva for Ti–Ta alloys and found that fluoride ions (F−) decreased the corrosion resistance of Ti–Ta and Ti6Al7Nb alloys. When F− ions interact with the hydrogen ions in the artificial saliva, the reaction produces a slightly acidic environment, which may deteriorate titanium oxide film by forming soluble complex as given in reaction 1 [24,28–30].

\[
\text{TiO}_2 + 4F^- + 4H^+ = \text{TiF}_4 + 2\text{H}_2\text{O}
\]  

(1)

Licausi et al. [31] compared the corrosion behavior of sintered and wrought Ti6Al4V in fluorinated artificial saliva and reported relatively higher corrosion resistance of sintered Ti6Al4V due to its porous microstructure and interaction of fluoride ions with the passive film. Similar to the sintering process, the additive manufacturing of Ti6Al4V also utilizes metal powder but in this process, a high energy laser or electron beam is used to selectively melt metal powder layer by layer [2,32,33]. In a recently published work, it is stated that SLM Ti6Al4V presented better corrosion resistance than electron beam melted (EBM) Ti6Al4V due to the formation of relatively thick passive titanium oxide film. Also, the small amount of thin beta phase (β) lamella was formed in the microstructure of Ti6Al4V manufactured via electron beam melting. This phase was possibly produced by the relatively high energy density of the electron beam compared to selective laser melting process [19]. Other chemical species that interact with the dental implant include calcium chloride and phosphate ions present in the body fluids [34].

Degradation of titanium-based alloys caused by these species has also been reported in the literature [35]. Lactic acid is secreted naturally by the bacteria present in the oral cavity and this may also enhance microbiologically influenced corrosion (MIC) of metallic implants [36,37]. Matono et al. [38] reported the evidence of titanium oxide or precipitation of corrosion by lactic acid produced by Streptococcus Mutans bacteria. Qu et al. [26] reported the pitting corrosion of titanium surface in artificial saliva containing lactic acid caused by the reaction of lactate ions (L−) with the hydrated titanium oxide ([Ti(OH)3] Cl) in the presence of chloride ions. In the above-cited literature, it is evaluated that chemical species present in the oral cavity could appreciably enhance the corrosion of titanium and could adversely affect the integrity of dental implants. On the other hand, the manufacturing of Ti6Al4V alloy via selective laser and electron beam melting are the emerging processes that would certainly induce local stresses and variations in the microstructure. These changes are pertinent to influence corrosion behavior of Ti6Al4V. Very scarce information is available in the literature that describes the corrosion tendency of selective laser melted Ti6Al4V in the presence of fluoride, calcium chloride and lactic acid in artificial saliva.

This study aims to explore the electrochemical behavior of both SLM and wrought Ti6Al4V in the artificial saliva containing various amounts of sodium fluoride, calcium chloride, and lactic acid. Besides, the effect of individual species i.e. fluoride, calcium chloride, and lactic acid dissolved in DI water is also investigated to explain their character in the artificial saliva.

2. Experimental

2.1. Materials

SLM Ti6Al4V samples were manufactured by AM 250 laser powder bed fusion system (Renishaw®) using Ti6Al4V metal powder (15–45 μm). This system is equipped with an ytterbium fiber laser (wavelength 1070 nm). SLM Ti6Al4V was fabricated at a laser power of 200 W, a layer thickness of 30 μm and a hatch distance of 105 μm. These process parameters were optimized to minimize the formation of surface defects and residual stresses in the samples [39]. During the process, the inert atmosphere was created by using argon gas containing a low level of oxygen (500 ppm). Wrought Ti6Al4V rod (diameter of 15.87 mm) purchased from onlinemetals.com was cut into disk shape samples having a thickness of 5.08 mm using high speed saw. Both SLM and wrought Ti6Al4V samples were ground with SiC papers from 180 to 1200 grit size sequentially. The ground samples were ultrasonically cleaned in ethanol for 15 min and rinsed in water. Cleaned samples were dried under nitrogen gas stream before using them as working electrodes for electrochemical testing. For microstructural analysis, ground samples were polished sequentially on the cloth decorated with 3 μm and 1 μm diamond particles in the form of a paste. The polished samples were etched in KROLL’s solution (85 mL H2O, 5 mL HNO3 and 10 mL HF) for 5 s and washed with plenty of DI water followed by drying in hot air.

2.2. Material characterization

X-ray diffraction (XRD) was performed using an X-ray diffractometer (Rigaku MiniFlexII Desktop). Cu Kα radiation source (λ = 0.154 nm) was used and XRD patterns were obtained within (2θ) range of 20–90°. The volume fraction of each phase was calculated using Equation (1) as follows:

\[
V_{\text{f,j}} = \frac{A_i}{\Sigma A_i}
\]  

(1)

Here V_{f,i} is the volume fraction of each phase, A_i is the total integrated area of each phase and ΣA_i is the total area of all phases. The integrated area of each phase was calculated by using the Origin Pro 2017 with Pearson VII function [40,41]. A scanning electron microscope (SEM) Hitachi 3400 N-II coupled with energy-dispersive X-ray spectroscopy (EDX) was used for microstructural analysis and to determine the chemical composition of both SLM and wrought Ti6Al4V samples, respectively as given in Table 1.

2.3. Electrochemical testing

The polished samples (ground up to 8 μm grit size) followed by ultrasonic cleaning and drying with nitrogen gas were used for electrochemical testing. AFNOR® artificial saliva was purchased from Pickering Laboratories Inc. and its composition is given in Table 2. All electrochemical experiments were performed at room temperature in artificial saliva and deionized water-based solutions as designated in Table 3. The solutions were divided into two groups: group A with a pH above 6 and group B with a pH below 6. Open circuit potential (OCP) was performed for 4 h to achieve potential stability of 0.01 mV/min. Electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PD) tests were performed in a three-electrode cell. Saturated calomel electrode (SCE) (0.249 V vs. SHE) reference, platinum counter electrode and Ti6Al4V (SLM and wrought) samples were used as working electrodes in the cell. EIS was performed in a frequency range of 10^5 to 10^-2 Hz and an AC potential amplitude of 5 mV was applied. The sample area exposed to the solution was 1.26 cm². PD scans were obtained by sweeping the potential from −0.5 V to a final potential of 2.5 V with respect to OCP at a 1 mV/s scan rate. All the electrochemical experiments were repeated three times to ensure the reproducibility in the results.

<table>
<thead>
<tr>
<th>Elements</th>
<th>SLM (weight %)</th>
<th>Wrought (weight %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>Balance</td>
<td>Balance</td>
</tr>
<tr>
<td>Al</td>
<td>5.99</td>
<td>6.09</td>
</tr>
<tr>
<td>V</td>
<td>3.76</td>
<td>3.57</td>
</tr>
</tbody>
</table>
3. Results

3.1. Microstructure and X-ray diffraction

The microstructure of SLM and wrought Ti6Al4V consisted of alpha (α/α’ dark areas) and β (bright phase) lamellae phases as shown in SEM images (Fig. 1). According to the ternary phase diagram [42] of Ti6Al4V, β phase is stable at 1066 °C and when the temperature decreases, alpha phase starts to nucleate and a binary (α + β) Widmanstätten type phase is formed [19,43]. From the SEM images, it can be seen that the morphology of the β lamella in SLM Ti6Al4V was relatively fine and higher in concentration than in wrought Ti6Al4V. Due to the high cooling rate during the selective laser melting process, preferential alpha phase formation is restricted and the enhanced nucleation of fine β phase is expected [44–46]. On the other hand, wrought Ti6Al4V showed coarse and irregular shaped β lamella. As a result of the rapid cooling rate during the selective laser melting process, the relatively high concentration of the β phase was formed. However, the microstructure of wrought Ti6Al4V was largely composed of α/α’ phase decorated with a relatively small amount of coarse β phase. Overall, both α/α’ and β phases coexist in SLM and wrought Ti6Al4V as validated from the XRD patterns as shown in Fig. 2.

As α and α’ have the same hexagonal close-packed (hcp) structure therefore, it is difficult to differentiate between these two phases [46]. Overall, β lamella is present as a minor phase compared to α/α’ in both SLM and wrought Ti6Al4V [47–49]. An additional peak at 2θ of 57.5° corresponding to the β phase is originated in the diffraction pattern of SLM Ti6Al4V peak [50]. The volume fractions of each phase were calculated from the XRD patterns by using Equation (1) and the quantitative information is given in Table 4. Compared to the wrought sample (volume fraction of β = 13.4%), the SLM Ti6Al4V contained relatively large volume fractions of the β (21.8%) phase as evident in the microstructure (Fig. 2a). These results are in support of the previously published work [16] that also suggested the formation of a relatively large amount of β phase in the SLM Ti6Al4V compared to wrought counterpart.

3.2. Electrochemical behavior of SLM and wrought Ti6Al4V in AS and DI water in the presence of F−, CaCl2 and lactic acid

Fig. 3 shows the bode plots of SLM and wrought Ti6Al4V in artificial saliva (AS) containing F−, CaCl2 and lactic acid solutions as designated in Table 3. Similarly, the Nyquist plots of both SLM and wrought Ti6Al4V in these solutions are shown in Fig. 4. It was observed that both SLM and wrought Ti6Al4V showed higher impedance at a lower frequency and non-ideal capacitive behavior as indicated from the phase angle greater than −90° (Fig. 3). As indicated by the deviation in the phase angle trends within the frequency range of 10−2 to 102 Hz, it is predicted that the electrochemical behavior of SLM Ti6Al4V was different than wrought Ti6Al4V in AS. This indicated the difference in the surface passive film characteristics and their electrochemical response in the presence of ionic species. Three different equivalent electrical circuit (EEC) models were used to simulate the impedance spectra. These EEC models (Fig. 5) were fitted by adjusting the individual parameters through iteration to minimize the residual errors in both real and imaginary impedance components by using Echem Analyst 5.26 software. These theoretical models were fitted to simulate the electrochemical processes at the electrolyte/electrode interface. The stability of the passive film that may form in the artificial saliva and DI water containing various species was estimated from the quantitative analysis of the impedance spectra by fitting with the EEC. The impedance spectra of both SLM and wrought Ti6Al4V in DI water containing F−, CaCl2 and lactic acid are shown in Fig. 6 and Fig. 7. One time constant EEC was well fitted on wrought Ti6Al4V in AS solution and designated as EEC-1. Two-time constants EEC were applied to simulate the impedance spectra of both alloys in all solutions (except SLM Ti6Al4V in DI solution and wrought Ti6Al4V in AS, DI, DI + CaCl2, DI + LA solutions) and designated as EEC-2. The inductive response in impedance spectra of SLM Ti6Al4V in DI solution and wrought Ti6Al4V in DI solution and wrought Ti6Al4V in DI, DI + CaCl2, DI + LA solutions was simulated to EEC-3 to extract the quantitative information. The addition of an inductor in the EEC-3 was associated with the positive phase shift (> 0°) as indicated in the bode plot (Fig. 6). From the impedance spectrum of wrought Ti6Al4V in AS solution, one-time constant EEC simulated to the capacitive and charge transfer characteristics of the compact passive film as schematically shown in Fig. 5(a). However, the fitting of EEC-2 corresponded to the layered structure of the passive film. The distribution of charge within the top porous and compact bottom oxide layers was indicated in the impedance spectra of SLM and wrought Ti6Al4V in all solutions mentioned in Table 3 (except SLM in DI solution and wrought in AS, DI, DI + CaCl2, DI + LA solutions) by a two time constant EEC-2. In contrast to wrought sample, the SLM Ti6Al4V presented variation in phase angle at approximately 1° as depicted in Fig. 3, which corresponded to the formation of pores within the compact oxide film due to the interaction of ionic species F− and other ionic species present in the AS solution and is simulated with EEC-2 (Fig. 5(b)). On the other hand, the formation of the relatively compact passive film on the surface of the wrought sample under similar conditions was evident associated with the barrier characteristics of the oxide film. Both SLM and wrought Ti6Al4V presented two-time constant impedance spectra in DI water in addition to the inductive response at high frequency. Similarly, the wrought Ti6Al4V in DI + CaCl2 and DI + LA solutions presented the inductive response and was

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Mass concentration (g/L)</th>
</tr>
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<tbody>
<tr>
<td>Potassium thiocyanate</td>
<td>0.3</td>
</tr>
<tr>
<td>Potassium phosphate monobasic</td>
<td>0.2</td>
</tr>
<tr>
<td>Sodium phosphate dibasic</td>
<td>0.2</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>0.7</td>
</tr>
<tr>
<td>Potassium chloride</td>
<td>1.2</td>
</tr>
<tr>
<td>Sodium bicarbonate</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Table 2

AFNOR artificial saliva composition.

<table>
<thead>
<tr>
<th>No.</th>
<th>Groups</th>
<th>Solutions</th>
<th>Abbreviations</th>
<th>Composition</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Group A</td>
<td>Artificial saliva</td>
<td>AS</td>
<td>Pure AS</td>
<td>7.8–8.4</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>Artificial saliva + sodium fluoride</td>
<td>AS + F</td>
<td>NaF 1.0 g/L</td>
<td>8.0–8.5</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>Artificial saliva + calcium chloride</td>
<td>AS + CaCl2</td>
<td>CaCl2 1.1 g/L</td>
<td>7.4–8.4</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>Deionized water</td>
<td>DI</td>
<td>Pure DI</td>
<td>6.2</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>Deionized water + sodium fluoride</td>
<td>DI + F</td>
<td>NaF 1.0 g/L</td>
<td>6.6</td>
</tr>
<tr>
<td>6</td>
<td>Group B</td>
<td>Deionized water + calcium chloride</td>
<td>DI + CaCl2</td>
<td>CaCl2 1.1 g/L</td>
<td>5.3</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>Artificial saliva + lactic acid</td>
<td>AS + LA</td>
<td>pH was adjusted by LA</td>
<td>2.5</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>Deionized water + lactic acid</td>
<td>DI + LA</td>
<td>pH was adjusted by LA</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Table 3

Solutions used for electrochemical experiments.
simulated to EEC-3 as shown in Fig. 5(c). The origin of inductive response at high frequency, particularly in these solutions neglected the chances of any hardware interferences in the cell setup and may be associated with the specific adsorption of ionic species on the surface. Using these EEC models, solution resistance (R_u), charge transfer resistance (R_{ct}), barrier film resistance (R_{po}), inductor (L), constant phase element of the porous film (Y_{po}), etc. were calculated. The capacitive response of the electrical double layer was replaced by the constant phase element (Y_{dl}) due to possible specific adsorption and non-homogeneous distribution of charge within the electrical double layer that would form within the porous structure of the top layer. On the other hand, the total resistance (R_{total}) of both SLM and wrought Ti6Al4V was observed. The R_{po} of SLM Ti6Al4V was found to be lower than wrought Ti6Al4V in AS, AS+F, and AS+CaCl_2, except in AS+LA solution in which the R_{ct} of wrought was slightly lower than SLM Ti6Al4V.

From PD curves of both SLM and wrought Ti6Al4V, it is predicted that the cathodic polarization behavior was almost similar in all solutions which corresponded to the kinetics of H_2O dissociation on the oxide passive film. However, the stability of the oxide film may also be influenced by the reduction of surface oxides to native metal. Furthermore, following the cathodic polarization, the surface oxidation of these samples would lead to the formation of a passive film as evident from the limiting anodic current density (termed as passive current density). Preceding to this passivation behavior, the increase in current within the Tafel region corresponded to the active dissolution of the surface oxide in the presence of ionic species i.e. F^-, CaCl_2, and lactic acid. The transition from active to passive behavior of SLM and wrought samples in AS was also influenced by the nature of the ionic species. For instance, the positive E_{corr} and relatively small current density of SLM compared to wrought Ti6Al4V in the anodic polarization (< ~350 mV) in AS, AS+F and AS+CaCl_2 indicated the slow dissolution of the former sample under oxidizing conditions. Whereas, the SLM transition from active to passive behavior was delayed and relatively large anodic current registered by this sample indicates its large dissolution tendency in AS-lactic acid solution. This may also be associated with the high acidity of the AS solution after the addition of lactic acid. Similarly, a slight difference in the E_{corr} values of SLM and wrought Ti6Al4V was observed in AS, AS+F, and AS+CaCl_2 solutions. Moreover, the E_{corr} values of SLM Ti6Al4V were relatively positive than wrought Ti6Al4V samples in these solutions. This stability of the oxide film in AS solution was estimated from the limiting current beyond the

Table 4
Phase volume fractions of both SLM and wrought Ti6Al4V calculated from XRD patterns.

<table>
<thead>
<tr>
<th>Material</th>
<th>Volume fraction of alpha (V_p, α/α')</th>
<th>Volume fraction of beta (V_p, β)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SLM</td>
<td>78.2%</td>
<td>21.8%</td>
</tr>
<tr>
<td>Wrought</td>
<td>86.6%</td>
<td>13.4%</td>
</tr>
</tbody>
</table>

Fig. 8 and Fig. 9 show the potentiodynamic polarization (PD) curves of SLM and wrought Ti6Al4V in all solutions as given in Table 3. From the anodic and cathodic polarization curves, the Tafel slopes (β_a and β_c, respectively) were determined from the Tafel region and the values of corrosion potential (E_{corr}) and corrosion current density (i_{corr}) were determined by extrapolating the curves, and are given in Table 6.

4. Discussion

4.1. Comparison of both alloys in AS, AS+F, AS+CaCl_2, and AS+LA

In Fig. 4, the relatively steep impedance spectra of SLM compared to wrought Ti6Al4V in AS, AS+F, and AS+CaCl_2 solutions were evident except for AS+LA as shown in Fig. 4(d). These trends highlighted the relatively large R_{total} of SLM compared to wrought Ti6Al4V in AS, AS+F, AS+CaCl_2 and AS+LA solutions that was largely dominated by the resistance of barrier oxide film. However, the minor difference in the R_{po} of both SLM and wrought Ti6Al4V was observed. The R_{po} of SLM Ti6Al4V was found to be lower than wrought Ti6Al4V in AS, AS+F, and AS+CaCl_2 except in AS+LA solution in which the R_{ct} of wrought was slightly lower than SLM Ti6Al4V.

From PD curves of both SLM and wrought Ti6Al4V, it is predicted that the cathodic polarization behavior was almost similar in all solutions which corresponded to the kinetics of H_2O dissociation on the oxide passive film. However, the stability of the oxide film may also be influenced by the reduction of surface oxides to native metal. Furthermore, following the cathodic polarization, the surface oxidation of these samples would lead to the formation of a passive film as evident from the limiting anodic current density (termed as passive current density). Preceding to this passivation behavior, the increase in current within the Tafel region corresponded to the active dissolution of the surface oxide in the presence of ionic species i.e. F^-, CaCl_2, and lactic acid. The transition from active to passive behavior of SLM and wrought samples in AS was also influenced by the nature of the ionic species. For instance, the positive E_{corr} and relatively small current density of SLM compared to wrought Ti6Al4V in the anodic polarization (< ~350 mV) in AS, AS+F and AS+CaCl_2 indicated the slow dissolution of the former sample under oxidizing conditions. Whereas, the SLM transition from active to passive behavior was delayed and relatively large anodic current registered by this sample indicates its large dissolution tendency in AS-lactic acid solution. This may also be associated with the high acidity of the AS solution after the addition of lactic acid. Similarly, a slight difference in the E_{corr} values of SLM and wrought Ti6Al4V was observed in AS, AS+F, and AS+CaCl_2 solutions. Moreover, the E_{corr} values of SLM Ti6Al4V were relatively positive than wrought Ti6Al4V samples in these solutions. This stability of the oxide film in AS solution was estimated from the limiting current beyond the
critical potential, which also corresponds to the aggressiveness of the ionic species. The large $R_{po}$ and small $i_{corr}$ (in the order of $10^{-8}$ A/cm$^2$) presented by both SLM and wrought samples assured the formation of the barrier oxide film in AS solution. However, the presence of F$^-$, CaCl$_2$ and lactic acid in AS could locally dissolve the barrier oxide film as reflected by the small $R_{ct}$ values (compared to $R_{po}$) in the impedance analysis.
(caption on next page)
4.2. Comparison of both alloys in DI, DI + F, DI + CaCl2, and DI + LA

Similar to AS based solutions, SLM Ti6Al4V showed comparatively steep impedance trend as compared to wrought Ti6Al4V in DI and DI + F solutions as shown in Fig. 7 (a, b). However, SLM Ti6Al4V showed a relatively gradual impedance trend in DI + CaCl2 solution (Fig. 7 (c)) as compared to wrought Ti6Al4V. The electrochemical parameters (R_total, Rpo, and Rct) associated with these impedance trends also showed the same behavior. For instance, the SLM Ti6Al4V presented relatively higher Rpo values in comparison to wrought Ti6Al4V in DI and DI + F solutions. From the polarization trends (Fig. 9), it was observed that oxide film formed in DI water based solutions varied considerably as predicted from the different anodic polarization trends but exhibiting similar cathodic polarization trends. From Table 6, it was also evident that the SLM Ti6Al4V showed lower i_corr (45.69 and 170.9 nA/cm²) values compared to wrought Ti6Al4V (56.99 and 199 nA/cm²) in DI water and DI + F solutions. Inversely, SLM Ti6Al4V showed relatively large i_corr values in DI + CaCl2 and DI + LA solutions compared to wrought Ti6Al4V due to slightly acidic pH (<6). During impedance scan, SLM Ti6Al4V showed higher Rpo values in comparison to wrought Ti6Al4V in DI + CaCl2 and DI + LA solutions, which could be due to the resistance offered by the pre-existing oxide film present on the surface of SLM Ti6Al4V [52]. This oxide would become unstable or may re-dissolve during a cathodic polarization scan thus exposing the active surface. In DI + CaCl2 and DI + LA solutions, SLM Ti6Al4V presented higher i_corr compared to wrought Ti6Al4V (group B in Table 3). Additionally, the existence of F−, CaCl2 and lactic acid in DI water also affected the barrier properties of the oxide film. For instance, both SLM and wrought Ti6Al4V showed significantly larger i_corr values in the DI + F solution as compared to the DI solution.

4.3. Effect of microstructure on the corrosion behavior of SLM and wrought Ti6Al4V

From the electrochemical trends, it can be predicted that SLM Ti6Al4V showed higher corrosion resistance than wrought Ti6Al4V in all solutions of group A (pH above 6) depicted in Table 3. In particular, i_corr of SLM Ti6Al4V was lower than wrought Ti6Al4V in group A solutions as shown in Fig. 10. It was noticed that the corrosion resistance of SLM Ti6Al4V was higher due to the presence of relatively higher β content in comparison to the wrought Ti6Al4V as given in Table 4. Alternatively, Dai et al. [39] reported inferior corrosion behavior of SLM Ti6Al4V as compared to wrought Ti6Al4V. The poor performance of SLM Ti6Al4V was considered primarily due to the lack of higher β contents in the SLM sample compared to the wrought sample. It has been found in the literature that β contents can be varied in SLM Ti6Al4V by printing in different build orientations that may ultimately improve its corrosion resistance [53]. Furthermore, the electrolyte used in this study was NaCl solution, which adds a significant amount of chloride ions that may locally produce HCl within the crevices and could adversely affect the integrity of the SLM Ti6Al4V dental implants. Analysis of β and α/α′ phases has revealed that these are primarily stabilized by the vanadium and aluminum additions, respectively [48]. Vanadium has a strong tendency to form a passive oxide layer on the surface of Ti6Al4V, which could enhance the corrosion resistance of Ti6Al4V [13,44]. Inversely, the corrosion resistance of SLM Ti6Al4V was decreased in the acidic solutions (pH below 6 designated as group B in Table 3 and Fig. 10) compared to wrought Ti6Al4V. In contrast to
SLM, wrought Ti6Al4V has a relatively higher aluminum enriched alpha phase, which was found to enhance corrosion resistance in the acidic solution. It has been reported that with the increase in the alpha phase in various heat-treated Ti6Al4V alloy, the corrosion resistance was significantly improved in 3.5 M HCl solution [54]. It is evaluated that due to the presence of a large α/α′ phase in the wrought Ti6Al4V than SLM Ti6Al4V, the samples of the former alloy presented relatively high corrosion resistance in group B solutions.

4.4. Effect of ionic species on the stability of passive oxide film

Various types of oxide species may form on the titanium surface such as TiO, TiO2, TiO2·H2O, TiO2·2H2O and Ti3O7 when it is exposed to aqueous media as reported in the literature [55]. Besides these oxides, the oxides of alloying elements i.e. Al2O3, Nb2O5 and VOx. Al2O3 may also form on Ti6Al4V that may contribute to the protection of Ti6Al4V from corrosion [31]. Mainly anhydrous TiO2 and small amounts of hydrous TiO2, Al2O3 and VOx contribute to the barrier characteristics of the passive film and its stability in various conditions under ambient conditions [19,45,55]. In this study, the effect of fluoride, calcium chloride and lactic acid on the stability of passive oxide film that may form on the surface of both SLM and wrought Ti6Al4V has been explained in the following sections.

4.4.1. Effect of fluoride (F)

It was observed that both SLM and wrought Ti6Al4V showed...
depressed impedance behavior in the presence of fluoride in AS and DI solutions. Further analysis revealed that both Ti6Al4V showed a minor increase in $i_{\text{corr}}$ values with the addition of F$^-$ ions in the AS solution. This behavior may be attributed to relatively large oxide film stability at slightly basic pH (8.0–8.5) changed by the addition of NaF in AS. The higher concentration of fluoride (1000 ppm) at near-neutral or at slightly basic pH is reported to be least corrosive towards titanium alloys. However, small concentrations of fluoride (500 ppm) could significantly increase the corrosion rate of titanium alloys in electrolytes having slightly acidic pH [56]. Similarly, significantly low corrosion resistance was presented by both samples in DI + F solution as predicted from the appreciably high $i_{\text{corr}}$ values (199 and 170.9 nA/cm$^2$ for wrought and SLM Ti6Al4V, respectively) due to decrease in pH to 6.6 by the addition of F$^-$ in DI water. The increase in $i_{\text{corr}}$ values indicated the deterioration of barrier oxide film on both Ti6Al4V. Licausi et al. [31] reported the behavior of fluoride ions in very mild acidic saliva (pH = 6.5) and confirmed that the formation of low concentrations of HF could affect the corrosion behavior of Ti6Al4V. Several other studies [24, 28, 29], also suggested the formation of small

![Fig. 9. Potentiodynamic polarization curves of SLM and wrought Ti6Al4V in (a) DI water (b) DI + F solution, (c) DI + CaCl$_2$ solution, and (d) DI + LA solution.](image)

Table 6

<table>
<thead>
<tr>
<th>Solutions</th>
<th>Materials</th>
<th>$E_{\text{corr}}$ (mV)</th>
<th>$i_{\text{corr}}$ (nA/cm$^2$)</th>
<th>$b_a$ (mV/decade)</th>
<th>$b_c$ (mV/decade)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AS</td>
<td>SLM</td>
<td>$-188 \pm 17$</td>
<td>$68.89 \pm 7.67$</td>
<td>278</td>
<td>$-121$</td>
</tr>
<tr>
<td>Wrought</td>
<td></td>
<td>$-226 \pm 15$</td>
<td>$80.14 \pm 7.48$</td>
<td>232</td>
<td>$-188$</td>
</tr>
<tr>
<td>AS + F</td>
<td>SLM</td>
<td>$-217 \pm 17$</td>
<td>$65.37 \pm 6.78$</td>
<td>262</td>
<td>$-117$</td>
</tr>
<tr>
<td>Wrought</td>
<td></td>
<td>$-260 \pm 28$</td>
<td>$76.78 \pm 4.60$</td>
<td>230</td>
<td>$-235$</td>
</tr>
<tr>
<td>AS + CaCl$_2$</td>
<td>SLM</td>
<td>$-165 \pm 5$</td>
<td>$68.31 \pm 6.27$</td>
<td>294</td>
<td>$-168$</td>
</tr>
<tr>
<td>Wrought</td>
<td></td>
<td>$-156 \pm 4$</td>
<td>$90.29 \pm 5.86$</td>
<td>238</td>
<td>$-230$</td>
</tr>
<tr>
<td>AS + LA</td>
<td>SLM</td>
<td>$-176 \pm 20$</td>
<td>$133.04 \pm 9.94$</td>
<td>219</td>
<td>$-240$</td>
</tr>
<tr>
<td>Wrought</td>
<td></td>
<td>$-101 \pm 18$</td>
<td>$90.66 \pm 6.16$</td>
<td>302</td>
<td>$-235$</td>
</tr>
<tr>
<td>DI</td>
<td>SLM</td>
<td>$-343 \pm 7$</td>
<td>$51.79 \pm 9.41$</td>
<td>225</td>
<td>$-304$</td>
</tr>
<tr>
<td>Wrought</td>
<td></td>
<td>$-263 \pm 5$</td>
<td>$59.79 \pm 9.75$</td>
<td>228</td>
<td>$-318$</td>
</tr>
<tr>
<td>DI + F</td>
<td>SLM</td>
<td>$-467 \pm 14$</td>
<td>$218.96 \pm 4.07$</td>
<td>181</td>
<td>$-351$</td>
</tr>
<tr>
<td>Wrought</td>
<td></td>
<td>$-397 \pm 19$</td>
<td>$249.66 \pm 21.15$</td>
<td>195</td>
<td>$-333$</td>
</tr>
<tr>
<td>DI + CaCl$_2$</td>
<td>SLM</td>
<td>$-314 \pm 7$</td>
<td>$58.46 \pm 4.80$</td>
<td>220</td>
<td>$-295$</td>
</tr>
<tr>
<td>Wrought</td>
<td></td>
<td>$-297 \pm 3$</td>
<td>$47.06 \pm 5.35$</td>
<td>217</td>
<td>$-309$</td>
</tr>
<tr>
<td>DI + LA</td>
<td>SLM</td>
<td>$-256 \pm 10$</td>
<td>$63.23 \pm 13.50$</td>
<td>167</td>
<td>$-153$</td>
</tr>
<tr>
<td>Wrought</td>
<td></td>
<td>$-222 \pm 18$</td>
<td>$45.03 \pm 2.79$</td>
<td>194</td>
<td>$-229$</td>
</tr>
</tbody>
</table>

![Fig. 10. Corrosion current density trend of SLM and wrought Ti6Al4V in group A and B solutions.](image)
amounts of HF as a result of fluoride addition with water. The passive titanium oxide may react with HF and form soluble titanium fluoride species as a result of the following reactions:

\[
\text{TiO}_2 + 4\text{HF} \rightarrow \text{TiF}_4 + 2\text{H}_2\text{O} \quad (2)
\]

\[
\text{TiO}_2 + 2\text{HF} \rightarrow \text{TiF}_2 + \text{H}_2\text{O} \quad (3)
\]

\[
\text{Ti}_2\text{O}_3 + 6\text{HF} \rightarrow 2\text{TiF}_3 + 3\text{H}_2\text{O} \quad (4)
\]

Among these species, TiF\(_4\) is soluble, and this chemical dissolution of titanium oxide film could expose the substrate to the solution. The bare surface of these alloys could experience severe corrosion of the substrate as evident for the large \(i_{corr}\) value. Other fluoride species may also adversely affect the pitting resistance of titanium as reported by Julio et al. [57].

4.4.2. Effect of calcium chloride (CaCl\(_2\))

In comparison to the AS solution, both SLM and wrought Ti6Al4V samples indicated enhanced total resistance value in the AS + CaCl\(_2\) solution. Due to the semi-conductive nature of TiO\(_2\), the calcium and phosphate interact with the surface layer and form complexes before precipitating [34,35]. In other words, this behavior could be due to the interaction of calcium and phosphate species with a TiO\(_2\) surface, which may adsorb on the oxide film and could further enhance its barrier characteristics. There are two types of hydroxyl groups attached to titanium oxide, which form hydrated titanium oxide as explained by Alkhateeb et al. in [58]. One of the hydroxyl groups attached to the hydrated titanium oxide (OH group) behaves like an acidic OH group, which attracts calcium and phosphate ions from the solution. Due to this attraction, calcium and phosphate ions may adsorb on both the SLM and wrought Ti6Al4V that resulted in the increase of \(R_n\) as mentioned in Table 5. During polarization scans, both SLM and wrought Ti6Al4V showed reduced corrosion resistance in AS + CaCl\(_2\) as compared to the AS solution. The increase in \(i_{corr}\) values could be due to the attack of chloride ions on the barrier oxide film present on both Ti6Al4V [59].

4.4.3. Effect of lactic acid (LA)

From Table 6, the \(i_{corr}\) of both Ti6Al4V was found to be increased by the addition of lactic acid in AS and DI water. Moreover, the \(R_n\) was also reduced by one order of magnitude in AS + LA solution compared to the \(R_n\) observed in plain AS solution. These electrochemical trends suggested the instability of passive oxide film in the presence of lactic acid, which could have possibly decreased the corrosion resistance of both Ti6Al4V samples. In other words, lactic ions (L\(^-\)) from the lactic acid caused the accelerated dissolution of titanium surface. The corrosion started with the complication of an oxide film with Cl\(^-\) ions that may be replaced by the L\(^-\) ions in the solution [26,60] according to reactions 5 and 6 given below.

\[
\text{TiO}_2^{3+} + \text{Cl}^- + 2\text{H}_2\text{O} \rightarrow [\text{Ti(OH)}_3]_\text{Cl} + \text{H}^+ \quad (5)
\]

For instance, [Ti(OH)\(_3\)]\(^+\) complex formed by the hydrolysis of Ti could locally decrease the pH at the surface (by the generation of H\(^+\)). These species could interact with the lactate ions (L\(^-\)) and may further enhance the dissolution of the oxide film.

\[
[\text{Ti(OH)}_3]_\text{Cl} + \text{L}^- \rightarrow [\text{Ti(OH)}_3]_\text{L} + \text{Cl}^- \quad (6)
\]

Similarly, the polarization trends of both Ti6Al4V indicated increased \(i_{corr}\) values in the DI + LA solution compared to in DI solution. These trends further confirmed the adverse effect of lactic acid on the corrosion resistance of both Ti6Al4V.

5. Conclusions

Corrosion behavior of the SLM Ti6Al4V and wrought Ti6Al4V was investigated in artificial saliva (AS, AS + F, AS + CaCl\(_2\), and AS + LA solutions) and deionized water (DI, DI + F, DI + CaCl\(_2\), and DI + LA solutions) based solutions. The following conclusions can be drawn:

1. Microstructural examination of SLM Ti6Al4V revealed a relatively fine and higher concentration of β content as compared to wrought Ti6Al4V. The rapid cooling during selective laser melting process resulted in the microstructural variations of SLM Ti6Al4V. XRD analysis also confirmed the presence of a higher β phase in the SLM Ti6Al4V as compared to wrought.

2. The corrosion resistance of SLM Ti6Al4V was higher as compared to wrought Ti6Al4V in AS, AS + F, AS + CaCl\(_2\), DI and DI + F solutions having pH > 6. In these solutions, higher β content enhanced the corrosion resistance of SLM Ti6Al4V as compared to wrought Ti6Al4V.

3. Wrought Ti6Al4V showed increased corrosion resistance in AS + LA, DI + CaCl\(_2\) and DI + LA solutions (pH below 6) due to higher α/α’ phase in comparison to SLM Ti6Al4V.

4. Both SLM and wrought Ti6Al4V depicted significantly reduced corrosion resistance in AS + LA and DI + F solutions.

CRediT authorship contribution statement

Hafiz Muhammad Hamza: Investigation, Writing - original draft, Validation, Formal analysis. Kashif Mairaj Deen: Conceptualization, Methodology, Writing - review & editing. Waseem Haider: Supervision, Resources, Project administration, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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