Titanium alloys are known for their excellent biocompatible properties. The development of additive-manufacturing technologies has increased the interest in the use of Ti-6Al-4V, produced by selective laser melting (SLM) method, also in dentistry, i.e., prosthetics and orthodontics. In the present paper, the effect of laser printing parameters in the selective laser melting (SLM) process on the porosity and corrosion behavior of Ti-6Al-4V dental alloy was metallographically and electrochemically studied. All the tests were performed in artificial saliva at 37 °C. Different forms of Ti-6Al-4V alloy were selected: a reference sample, i.e., pre-fabricated milling disc in wrought condition and four different 3D-printed samples made from Ti-6Al-4V powder using the SLM method, one being heat treated. Electrochemical, spectroscopic and hardness measurements were employed in the study. It was shown that the SLM-produced Ti-6Al-4V samples with different printing parameters have similar microstructural and electrochemical properties, while the electrochemical properties of a reference and thermally treated 3D-printed sample were different, most probably due to the change in the microstructure of the alloys. The corrosion properties were related to the microstructural properties as well as to the pore density.

Keywords: Ti-6Al-4V, dental alloys, artificial saliva, selective laser melting, corrosion

Titanium and titanium-based alloys are widely applied in biomedical and dental applications. They possess favorable mechanical properties such as high tensile strength, toughness and ductility.1 The most important feature for biomedical and dental application is thus their chemical inertness through corrosion resistance and biocompatible properties.2

In dentistry, Ti and titanium alloys are used for different applications, such as dental implants, crowns and bridges, posts and cores in prosthodontics and NiTi archwires in orthodontics.3 With the recent rapid development of additive-manufacturing technologies, the selective laser melting (SLM) procedure replaces precision metal casting technology and is being employed in dentistry for custom-made options, rapid in-lab fabrication and lower material usage.4

The biocompatible properties of Ti and Ti alloys are due to a thin oxide layer that forms at the surface.5 This oxide layer is approximately 2–5 nm thick, if grown naturally upon exposure to air.6 If grown in a corrosive solution such as simulated body fluid, its thickness was reported7 to be 9 nm at 2.5 V, if fretted, thicker oxide layers were reported to increase to 30 nm, studied by XPS.9 In simulated saliva the oxides on Ti, Ti-6Al-4V and Ti-6Al-7Nb vary and reach up to 21 nm, while in the presence of 0.25 % NaF, the oxide thickness was reduced.10,11 Oxide layers are formed in the anodic regime than in the cathodic regime.8 In general, the passive film consists of a dense inner oxide layer and a porous outer layer, which was confirmed electrochemically and spectroscopically decades ago.10,11

In simulated saliva the oxides on Ti, Ti-6Al-4V and Ti-6Al-7Nb vary and reach up to 21 nm, while in the presence of 0.25 % NaF, the oxide thickness was reduced. In simulated saliva the oxides on Ti, Ti-6Al-4V and Ti-6Al-7Nb vary and reach up to 21 nm, while in the presence of 0.25 % NaF, the oxide thickness was reduced. In simulated saliva the oxides on Ti, Ti-6Al-4V and Ti-6Al-7Nb vary and reach up to 21 nm, while in the presence of 0.25 % NaF, the oxide thickness was reduced.
plasma and thermal oxidation.\textsuperscript{6,13,14} The thickness of the oxide can be tailored with artificial passivation\textsuperscript{6} in H\textsubscript{3}PO\textsubscript{4}, H\textsubscript{2}O\textsubscript{2} or nitric acid, reaching thicknesses up to 400 nm by anodization in NaOH.

With the implementation of Ti-6Al-4V products, produced by selective laser melting, the need for knowledge of their mechanical, microstructural and corrosive behavior increases in order to understand differences and possible effects when compared to wrought alloys and cast procedures. The research in the field has increased immensely with different focuses in their studies: the effect of recycled powder, the position on the SLM printing board, the effect of laser power density and similar.

Titanium alloys comprising both \(\alpha\)-Ti and \(\beta\)-Ti are most often used in aircraft. Ti-6Al-4V is the most common \(\alpha + \beta\)-Ti alloy, which possesses a high creep resistance and toughness (from the \(\alpha\)-Ti) and high strength and fatigue resistance (from the \(\beta\)-Ti).\textsuperscript{15,16} The microstructure is affected to a great extent by the production technology and post heat treatments.\textsuperscript{17}

In this paper different laser powers and laser speeds, i.e., laser power densities, both as printed and heat treated, are studied and compared to the reference wrought alloy. The microstructural, physical and corrosive properties of the different forms of Ti-6Al-4V alloys were defined and compared. The effects of microstructure, porosity, and hardness were sought in relation to the properties of corrosion and performance.

2 EXPERIMENTAL PART

For samples produced by the SLM procedure, the Ti-6Al-4V powder was from S&S Scheftner GmbH as powder (Starbond Ti4Powder 45) with the chemical composition 89.0 w/% Ti, 6.0 w/% Al, 4.0 w/% V with N, C, H, Fe and O < 1.0 w%. The following printing parameters were used: laser power 60 W, 75 W and 90 W with various travel velocities of 520 mm/s and 805 mm/s, with a hatch distance of 0.025 mm and a layer thickness 0.025 mm. The calculated energy density and sample description are given in Table 1. One sample was heat treated in argon at 1000 °C for 1 h and cooled down to 500 °C in the furnace, followed by cooling in the air. The reference sample of Ti-6Al-4V was supplied by Goodfellow in the wrought and annealed condition, with chemical composition consisting of 90.0 w/% Ti, 6.0 w/% Al and 4.0 w/% V.

Light microscopy on the metallographically prepared samples at different magnifications was executed using a Carl Zeiss metallographic microscope (Germany, 2009) to reveal the microstructure as well as the pore share at the cross-section of the samples (metallographic photographs were analyzed by ImageJ software to determine the percentage of porosity). The relative density was estimated by Archimedes’ method in 96 % ethanol. Vickers hardness measurements (HV 0.3) were conducted according to the standard\textsuperscript{18} ISO 6507-1: 2018 using a EMCO DuraScan 70 G5 hardness-testing machine (Austria, 2022).

Electrochemical tests were conducted using a Gamry ref 600+ Potentiostat/Galvanostat (USA, 2015). First, the open-circuit potential (OCP) was measured for at least 1 h, or until a steady state was reached. Linear polarization measurements followed at a scan rate of 0.1 mV/s in the potential range \(\pm 20\) mV vs \(E_{\text{corr}}\) (results not shown in this study). Electrochemical impedance spectroscopy measurements were then conducted by measuring the impedance at frequencies between 65 kHz and 1 mHz, applying a perturbation signal of 20 mV and measuring 7 points per decade. Finally, potentiodynamic measurements were executed, starting \(-250\) mV cathodically vs \(E_{\text{corr}}\), progressing in the anodic direction up to 3.2 V or 1 mA/cm\(^2\) at a scan rate of 1 mV/s. Then, the electrochemical parameters were extracted from electrochemical measurements using Echem Analyst Software.

The corrosion cell for the electrochemical tests consisted of an assembly of three electrodes in a jacked cell with a volume of \(V = 350\) cm\(^3\), using an Ag/AgCl reference electrode and a graphite rod as a counter electrode. The areas of the working electrodes were 0.64 cm\(^2\) for the 3D-printed samples and 0.785 cm\(^2\) for a reference sample in the form of a disc with 15 mm diameter. All the results presented were normalized.

Artificial saliva\textsuperscript{15} was prepared to contain 0.6 g/L NaCl, 0.72 g/L KCl, 0.22 g/L CaCl\(_2\)-2 H\textsubscript{2}O, 0.68 g/L KH\textsubscript{2}PO\textsubscript{4}, 0.856 g/L Na\textsubscript{2}HPO\textsubscript{4}·12 H\textsubscript{2}O, 0.060 g/L KSCN, 1.5 g/L KHCO\textsubscript{3} and 0.03 g/L citric acid with a pH 6.5. All the measurements were conducted at 37 °C.

All the specimens were wet grinded with 1200–grit SiC emery paper and afterwars ultrasonically cleaned in acetone for 3 min.

<table>
<thead>
<tr>
<th>Ti-6Al-4V sample</th>
<th>Laser power (W)</th>
<th>Laser speed (mm/s)</th>
<th>Energy (J/mm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>SLM-60-520</td>
<td>60</td>
<td>520</td>
<td>132</td>
</tr>
<tr>
<td>SLM-75-805</td>
<td>75</td>
<td>805</td>
<td>106</td>
</tr>
<tr>
<td>SLM-75-805-HT   (heat treated)</td>
<td>75</td>
<td>805</td>
<td>106</td>
</tr>
<tr>
<td>SLM-90-520</td>
<td>90</td>
<td>520</td>
<td>198</td>
</tr>
<tr>
<td>Ti-6Al-4V-reference</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

3 RESULTS AND DISCUSSION

3.1 Microstructure, porosity and hardness

First, the SLM-manufactured Ti-6Al-4V samples were metallographically prepared (Figure 1). The microstructural investigation is presented in Figure 1 and the porosity study is presented in Figure 2 using light microscopy.

The microstructures of the SLM-fabricated samples are similar, regardless of the different printing parameters and consist of martensite (\(\alpha'\)), as can be observed from Figure 1c. The inset in Figure 1b presents a
heat-treated sample where a more defined microstructure is observed. A previous martensitic microstructure underwent temperature transformation above β-transus and during cooling to the room temperature, it transformed to the so-called Widmanstätten/basket-weave microstructure consisting of α-phase lamellas separated by β plates within large (100–250 μm) primary β grains and α-phase along the grain boundaries. The reference sample in Figure 1d consisted of globular α + β microstructure (dark regions represent β-phase), typical for a wrought Ti-6Al-4V alloy in the annealed condition.

The porosity of each sample was defined at a 12.5× magnification with image analysis using ImageJ software according to the standard ASTM E2109-01. Hardness measurements were then executed with a minimum of six measurements taken for each sample. The results of the porosity, relative density determined by Archimedes’ method and hardness are presented in Table 2.

All the observed SLM-manufactured Ti-6Al-4V samples were very rough at the surface since no post surface treatment was made at the supplier. The porosity of the SLM printed samples is related to the laser power density. Lower laser-power densities (samples SLM-60-520 and SLM-75-805) resulted in a higher porosity. For these two samples it was 0.4 % and 0.5 %, respectively. The lowest laser-power density and heat treatment for sample SLM-75-805, as well as the highest laser-power density resulted (SLM-60-520) in the lowest porosity of 0.1 % (Figures 2c and 2d). The relative density, estimated by Archimedes’ method, was the highest for the heat treated SLM-75-805, which indicates the lowest porosity as determined by microscopic method. On the other hand, the
The lowest relative density was measured for the specimen SLM-90-520 with the lowest porosity. It can be assumed that the relative density is strongly related to the surface roughness and not so much to the internal porosity of the specimens. The relative density of the other two specimens (SLM-75-805 and SLM-60-520) was in between the previously mentioned two specimens.

The Vickers hardness was measured as well. This depends on the microstructure, since there are two distinctive HV values, i.e., for a sample that was heat treated it was lower at (318 ± 25) HV, but for the other SLM-printed sample it was higher and with similar values at (393 ± 26) HV and (394 ± 25) HV for SLM-60-520 and SLM-75-805, respectively. However, the specimen SLM-90-520 printed with the highest laser energy density has the highest hardness, which is very probably the result of the highest temperature difference between the melted surface and the environment, and subsequently the fastest cooling rate.

### Table 2: Vickers hardness and porosity values for 3D-printed Ti-6Al-4V samples

<table>
<thead>
<tr>
<th>Ti-6Al-4V sample</th>
<th>Porosity (%)</th>
<th>Density (g/cm³)</th>
<th>HV 0.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>SLM-60-520</td>
<td>0.4</td>
<td>4.364 ± 0.022</td>
<td>393 ± 26</td>
</tr>
<tr>
<td>SLM-75-805</td>
<td>0.5</td>
<td>4.357 ± 0.054</td>
<td>394 ± 25</td>
</tr>
<tr>
<td>SLM-75-805-HT</td>
<td>0.1</td>
<td>4.389 ± 0.038</td>
<td>318 ± 25</td>
</tr>
<tr>
<td>SLM-90-520</td>
<td>0.1</td>
<td>4.333 ± 0.033</td>
<td>420 ± 26</td>
</tr>
</tbody>
</table>

### 3.2 Open-circuit potential measurements

Corrosion studies included a measurement of the open-circuit potential, a linear polarization measurement, the electrochemical impedance spectroscopy and potentiodynamic measurements. The results of the linear polarization measurements are not presented in this study.

When the Ti-6Al-4V samples were immersed in artificial saliva at 37 °C, the potential slowly started to increase (Figure 3). The increase in potential upon exposure to the saliva indicates the growth of a passive layer. The lowest potential was measured for the reference Ti-6Al-4V sample, reaching a value of −0.50 V after 1 h of exposure time, with very similar value for SLM-60-520, i.e., −0.46 V.

The most positive OCP potential of the SLM-fabricated SLM-75-805 was at −0.397 V after 1 h of exposure in saliva at 37 °C. The SLM-fabricated samples with a higher or lower laser power (SLM-90-520) had a more negative potential (between the reference and the SLM-75-805 fabricated sample) after 1 h of exposure to artificial saliva at 37 °C. The small potential change during the exposure of the TiAlV alloy to simulated saliva points to a relatively stable process observed between the Ti oxide and the artificial saliva.
3.3 Electrochemical impedance measurement

The electrochemical impedance measurements (EIS) were taken once the steady state was reached (Figure 4). It can be observed that the impedance responses for the Ti-6Al-4V reference and SLM samples are different. The highest impedance response was measured for the SLM-75-805, where the absolute impedance at the lowest measured frequency was 1.27 MΩ·cm². This particular sample also had the highest porosity of 0.5 %. A higher porosity resulted in a larger specific area and thus a higher value of the impedance response. A similar observation was reported earlier, where the high porosity was reflected in the higher corrosion-resistance values of the CoCr alloys as well.22 The thermally treated (SLM-75-805-HT) sample had the lowest absolute impedance at 0.577 MΩ·cm². The reference Ti-6Al-4V sample had an absolute impedance value of 0.724 MΩ·cm².

Minor differences can be observed from the EIS results, but no distinctive difference could be revealed when the SLM-printed samples were compared to the reference wrought alloy of Ti-6Al-4V. The differences were related to the presence of pores and not directly correlated to the laser energy density of the studied samples. Microstructural changes of the heat-treated sample resulted in a lower corrosion resistance.

3.3 Potentiodynamic polarization measurement

Potentiodynamic curves for the reference material and the SLM-printed Ti-6Al-4V alloy are given in Figure 5 and the electrochemical parameters are extracted in Table 3. The corrosion potential, \(E_{\text{corr}}\), was similar in all the samples. The values of the corrosion-current density, \(j_{\text{corr}}\), were also similar for all the samples, with values between 25.8 nA/cm² and 58.4 nA/cm².

Potentiodynamic curves for the studied samples had similar cathodic behavior. In the anodic region, passive behavior was observed with a constant passive-current density of the order of 4–5 μA/cm², similar for all the samples up to 1.2 V. Then, some differences in the anodic behavior were observed. Namely, for the reference Ti-6Al-4V and the heat-treated sample 75-805-HT, an anodic peak was observed, which showed similarities between these two samples. That might be due to the fact that the microstructures of these two specimens do not contain \(\alpha'\) martensitic phase, but \(\alpha + \beta\). A similar current peak was observed in the survey of Aziz-Kerrzo for a Ti-6Al-4V alloy.10 From the literature, there is no consensus as to which microstructure of this alloy has the best corrosion properties (martensitic \(\alpha'\) or \(\alpha + \beta\)). How-
ever, in the literature we found that between $\alpha$ lamellas and $\beta$ plates in $\alpha + \beta$ microstructure the galvanic effect could affect the preferential corrosion of the $\beta$-phase.\textsuperscript{23} In addition, martensitic $\alpha'$ microstructure enables the formation of a more homogenous passive layer than the $\alpha + \beta$, and thus a better corrosion performance.\textsuperscript{24}

3.3 Optical microscopy

Following the potentiodynamic (PD) scans, the surfaces exposed to artificial saliva were inspected. As observed from the images after the PD scans, defects in the form of spots can be seen.

The 3D-printed sample with a higher porosity (SLM-60-520 and SLM-77-805) showed the highest number of spots with a discoloured surface in Figure 6. One spot was found on the SLM-90-520 specimen, and no spots are present after the PD measurements on the SLM-75-805-HT and the reference specimens.

4 CONCLUSIONS

This research investigated a Ti-6Al-4V dental alloy in artificial saliva at 37 °C. Different forms of Ti-6Al-4V alloy were studied, i.e., three samples made from Ti-6Al-4V powder using the selective laser melting (SLM) method, one sample being also thermally treated and compared to a reference Ti-6Al-4V alloy.

The microstructural, physical and corrosion studies showed that:
1) All the SLM-printed samples contained a certain amount of porosity, whereas the reference sample did not. The high porosity is related to the printing parameters with lower laser energy density. The higher energy density and heat treatment resulted in a lower micro-porosity.
2) After 1 h of immersion in the artificial saliva the corrosion potential was more positive in the SLM-printed Ti-6Al-4V samples when compared to the reference sample.
3) Electrochemical impedance spectroscopy measurements and potentiodynamic measurements showed complementary electrochemical properties; the reference and heat-treated samples had very similar properties observed by potentiodynamic scans, while the EIS showed diverse properties due to different levels of porosity.
4) When comparing the hardness of the different SLM-fabricated Ti-6Al-4V samples, the heat-treated sample had a lower hardness due to the globular microstructure consisting of $\alpha + \beta$. The highest porosity was measured for the SLM-90-520 specimen, printed with the highest laser-power density and it can be contributed to the highest cooling rate due to the highest temperature difference.
5) Due to the characteristics of the printed samples it can be concluded that metal frameworks fabricated by SLM technology in clinical practice are suitable for long-span bridges in fixed prosthodontics.

Acknowledgments

The financial support of the Slovenian Research Agency (SRA), under grant No L2-1831, is hereby gratefully acknowledged. Great thanks to Tanja Antičič for preparing the metallographic specimen and Jošt Oblak for performing electrochemical experiments. The financial support of Imedika, Prodent, Dentalia, AO American Orthodontics, Dentas, Zavod MD-RI Institut za raziskavo materialov v medicini is greatly acknowledged.

5 REFERENCES

7 I. Milošev, M. Metikos-Huković, H. H. Strehblow, Passive film on orthopaedic TiAlV alloy formed in physiological solution investi-
gated by X-ray photoelectron spectroscopy, Biomaterials, 21 (2000), 2103–2113, doi:10.1016/s0142-9612(00)00145-9
20 ASTM E2109-01, Standard test methods for determining area percentage porosity in thermal sprayed coatings, doi:10.1520/E2109-01R14