Manufacture by selective laser melting and mechanical behavior of a biomedical Ti–24Nb–4Zr–8Sn alloy

L.C. Zhang, a,* D. Klemm, b J. Eckert, b,c Y.L. Hao d and T.B. Sercombe a

School of Mechanical and Chemical Engineering, M050, The University of Western Australia, 35 Stirling Highway, Crawley, Perth, WA 6009, Australia

b IFW Dresden, Institute for Complex Materials, P.O. Box 27 01 16, D-01171 Dresden, Germany

c TU Dresden, Institute of Materials Science, D-01062 Dresden, Germany

d Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang 110016, China

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In this paper, we present the results of using selective laser melting (SLM) to produce biomedical beta Ti–24Nb–4Zr–8Sn components, including the manufacture of a sample acetabular cup. The density of the material increases with increasing incident laser energy (i.e. decreasing laser scan speed) and reaches a near full density value of >99% without any post-processing. The mechanical properties of the as-processed material are also compared to those of conventionally processed material.

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Titanium alloys are receiving a great deal of attention with regard to both medical and dental applications [1,2]. One of the significant drawbacks of the traditional biomedical α + β titanium alloys (such as the ubiquitous Ti–6Al–4V) is that they have a modulus ~10 times that of bone. Mismatch of the moduli between the implant and surrounding bone can cause stress shielding in bone [1,2]. This eventually leads to bone resorption, and is one of the primary causes of implant loosening, which requires painful revision surgery [1]. Low-modulus beta titanium alloys comprising non-toxic and non-allergic elements are currently being developed for the next generation of metallic implant material [1,3]. Gum Metal (Ti–36Nb–2Ta–3Zr–0.3O) [4–6] and Ti2448 (Ti–24Nb–4Zr–8Sn) [7,8] (all compositions in wt.%) are two groups of representative beta titanium alloys which possess an improved balance of low modulus and high strength. For example, Gum Metal has a high strength of 1000–1200 MPa and a large reversible elastic strain (superelasticity) of ~2.5%, coupled with a low modulus of 55–75 GPa [4]. The Ti2448 alloy exhibits a low modulus of 42–55 GPa as well as strength between 800 and 1200 MPa depending on processing and heat treatment [7–9]. Both alloys exhibit the unusual deformation behavior of nonlinear elasticity and highly localized plasticity [7–10] in spite of the significant differences in composition and processing [5,6,9,10].

For patients with extensive bone loss or deformities, standard off-the-shelf orthopedic implants often do not provide an acceptable clinical solution. In order to successfully treat such patients, customized devices with the external geometry derived from the patient’s computed tomography or magnetic resonance imaging data must be manufactured. Such customized devices have the potential to reduce surgery, recovery and rehabilitation times, restore correct joint kinetics, improve implant fixation and reduce the likelihood of revision surgery [11]. These combined factors reduce the patients’ pain and suffering, and should result in a considerable reduction in hospitalization time and medical costs. Emerging advanced manufacturing technologies such as selective laser melting (SLM) are providing the ideal platform for the creation of these customized devices. SLM facilitates the manufacture of parts with almost no geometric constraints and is economically feasible down to a batch size of one. It is a powder-based, layer-additive manufacturing technology, whereby parts are built by melting selected areas of a powder layer using a high-intensity laser beam. Three-dimensional parts are then
manufactured by sequential production of these two-dimensional layers. Although SLM has been applied to the manufacture of titanium components, this has been limited to the traditional $\alpha + \beta$ alloys Ti–6Al–4V [12,13] and Ti–6Al–7Nb [14].

In this work, we used SLM to produce low-modulus, biomedical beta titanium components. The processing–microstructure–property relationship and the deformation behavior of the material have also been investigated. In addition, we have successfully manufactured a sample acetabular cup, complete with complex outer scaffold structure.

The Ti–24Nb–4Zr–8Sn powder used in this work was gas atomized from a Ti2448 ingot fabricated by vacuum arc remelting [7]. The powder was spherical, and between 45 and 100 $\mu$m in diameter. Parts were manufactured using an MTT SLM 250 HL machine under a high-purity Ar atmosphere containing no more than 100 parts per million oxygen. The machine was equipped with a 400 W Yb:YAG fiber laser, which had a spot size of 80 $\mu$m. Small cubes (7 $\times$ 7 $\times$ 7 mm) were manufactured using a laser power of 200 W and laser scan speeds of between 50 and 900 mm s$^{-1}$. The layer thickness was kept constant at 100 $\mu$m. X-ray diffraction (Siemens D5000 diffractometer) was used to confirm that all samples consisted of a single $\beta$ phase after building. The density was measured using Archimedes’ method and is presented as a percentage of the solid ingot density, which was assumed to be fully dense. For each condition, three specimens were measured and the results were averaged. The deviation in these measurements was less than 0.3%. The microstructure of $X$–$Y$ cross-sections (i.e. in the plane of one layer) of the cubes was examined by mounting them in epoxy, polishing using standard metallographic techniques and finishing on 0.04 $\mu$m colloidal silica. Samples were etched with Kroll’s Reagent and investigated using an Olympus PMG 3 microscope. Fracture morphologies were observed with a Zeiss 1555 scanning electron microscope (SEM). The Vickers hardness was measured on the polished cross-sections using a Mitutoyo AVK-C2 Hardness Tester with a 50 g load. An average of 10 indents was taken for each condition. Tensile specimens with a rectangular cross-section of 4 $\times$ 5 mm and a gauge length of 12 mm were machined from manufactured bars and tested in the build (Z) direction. The tensile tests were carried out using either loading/unloading cycles or until rupture in an Instron 5584 machine at a strain rate of $1.3 \times 10^{-4}$ s$^{-1}$. For cyclic testing, six loading/unloading cycles were conducted in 1% steps up to 6% strain [7,8]. The reported tensile properties are the average of three individual samples. The oxygen content of the as-received powder and of the manufactured samples was measured by carrier gas hot extraction to be 0.17 and 0.21 wt.%, respectively.

Figure 1 shows the effect of laser scan speed on the density of the laser melted samples. There is a general decrease in density and hardness with increasing scan speed. Individual points are an average of 3 and 10 tests for density and hardness, respectively. Error bars in the hardness data show one standard deviation. For the density data, the error bars are smaller than the data point (0.3%).

The Vickers hardness at different laser speeds is also shown in Figure 1. For speeds higher than 300 mm s$^{-1}$ there is a strong correlation between Vickers hardness and density. At speeds less than 300 mm s$^{-1}$ the hardness remains high, despite the decreasing density. This is ascribed to the fact that these samples are internally fully dense but have a poor surface finish, which reduces the overall density. It is therefore apparent that, in order to manufacture near full density parts with an acceptable surface finish, the optimum laser scan speed (under the conditions used) is between 300 and 600 mm s$^{-1}$. However, since the speed (and therefore the cost) of manufacturing is directly related to the laser scan speed, there is considerable benefit in using values at the upper end of this range. As such, the production of fully dense tensile bars and the sample acetabular cup was performed at a speed of 550 mm s$^{-1}$.

Figure 2a–c illustrates the microstructure of the manufactured samples in three conditions: near full density (99.3%) at 550 mm s$^{-1}$, at intermediate density (98.2%) at 650 mm s$^{-1}$ and at low density (95.8%) at 800 mm s$^{-1}$. The laser tracks created during the SLM process, represented by the dark bands, are clearly visible in all micrographs. These tracks are typical microstructural features in samples manufactured by SLM [13,16]. For the near fully dense sample at 550 mm s$^{-1}$
(Fig. 2a), the powders have completely melted/resolidified and there is no apparent porosity in the microstructure. For the sample with an intermediate density (Fig. 2b), unmelted particles are evident in the microstructure (arrowed in Fig. 2b); it may therefore be concluded that the laser energy was not sufficient to completely melt all of the powder particles. In the sample with the lowest density (Fig. 2c), the number of unmelted particles has increased and porosity is clearly present. In Figure 2d a sample acetabular prosthesis manufactured by SLM with a laser power of 200 W and a laser speed of 550 mm s$^{-1}$ is shown. The cup has a complex, fine-scale scaffold structure on its outer surface, which is aimed at enhancing bone in-growth.

![Figure 2. Optical microstructures of the parts manufactured at laser scan speeds of: (a) 550 mm s$^{-1}$, (b) 650 mm s$^{-1}$ and (c) 800 mm s$^{-1}$. The gray bands are the laser tracks. (d) An example of precise acetabular cup produced by SLM with laser power of 200 W and a laser scan speed of 550 mm s$^{-1}$. The inset shows the fine-scale scaffold that has been created on the surface, which is aimed at enhancing bone in-growth.](image)

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Typical stress–strain curves of the samples manufactured by SLM at different scan speeds are shown in Figure 3. All samples exhibit a low Young’s modulus of $\sim$53 GPa, an ultimate tensile strength of $\sim$660 MPa and a ductility exceeding 10%. Although the strength and modulus are independent of the scan speed, the ductility is closely linked to the scan speed and therefore to the density of the specimens. Table 1 compares the mechanical properties of the Ti2448 alloy manufactured by SLM with those of conventionally processed material. Although the SLM Ti2448 has a similar Young’s modulus and ductility, it has lower ultimate tensile strength and perhaps slightly lower yield strength than hot-rolled or hot-forged material. These samples were tested with the tensile load applied to the build (Z) direction. It is well known [17] that this is the weakest direction for samples produced by SLM. Hence, in spite of this, the yield strength is only slightly lower than conventionally processed material. The inset in Figure 3 shows the stress–strain curves of cyclic loading–unloading deformation with 1% strain steps. There is no pronounced superelastic behavior.

![Figure 3. Typical stress–strain curves of parts processed at laser scan speeds of 550, 650 and 800 mm s$^{-1}$. Unlike the ductility, the modulus and strength do not depend on the scan speed. The inset shows cyclic loading/unloading stress–strain curves with 1% strain steps. There is no pronounced superelastic behavior.](image)

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![Figure 4. Secondary electron SEM images of the fracture surfaces of the samples produced at laser scan speeds of: (a) 550 mm s$^{-1}$, (b) 650 mm s$^{-1}$ and (c) 800 mm s$^{-1}$. (d) An overview of the fracture surface for the sample produced at a scan speed of 550 mm s$^{-1}$.](image)

Figure 4. Secondary electron SEM images of the fracture surfaces of the samples produced at laser scan speeds of: (a) 550 mm s$^{-1}$, (b) 650 mm s$^{-1}$ and (c) 800 mm s$^{-1}$. (d) An overview of the fracture surface for the sample produced at a scan speed of 550 mm s$^{-1}$.

![Table 1. Comparison of the tensile properties for the Ti-24Zr-4Nb-8Sn alloys manufactured by SLM (laser powder: 200 W; laser scan speed: 550 mm s$^{-1}$) and by conventional processing methods: Young’s modulus $E$, yield strength $\sigma_{0.2}$, ultimate tensile strength $\sigma_{UTS}$ and elongation $\delta$.](table)

<table>
<thead>
<tr>
<th>Processing methods</th>
<th>$E$ (GPa)</th>
<th>$\sigma_{0.2}$ (MPa)</th>
<th>$\sigma_{UTS}$ (MPa)</th>
<th>$\delta$ (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selective laser melting</td>
<td>53 ± 1</td>
<td>563 ± 38</td>
<td>665 ± 18</td>
<td>13.8 ± 4.1</td>
<td>This work</td>
</tr>
<tr>
<td>Hot rolling</td>
<td>46</td>
<td>700</td>
<td>830</td>
<td>15.0</td>
<td>[10]</td>
</tr>
<tr>
<td>Hot forging</td>
<td>55</td>
<td>570</td>
<td>755</td>
<td>13.0</td>
<td>[8]</td>
</tr>
</tbody>
</table>
deformation in the new-developed beta titanium alloys are still not fully understood [3,4,6,7,18], interstitial oxygen in the β phase improves the phase stability, thereby preventing the potential phase transformation. Consequently, in alloys with a high oxygen content, the amount of nonlinear recoverable strain is reduced and the double yielding phenomenon can also be obscured [18]. For example, the nonlinear, recoverable strain of Ti2448 decreases from 1.2% to near 0% when the oxygen level increases from 0.08 to 0.40 wt. % [18]. Hence, it is proposed that the high oxygen content of the SLM processed material (0.21 wt. %) is the reason for the absence of the superelastic behavior. The source of the high oxygen content is the starting powder (0.17 wt. %) rather than the processing conditions. During the SLM process, the oxygen enrichment is only very small (~0.04 wt. %), which suggests that the use of lower oxygen content powder may result in a recovery of pronounced superelastic behavior.

Figure 4 shows the fracture surfaces of samples produced at scan speeds of 550, 650 and 800 mm s⁻¹. At a speed of 550 mm s⁻¹, elongated dimple (cup and cone) features are clearly visible on the fracture surface (Fig. 4a). An overview of the fracture surfaces (Fig. 4d) reveals that cracks initiate at defects, such as around weakly bonded grains, as indicated by the arrows. At a scan speed of 650 mm s⁻¹ more defects and/or incompletely melted powder particles are present and therefore the fracture surface (Fig. 4b) shows a mixture of smooth zones related to intergranular fracture, as well as elongated dimple features. Cracks are also observed at some grain boundaries. Intergranular fracture and transgranular cleavage fracture (coarse zones) dominate the fracture of the sample produced at 800 mm s⁻¹ scan speed (Fig. 4c).

In summary, components from a novel biomedical beta Ti–24Nb–4Zr–8Sn alloy were, for the first time, manufactured using SLM. The density and microhardness generally increase with decreasing the laser scan speed, which corresponds to a higher laser energy density. Near full density parts (~99%) have been obtained at a laser power of 200 W and with a scan speed range of 300–600 mm s⁻¹. Compared with material prepared by conventional processing routes, SLM processing produces samples with similar mechanical properties but without pronounced superelastic deformation due to the high oxygen of the starting powder. An example of an acetabular hip cup complete with complex outer scaffold has been manufactured.

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