Ti6Al4V titanium alloy used as a modern biomimetic material

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ABSTRACT

Purpose: The principal aim of the article is to characterise titanium alloy Ti6Al4V as a biomimetic material. The work presents in particular the application of this alloy in regenerative/aesthetic medicine for implants of craniofacial elements against other its other applications in various branches of industry. The article presents a rapid manufacturing (RM) method of fabrication of elements to be used as implants from Ti6Al4V powder. It was demonstrated that the scaffolds created in Selective Laser Melting (SLM) have strictly defined geometric dimensions of an object and open pores, and the pores are regular and repeat within the whole volume of the object.

Design/methodology/approach: Scanning electron microscopy was applied for showing the structure of innovative biomimetic materials made of Ti6Al4V powder.

Findings: It was confirmed in SEM examinations that the structure of laser-sintered objects consists, within its entire volume, of regularly occurring pores with strictly specified geometric dimensions.

Practical implications: Biomimetic materials can be used in regenerative/aesthetic medicine as implants. The purpose of the scaffolds produced is to enable the growth of soft tissue or bone tissue in craniofacial elements.

Originality/value: Biomimetic materials can be used in regenerative/aesthetic medicine as implants. The purpose of the scaffolds produced is to enable the growth of soft tissue or bone tissue in craniofacial elements.

Keywords: Biomaterials; Ti6Al4V; Scaffolds; Porous structure; Implants, SLM

Reference to this paper should be given in the following way:

MATERIALS MANUFACTURING AND PROCESSING

1. Introduction

In today’s world, the automotive and aviation industries have been seeking new and innovative lightweight structure with goods mechanical properties, and light metal alloys, apart from composites, play a crucial role here. The activities of designers and constructors are aimed at mass reduction and energy reduction while improving the safety of constructions made of newly created materials. The following have been the drivers of intensive development of lightweight structures: a fuel market downturn, shrinking oil resources and the gradual greenhouse effect [1].
Titanium alloys have also advanced sharply in the field of medicine owing to their biocompatibility with a human organism [2]. Works have been carried out since long over solid implants and prostheses made of such alloys. Additive manufacturing used in biomedicine and in the aviation and motor industry has strongly evolved recently. Works are being now conducted to develop scaffolds made of titanium alloys finding their application as porous bone [3-4] and palate [5-7] implants. The article provides a detailed characterisation of titanium alloys against other light metal alloys. Special emphasis is laid on the usage of Ti6Al4V titanium alloys as an innovative porous biomimetic material in Selective Laser Melting (SLM).

2. Properties of titanium and titanium alloys versus other light metals

Light metals are metals whose density is below 4.5 [g/cm³]. Light metals include aluminium, titanium, magnesium, beryll [8-11]. Table 1 compares the selected properties of light materials. Titanium, whose density is slightly over 4.5 [g/cm³] and is 4.507 [g/cm³], is classified to the group of light metals [1,9]. Technically pristine titanium is silver-grey. Pristine titanium and its alloys are classified as paramagnetics. They are characterised by excellent corrosion resistance in the majority of aggressive environments. The maximum working temperature of titanium and its alloys is limited by small resistance to oxidation at air temperature. The limit working temperature of such materials in a strongly oxidising environment is 500 °C. Titanium and its alloys are strongly reactive. It is recommended to perform heat treatment, welding and rapid manufacturing processes in the environment of shielding gases [1,6-7,9-10]. It is because they tend to self-ignition when in contact with oxygen. Table 2 presents the influence of temperature on the physical properties of titanium. This element has two allotrope types: Tiₐ and Ti₇. The α allotrope type endures to the temperature of 882°C and crystallises in a hexagonal structure with a compact lattice (A3). The β allotrope type endures to the temperature of 882°C to 1068°C being a melting point. It crystallises in a regular structure with a centred spatial lattice (A2). Crystalline structure reconstruction is a result of the changes taking place during heating and cooling pristine titanium. Grain growth is experienced during the α→β transformation caused by titanium heating above 882°C. It is a characteristic trait of titanium and its alloys. The both allotrope types possess good plasticity [1,9, 10-14].

Alloy elements influence the titanium allotrope temperature transformation. They are grouped into neutral ones and ones stabilising the phase α and stabilising the phase β. Neutral elements include Zr, Sn (influence transformation temperature), the phase α stabilising elements include: Al, O, N, C, the phase β stabilising elements include: Mo, V, Ta, Nb, Fe, Mn, Cr, Co, Ni, Si, H. Titanium alloys containing elements stabilising the phase β have higher density than alloys containing the phase α, and α and β. It is due to the fact that they contain elements with high density – molybdenum and vanadium [1,9,11].

Titanium alloys are classified as single-phase α and β, double-phase α+β and pseudo-α and pseudo-β. The alloys α include pristine titanium and titanium with additive of elements stabilising the phase α and with an addition of neutral elements. If additional alloys stabilising the phase β are found in the microstructure in a small quantity, it is the pseudo-α alloy. β alloys contain a large quantity of elements stabilising the phase β in their microstructure. Double-phase α+β alloys are the most popular, widely used group of titanium alloys. The content of the phase β in the microstructure are within the range of 5-40 %. A pseudo-β alloy is the double-phase α+β alloy, but the content of elements stabilising the phase β in the microstructure is so high that it prevents phase β stabilisation at room temperature after a water cooling process in the range of phase β occurrence [1,9-14].

The properties of titanium alloy are depending on their microstructure. Chemical composition influences the properties of the phases α and β. The microstructure is characterised by the grain size and alignment of the phases α and β. A fine-grained structure and coarse-grained structure is distinguished depending on the grain size, and a plate microstructure and equiaxial microstructure are distinguished according to the shape and arrangement of phases [1,9-11]. Table 3 shows the influence of a microstructure on the properties of titanium alloys, and table 4 presents the selected properties of particular titanium alloys. The α alloys are mainly used in the chemical industry. This is largely influenced by their high corrosion resistance and deformability. Pseudo-α alloys, due to their high creeping resistance, are used for work at a high temperature of up to 550 °C. The β alloys are applied as alloys with very high corrosion resistance, which do not exhibit the tendency to self-ignite. The α + β alloys have good strength and plastic properties. This group includes the most popular Ti6Al4V titanium alloy, which is broadly employed in the automotive, aviation, space and medical industry. The pseudo-β alloys are characterised by high tensile strength, good plastic properties, strength properties and cracking resistance. A disadvantage of such alloys is their high density, small resistance to oxidation and high costs. Titanium and titanium alloys are used in the arms, chemical, automotive, aviation, power and transport sector, in medicine, architecture and sports. Due to their properties, they are used in many branches of industry [1,9-14,16].
Table 1. Comparison of selected properties of light alloys [9,10-14]

<table>
<thead>
<tr>
<th>Properties</th>
<th>Ti</th>
<th>Al</th>
<th>Mg</th>
<th>Be</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic number</td>
<td>22</td>
<td>13</td>
<td>12</td>
<td>4</td>
</tr>
<tr>
<td>Atomic mass</td>
<td>47,867</td>
<td>26,981</td>
<td>24,305</td>
<td>9,012</td>
</tr>
<tr>
<td>Crystalline structure</td>
<td>α A3, β A2</td>
<td>A1</td>
<td>A3</td>
<td>α A3, β A2</td>
</tr>
<tr>
<td>Density at 20°C, [g/cm³]</td>
<td>4,507</td>
<td>2,698</td>
<td>1,738</td>
<td>1,848</td>
</tr>
<tr>
<td>Melting point</td>
<td>1068</td>
<td>660,4</td>
<td>650</td>
<td>1283</td>
</tr>
<tr>
<td>Boiling point</td>
<td>3260</td>
<td>2494</td>
<td>1107</td>
<td>2770</td>
</tr>
<tr>
<td>Thermal expansion coefficient [10⁻⁶ 1/K]</td>
<td>8.41</td>
<td>18</td>
<td>25,2</td>
<td>11,6</td>
</tr>
<tr>
<td>Specific heat capacity [kJ/(kg K)]</td>
<td>0.993</td>
<td>0.9</td>
<td>1,025</td>
<td>1,886</td>
</tr>
<tr>
<td>Heat conductivity [W/(m·K)]</td>
<td>11,4</td>
<td>247</td>
<td>418</td>
<td>210</td>
</tr>
<tr>
<td>Resistivity [nΩ·m]</td>
<td>420</td>
<td>0,1145</td>
<td>44,5</td>
<td>40</td>
</tr>
<tr>
<td>Tensile strength R_m [Mpa]</td>
<td>235</td>
<td>45</td>
<td>180-220⁸⁻¹⁷</td>
<td>483-690⁸⁻¹⁷</td>
</tr>
<tr>
<td>Yield point R_{p0,2} [MPa]</td>
<td>140</td>
<td>10</td>
<td>115-140⁸⁻¹⁷</td>
<td>310</td>
</tr>
<tr>
<td>Elongation [%]</td>
<td>54</td>
<td>50</td>
<td>2-10⁸⁻⁶⁷</td>
<td>5-20</td>
</tr>
<tr>
<td>Young modulus [GPa]</td>
<td>250</td>
<td>30-58</td>
<td>45-47⁻⁸⁻¹⁷</td>
<td>75-85</td>
</tr>
</tbody>
</table>

Table 2. Influence of temperature on physical properties of titanium [1,14,16]

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>Thermal expansion coefficient [10⁻⁶ 1/K]</th>
<th>Heat conductivity [W/(m·K)]</th>
<th>Specific heat capacity [J/kg·K]</th>
<th>Young modulus [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>-</td>
<td>17</td>
<td>500</td>
<td>110</td>
</tr>
<tr>
<td>100</td>
<td>7.6</td>
<td>16</td>
<td>550</td>
<td>101</td>
</tr>
<tr>
<td>200</td>
<td>8.9</td>
<td>15</td>
<td>580</td>
<td>92</td>
</tr>
<tr>
<td>300</td>
<td>9.5</td>
<td>15</td>
<td>595</td>
<td>85</td>
</tr>
<tr>
<td>400</td>
<td>9.6</td>
<td>15</td>
<td>605</td>
<td>78</td>
</tr>
<tr>
<td>500</td>
<td>9.7</td>
<td>15</td>
<td>615</td>
<td>72</td>
</tr>
<tr>
<td>600</td>
<td>-</td>
<td>16</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 3. Influence of microstructure on properties of titanium alloys [1,14,16]

<table>
<thead>
<tr>
<th>Fine-structure</th>
<th>Coarse-structure</th>
<th>Properties</th>
<th>Plate</th>
<th>Equiaxial</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cerr</td>
<td>Strength</td>
<td>↑</td>
<td>↑</td>
</tr>
<tr>
<td></td>
<td>cerr</td>
<td>Plasticity</td>
<td>↓</td>
<td>↑</td>
</tr>
<tr>
<td></td>
<td>cerr</td>
<td>Creeping</td>
<td>↑</td>
<td>↓</td>
</tr>
<tr>
<td></td>
<td>cerr</td>
<td>Creeping resistance</td>
<td>↑</td>
<td>↓</td>
</tr>
<tr>
<td></td>
<td>cerr</td>
<td>Oxidisation resistance</td>
<td>↑</td>
<td>↓</td>
</tr>
</tbody>
</table>

Biomimetics (from Greek bios – life, mimesis – imitation) is a term which relates to a field of science observing and imitating the behaviour and functioning of nature, and then its adaptation for practical reasons. Its purpose is to construct better materials, devices, machines by using the solutions created by nature for millions of years [17-18].

Scaffolds are biomimetic materials whose task is to replace and mimic the biological functions of a bone/tissue. Such materials also have a structure of the material being replaced (e.g. open bone pores with a specific structure and geometrical dimensions) and allow the growth of living cells on their surface. The possibility of cells growth is influenced by the porous structure of a scaffold. It allows to supply nutrients to the cells developing on its surface. Scaffolds may be used in an organism in a long-term period as biocompatible materials or may be subject to degradation and resorption [19-24].

3. Materials and methodology

A material used in a selective laser melting process is Ti6Al4V alloy in the form of spherically-shaped powder. The powder grain size is 15-45 µm. Table 5 presents chemical composition of Ti6Al4V powder according to the manufacturer’s specifications.

Virtual models with a complex shape and a regular porous structure are designed by means of CAMD.
soft enumeration. Figures 1-3 show models with complex geometric dimensions and a regular, porous structure. The model is designed as a patient’s a palate piece loss.

![Fig. 1. A scaffold model created by means of CAMD software, top view](image1)

![Fig. 2. Scaffold model created by means of CAMD software, bottom view](image2)

Metal scaffolds were produced in a selective laser sintering process (SLM) (Fig. 4) with Ti6Al4V powder. The process consists of producing, on a point-by-point and layer-by-layer basis, an object from metal powder using a high-performance laser. An object is created based on a model designed earlier. Ti6Al4V titanium powder was preheated at 160°C for 12h in the argon protective atmosphere, which ensures that humidity affecting a sintering process is removed. An SLM process was carried out with a scanning rate of 1000 mm/s with the laser power of 100 W using a laser point of 60 µm in a protective atmosphere of argon.

![Fig. 3. Scaffold model created by means of CAMD software, side view](image3)

![Fig. 4. Diagram of device for Selective Laser Sintering [25-27]](image4)

Microscope observations of the structure of porous materials were performed using a scanning electron microscope Zeiss Supra 35 equipped with EDS and WDS detectors for chemical composition analysis. Porosity tests along a profile of metal scaffolds were carried out using a confocal microscope CLSM Exciter 5 by Zeiss allowing observations at magnification of up to 2000x m and equipped with four lasers with different power rating and a 2D and 3D image of the studied objects was generated.

<table>
<thead>
<tr>
<th>Powder</th>
<th>Al</th>
<th>V</th>
<th>C</th>
<th>Fe</th>
<th>O</th>
<th>N</th>
<th>H</th>
<th>Other together</th>
<th>Other together</th>
<th>Ti</th>
</tr>
</thead>
</table>
| Ti6Al4V    | 6.35| 4.0 | 0.01| 0.2 | 0.15| 0.02| 0.003| ≤ 0.4          | ≤ 0.1          | other

Table 5. Fraction of particular chemical elements in composition of powders subject to experiments in per cents
4. Results and discussion

A top and bottom view of a metal scaffold created from Ti6Al4V titanium powder by selective laser sintering is presented, respectively, in Figures 5 and 6. The object has geometrical dimensions determined at the stage of design.

Surface topography of the scaffolds produced was viewed with a Supra 35 SEM microscope. It was observed that the studied material has a porous, regular latticework-shaped structure. It was also found that the pores of the scaffold produced are open (Fig. 7-10), which was one of the designers’ key assumptions. It can be confirmed by comparison to bone tissue that the material is biomimetic. Microscope observations of the studied material’s surface topography indicate the presence of singular spherically-shaped powder grains on its surface, which were deposited there due to adhering to the scaffold surface remelted in the SLM process. A metal melting effect was also observed on the surface of the created scaffold, created due to powder melting with a high performance laser.

A confocal microscope allowed to achieve a 2D image (Fig. 9) and 3D image (Fig. 10) of the developed metal scaffolds and to examine their porosity Ra along the set profile (Fig. 11). The observations have confirmed the occurrence of open pores (Fig. 9-10) in the studied object and that the surface of the created object is porous. The porosity value $R_a$ is 26 [µm].

Fig. 5. Scaffold produced in SLM process, top view

Fig. 6. Scaffold produced in SLM process, bottom view

Fig. 7. Scaffold produced with Ti6Al4V powder in SLM, SEM process, magnification of 200X

Fig. 8. Scaffold produced with Ti6Al4V powder in SLM, SEM process, magnification of 300X

Fig. 9. Scaffold produced with Ti6Al4V powder in SLM, SEM process, magnification of 500X
5. Conclusions

The designing and fabrication of modern materials with predefined, unique properties is a key task for today’s engineers. Considering the efforts to achieve better and better functional characteristics of innovative products, modern engineering materials are facing very high requirements. The article presented indicates that it is possible to fabricate modern innovative porous biomimetic materials using Ti6Al4V titanium alloy. Specialist CAMD software enables the designer to create an object with any geometric dimensions and any shape of open pores. In such case, the dimensions of the scaffold manufactured correspond to dimensions of a patient’s palate loss. Due to the dimensions and shape of the implant and its pores, the material can be considered biomimetic. The dimensions correspond, in particular, to the patient’s palate loss, the pores are regular, and their dimensions correspond to pores existing in the human bone tissue. Additive manufacturing methods are beyond doubt another step for intensive development of biomimetic materials, which in consequences is contributing to the development of modern branches of transplantation medicine.

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References


[18] International project entitled “Investigations of structure and properties of newly created porous biomimetic materials fabricated by selective laser sintering BIOLASIN” headed by Prof. L.A. Dobrzański funded by the Polish National Science Centre under the decision DEC 2013/08/M/ST8/00818.


