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## SELECTIVE LASER SINTERING AND MELTING OF PRISTINE TITANIUM AND TITANIUM Ti6Al4V ALLOY POWDERS AND SELECTION OF CHEMICAL ENVIRONMENT FOR ETCHING OF SUCH MATERIALS

## SELEKTYWNE SPIEKANIE I TOPIENIE LASEROWE PROSZKÓW CZYSTEGO TYTANU I JEGO STOPU Ti6Al4V ORAZ DOBÓR ŚRODOWISKA CHEMICZNEGO DO TRAWIENIA TYCH MATERIAŁÓW

The aim of the investigations described in this article is to present a selective laser sintering and melting technology to fabricate metallic scaffolds made of pristine titanium and titanium Ti6Al4V alloy powders. Titanium scaffolds with different properties and structure were manufactured with this technique using appropriate conditions, notably laser power and laser beam size. The purpose of such elements is to replace the missing pieces of bones, mainly cranial and facial bones in the implantation treatment process. All the samples for the investigations were designed in CAD/CAM (3D MARCARM ENGINEERING AutoFab (Software for Manufacturing Applications) software suitably integrated with an SLS/SLM system. Cube-shaped test samples dimensioned 10x10x10 mm were designed for the investigations using a hexagon-shaped base cell. The so designed 3D models were transferred to the machine software and the actual rapid manufacturing process was commenced. The samples produced according to the laser sintering technology were subjected to chemical processing consisting of etching the scaffolds' surface in different chemical mediums. Etching was carried out to remove the loosely bound powder from the surface of scaffolds, which might detach from their surface during implantation treatment and travel elsewhere in an organism. The scaffolds created were subjected to micro- and spectroscopic examinations

Celem badań, opisanych w niniejszym artykule jest zaprezentowanie technologii selektywnego spiekania i topienia laserowego w celu wytworzenia metalowych scaffoldów z proszków: czystego tytanu oraz jego stopu Ti6Al4V. Technika tą przy zastosowaniu odpowiednich warunków wytwarzania między innymi mocy lasera i wielkości plamki lasera wytworzono tytanowe scaffoldy o różnych własnościach i strukturze. Tego typu elementy mają za zadanie zastąpić brakujące fragmenty kości głównie kości szczękowo-twarzowych w procesie leczenia implantacyjnego. Wszystkie próbki do badań zaprojektowano w odpowiednio zintegrowanym z systemem SLS/SLM oprogramowaniem CAD/CAM (3D MARCARM ENGINEERING AutoFab, Software for Manufacturing Applications). Przy wykorzystaniu komórki bazowej o kształcie heksagonalnym zaprojektowano próbki do badań w kształcie sześcianu o wymiarach 10x10x10 mm. Tak zaprojektowane trójwymiarowe modele przetransportowano do oprogramowania maszyny gdzie rozpoczęto właściwy proces wytwarzania przyrostowego. Wykonane w technologii spiekania laserowego próbki poddano obróbce chemicznej polegającej na trawieniu powierzchni scaffoldów, w różnych ośrodkach chemicznych. Trawienie wykonano w celu usunięcia z powierzchni scaffoldów luźno związanego proszku, który mógłby podczas leczenia implantacyjnego oderwać się od ich powierzchni i przedostać się w inne miejsce organizmu. Wytworzone scaffoldy poddano badaniom mikro- i spektroskopowym.

### 1. Introduction

Rapid manufacturing technologies, including the laser sintering technology, have been known for over 30 years [1]. The main idea on which rapid manufacturing technologies are based is a combination of individual layers of the material from which the given element is to be created. Rapid manufacturing thus enables to create objects with the final shape, while allowing to control the fabricated element in each part of its volume. Numerous various rapid manufacturing technologies are used in industry these days, which may differ in the type

and form of the materials used, a combination method of particular layers, as well as construction possibilities. These are always computer-controlled technologies, though, requiring the earlier preparation of appropriate 3D CAD models of the object produced. The elements produced can therefore be of any shape, often very complicated, offering application possibilities in various branches of industry [2-9].

Medicine is one of the fields where advantages of rapid manufacturing technologies have emerged. The construction of organs, bones or human tissues can be represented very accurately anatomically by being able to produce parts with any

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shape. The following is produced by means of RM technologies:

- physical models of anatomical organs;
- surgical instruments;
- dental and orthodontic models;
- dental implants and bridges;
- individualised implants accommodated to a patient based on the results of Computer Tomography or Nuclear Magnetic Resonance,
- scaffolds being a support structure of tissues, whose purpose is to restore the original biological functions [2-3, 10-15].

**2. Computer aided materials design**

An appropriate CAMD (Computer Aided Materials Design) tool enabling to ensure appropriate properties for a model needs to be used to produce a suitable model with selective laser sintering and melting. All the models presented in the article have been designed with 3D MARCARM ENGINEERING AutoFab software created for computer-aided designing, whose results are obtained directly in CAD/CAM in the SLS/SLM rapid manufacturing technique. A designer can select such parameters as:

- the size of the designed model;
- external and internal structure;
- the type and shape of filling of the model volume;
- the size and shape of an elementary cell creating the whole model [2-3, 16].

A hexagon-shaped base cell (Fig. 1) dimensioned 500x500x500 μm was used to design a scaffold model. A cube model dimensioned 10x10x10 mm, shown in Fig. 2, was created with this cell.

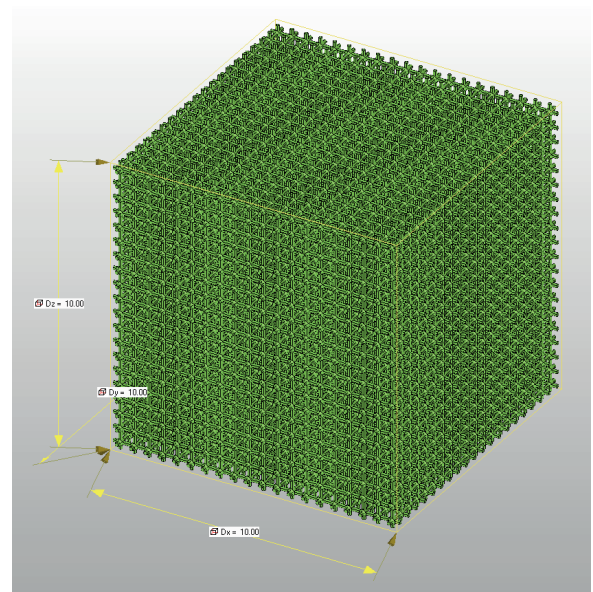


Fig. 2 a) Scaffold model, a)3D, b) top view, c) side view

After selecting the right structure of the model and determining the appropriate fabrication conditions, the entire model was divided into layers with specific thickness corresponding to the number of powder layers subjected to the sintering process until a ready object is obtained. A layer model is transferred to the software of a machine where, after producing a vacuum, and then after reaching an appropriate oxygen concentration which should not exceed 100 ppm, the actual fabrication process is taking place in a protective atmosphere of argon.

**3. Materials and methodology**

A material used for manufacturing the actual objects is pristine titanium powder (0-45 μm) and Ti6Al4V titanium alloy powder (15-45 μm). The chemical composition of the pristine titanium powder and Ti6Al4V powder according to the manufacturer’s specifications is given in table 1. Powder grains in the both cases are spherically shaped.

A virtual 3D cube model was created before the laser selective sintering and melting process directly using the software bundled into a Renishaw AM 125 device. The particular steps of the task are presented in chapter 2 of this article. The so created model is virtually placed in a work chamber. The model position is largely influencing the addition of supports supporting the element being produced and securing it against collapse under its own weight. In

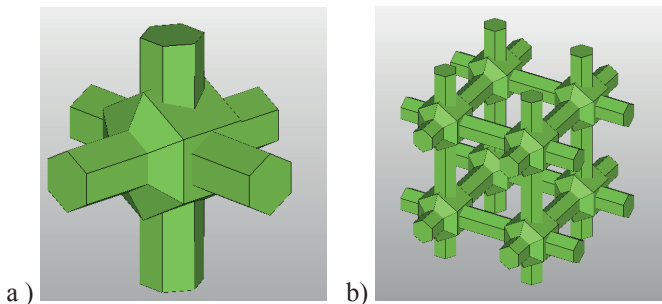


Fig.1 a) Hexagonal base cell used in scaffold modelling process, b) example of use of hexagonal cell to create a spatial porous structure.

TABLE 1

Fraction of particular chemical elements in composition of powders subject to experiments in per cents

Powder	Al	V	C	Fe	O	N	H	Others total	Others each	Ti
Ti	--	--	0.01	0.03	0.14	0.01	0.004	<0.4	<0.01	remainder
Ti6Al4V	6.35	4.0	0.01	0.2	0.15	0.02	0.003	≤ 0.4	≤ 0.1	

addition, the higher the model the longer the manufacturing time as more layers are sintered. The thickness of an individual layer is determined at the next stage of the procedure. The model is divided into individual layers with specific thickness along the cross section of the model in the axis perpendicular to the work chamber substrate in relation to which it had been oriented in advance taking into account only the points to be sintered in a given layer.

Titanium and titanium Ti6Al4V alloy powder was preheated at 150°C before starting the actual process in a protective atmosphere of argon. The selective laser sintering and melting process (SLS/SLM) was carried out within the following range of parameters: the scanning speed of 500-1200 mm/s; laser power: 50-120 W; laser point size of 35-80  $\mu\text{m}$ ; a protective atmosphere of argon. A manufacturing process of the actual object in the selective laser sintering and melting process was performed from the bottom. Each layer produced is adhering to the preceding one until the process is completed [2-3, 17-24]. Microscope observations of the metal scaffolds produced by SLS/SLM were carried out in a Supra 35 scanning electron microscope (SEM) by Carl Zeiss and an LSM 5 Exciter confocal microscope by Zeiss before and after surface treatment.

The surface of the scaffolds fabricated using titanium powder as well as Ti6Al4V alloy is rough. Surface treatment by chemical etching using different acid solutions and at different time was applied to reduce surface roughness (Ra) of the scaffolds created. The literature asserts that the most appropriate medium for the process for such a type of porous materials made of Ti6Al4V alloys is a hydrofluoric acid solution (HF) [25-26]. An HF solution with a concentration of 14 [%] with water at a rate of 0.5 [ml] HF + 50 [g] H<sub>2</sub>O was used. Optional etching methods with aqua regia (rate of 3:1 of sulphur acid 36.5% and nitric acid – 65%) and a sulphur acid solution (35-38%) with sulphuric acid (95%) at a rate of 1:1m, which was heated to 100°C, were employed due to high toxicity of hydrofluoric acid. The object was placed in polymeric (for a hydrofluoric acid solution) and glass (for other acid solutions) containers and etched, respectively, for 8 [min.] for a hydrofluoric solution with water, for 6 min. for hydrochloric acid with sulphuric acid and by 1 [h] for aqua regia.

#### 4. Results and discussion

A Scanning Electron Microscope Supra 35 by Carl Zeiss allowed to observe the surface topography of the scaffolds created. It was observed that the studied material has a porous, regular latticework-shaped structure. It was also confirmed that the pores in the scaffolds produced are open (Fig. 5). It was found, when analysing the results obtained for the scaffolds made of Ti6Al4V alloy, that their surface is rough as individual spherically-shaped powder balls exist. They were created as a result of remelting Ti6Al4V powder grains to the surface of the remelted material during the SLS/SLM process. Figure 6 shows a scaffold after etching in a hydrofluoric acid solution with water for 8 minutes. It was observed that the number of titanium powder grains on the surface has

decreased and no large pits were seen due to the etching process. It was also found that the unmolten powder was removed as a result of the process, but the arms produced were intact. Observations confirm that a flow effect of the material being melted is seen despite the etching process. The particular pores are shaped more regularly after the etching process. Figure 7 shows a scaffold made of Ti6Al4V after etching in a hydrochloric acid solution with sulphuric acid at a rate of 1:1 for 6 minutes. It was found that the structure is torn as a result of an intensive etching process. The structure is torn but regular. No metal flow effect was found for the structure meaning that the etching process influences not only the unmolten powder but also the basic scaffold produced in the SLS/SLM process. No changes in the structure of the created object were caused due to etching the titanium alloy in aqua regia. Unmolten powder and a metal flow effect were observed (Fig. 8).

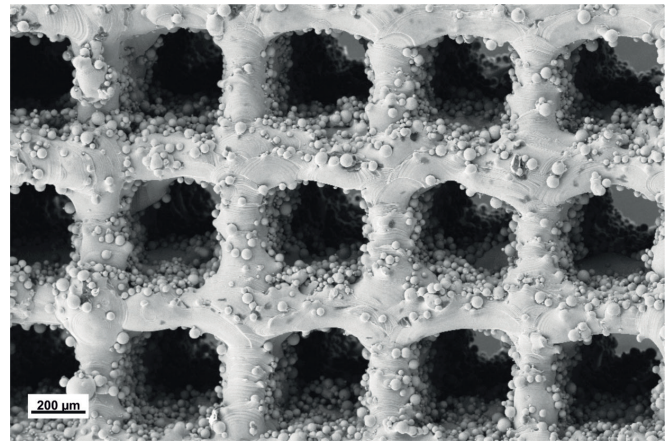


Fig. 5. Scaffold made of Ti6Al4V alloy in SLS/SLM process before chemical etching, SEM, magnification of 150x

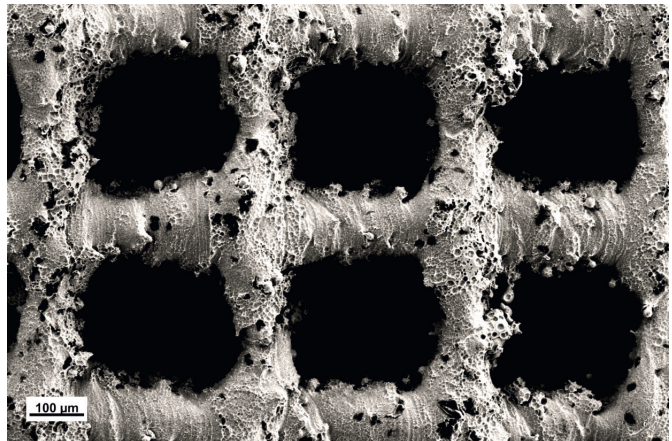


Fig. 6. Scaffold made of Ti6Al4V alloy in SLS/SLM process after etching in water solution with hydrofluoric acid for 8 minutes, SEM, magnification of 200x

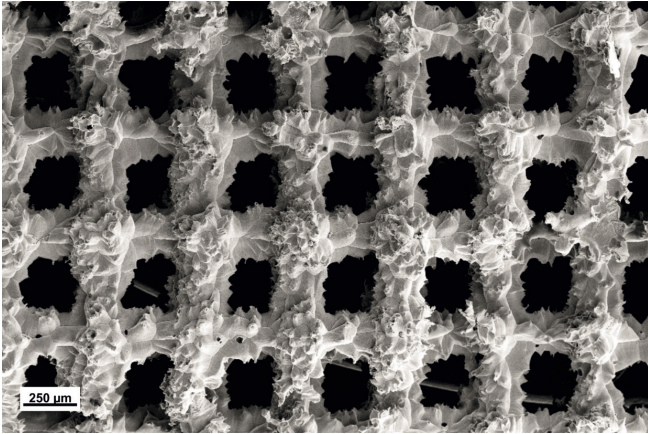


Fig. 7. Scaffold made of Ti6Al4V alloy in SLS/SLM process after etching in hydrochloric acid solution with sulphuric acid for 6 minutes, SEM, magnification of 100x

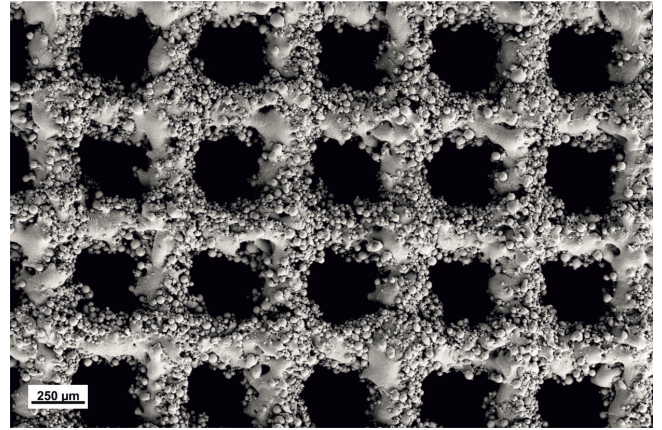


Fig. 9. Scaffold made of pristine titanium in SLS/SLM process before etching process, SEM, magnification of 100x

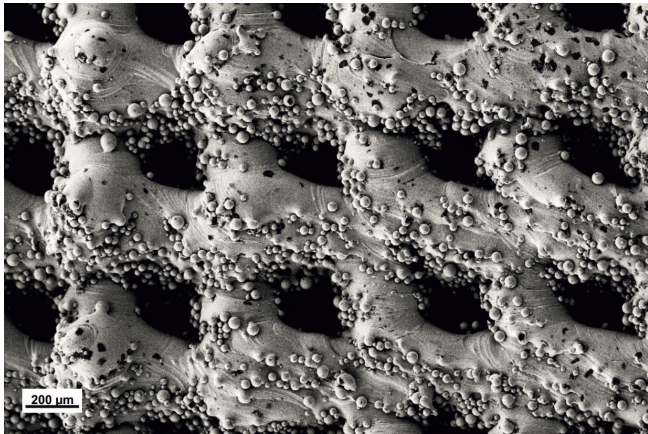


Fig. 8. Scaffold made of Ti6Al4V alloy in SLS/SLM process after etching in aqua regia for one hour, SEM, magnification of 150x

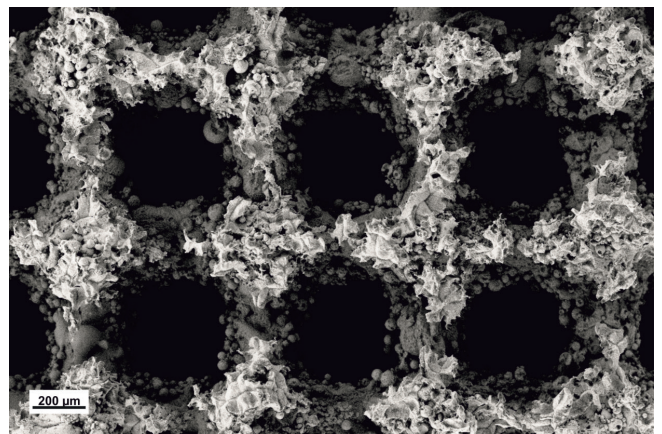


Fig. 10. Scaffold made of pristine titanium in SLS/SLM process after etching process in hydrochloric acid solution with sulphuric acid for 6 minutes, SEM, magnification of 150x

A scaffold made of pristine titanium is shown in figure 9. Sinters and particles of unsintered powder grains are visible on the surface. The object obtained has regularly shaped pores. The shape of the structure is similar to latticework. Figure 10 shows a scaffold made of Ti subjected to the etching process in a hydrochloric acid and sulphuric acid solution at a rate of 1:1 for 6 minutes. The object obtained features a torn, but regularly shaped structure. The unsintered powder grains have been removed. Sintors are still visible. The effect of the acid has created a more regular structure and pores in relation to an object prior to the etching process. Figure 11 presents a titanium scaffold subjected to the activity of aqua regia for 1 hour. Small influence of this chemical environment on the structure was observed, which caused partial removal of the unsintered powder grains. Sintors and unsintered powder grains occur in the structure. Differences in the structure were observed when comparing figures 5-8 and 9-11. The titanium alloy consists of a solid melted material, while the pristine titanium consists of sintered elements. The differences derive from applying different materials and different process parameters.

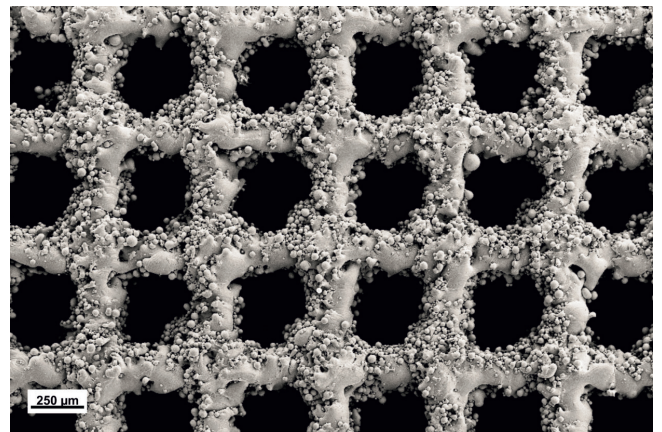


Fig. 11. Scaffold made of pristine titanium in SLS/SLM process after etching process in aqua regia for one hour, SEM, magnification of 100x

### 5. Roughness research

The roughness of solid scaffolds made of pristine titanium and Ti6Al4V alloy manufactured in SLS/SLM processes was examined along the profile line with a confocal microscope prior to an etching process and directly after the process, in different chemical mediums. The results of the examinations are presented in Fig. 12 - 18. It was found during microscopic observations that – compared to the scaffold prior to the etching process (Fig. 12) – the smoothest and most regular surface following the etching process was achieved by applying a hydrofluoric acid solution (HF) with water (Fig. 13). Etching with aqua regia allowed to achieve solid results with reduced surface roughness for a scaffold made of titanium and its alloy, as shown, respectively, in Fig. 15 and 18. The worst result, equivalent to high roughness, was seen for a scaffold subjected to the etching process in a hydrochloric acid and sulphuric acid solution made of titanium (Fig. 17) and Ti6Al4V alloy (Fig. 14).

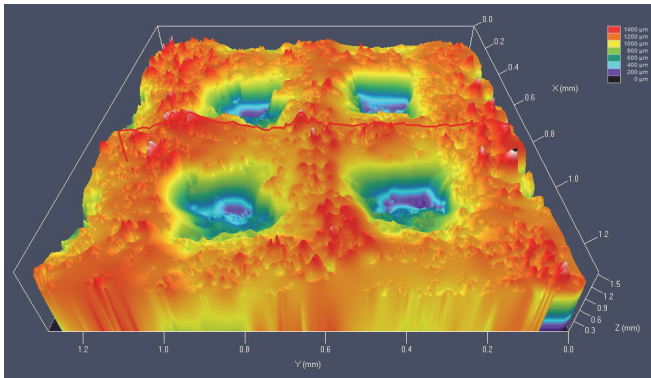


Fig. 12. Scaffold made of Ti6Al4V alloy in SLS/SLM process before chemical etching; porosity measurement along the set profile; CSLM

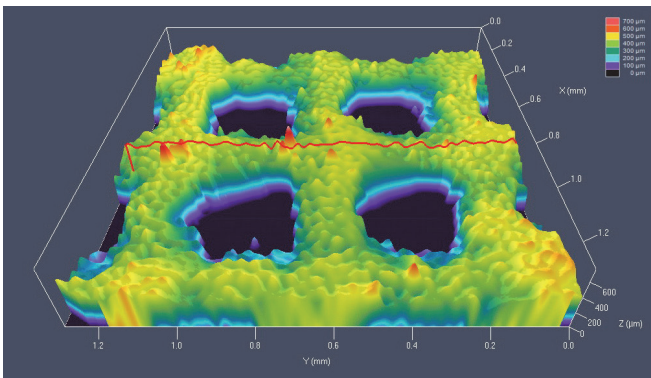


Fig. 13. Scaffold made of Ti6Al4V alloy in SLS/SLM process after etching in HF solution with water lasting 8 minutes; porosity measurement along the set profile; CSLM

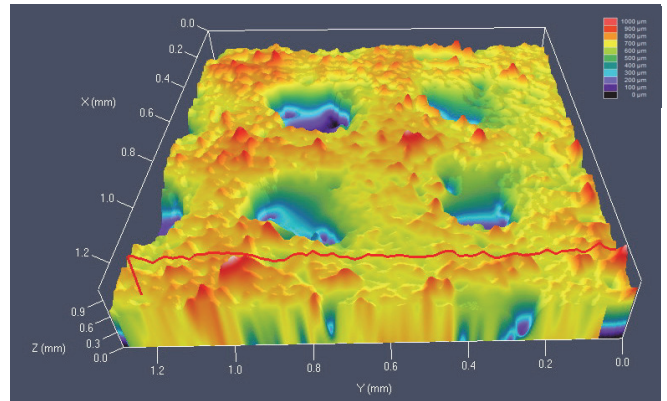


Fig. 14. Scaffold made of Ti6Al4V alloy in SLS/SLM process after etching in hydrochloric acid solution with sulphuric acid lasting 6 minutes; porosity measurement along the set profile; CSLM

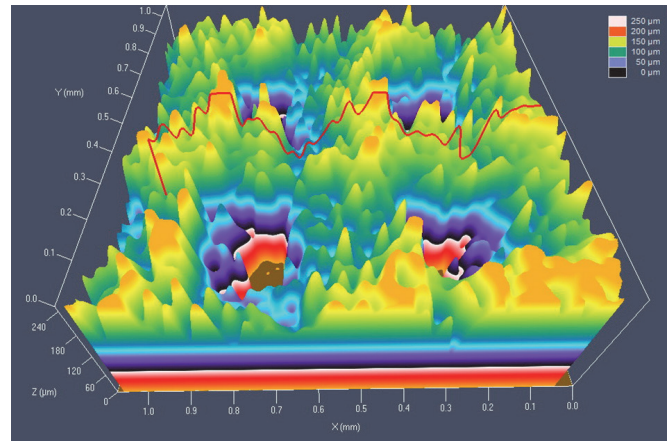


Fig. 15. Scaffold made of Ti6Al4V alloy in SLS/SLM process after etching in aqua regia lasting one hour; porosity measurement along the set profile; CSLM

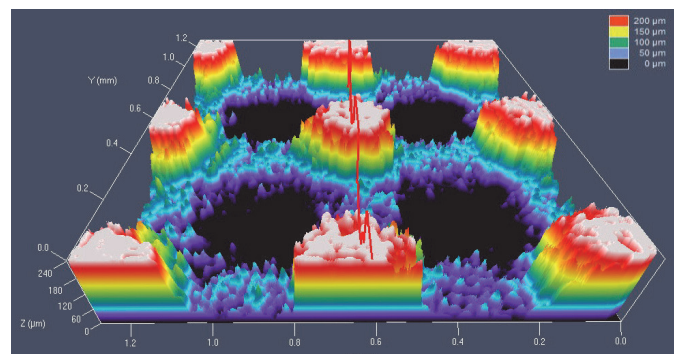


Fig. 16. Scaffold made of pristine titanium in SLS/SLM process before chemical etching; porosity measurement along the set profile; CSLM

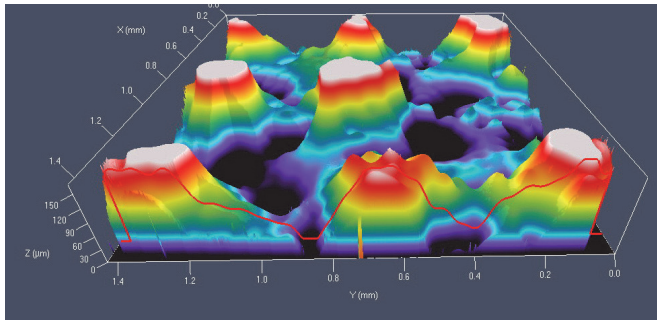


Fig. 17. Scaffold made of pristine titanium in SLS/SLM process after etching in hydrochloric acid solution with sulphuric acid lasting 6 minutes; porosity measurement along the set profile; CSLM

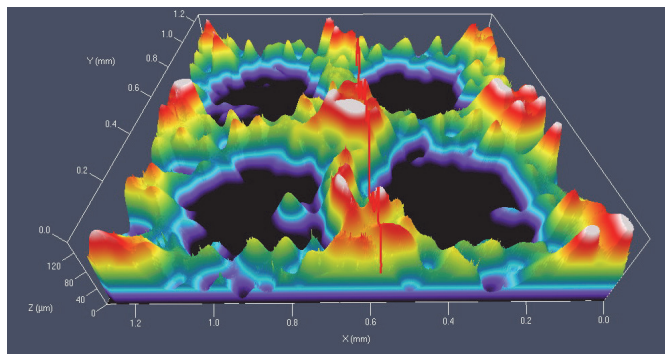


Fig. 18. Scaffold made of pristine titanium in SLS/SLM process after etching in aqua regia lasting one hour; porosity measurement along the set profile; CSLM

Table 2 presents the values of an average arithmetic deviation of the profile from the average line (Ra) of scaffolds made of titanium and Ti6Al4V alloy made after etching processes in different mediums. Roughness values for titanium and Ti6Al4V alloy are subject to reduction using etching with a hydrofluoric acid solution (HF) with water. Roughness is also subject to reduction in case of applying etching in aqua

regia and in a mixture of hydrochloric acid and sulphuric acid. Table 3 presents a percentage mass loss for particular actual objects after an etching process in relation to their initial mass. The results of the investigations show that etching in an HF solution with water is not the best solution. In case of this solution, the roughness value (Ra) is smaller, however, a mass loss corresponding to a titanium scaffold is 9.72%, and 7.6% for a scaffold made of Ti6Al4V alloy. Etching in aqua regia produces slightly higher average roughness values (Ra), but a mass loss is much smaller, of 3%, for a titanium scaffold, and only 1.8% for the examined titanium alloy. Roughness reduction (Ra) is achieved by employing etching for a mixture of hydrochloric acid with sulphuric acid for the both investigated materials, but is also related to a very high mass loss of 30.9% for Ti6Al4V and as much as 50.6% for pristine titanium. The investigations' results are shown in charts (Fig. 19) corresponding to the roughness values (Ra) and presenting a percentage mass loss (Fig. 20) for particular objects made of titanium and Ti6Al4V alloy etched in different chemical mediums.

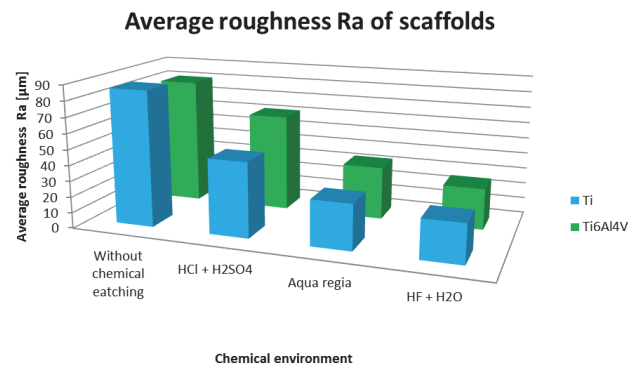


Fig. 19. Chart of average roughness of scaffolds made of pristine Ti and Ti6Al4V alloy using etching in different types of acids

TABLE 2

Results of average roughness of scaffold for pristine titanium and Ti6Al4V alloy before and after etching process in different chemical mediums

		MATERIAL		Unit
		Ti6Al4V	Ti	
SOLUTION	-	80,45	86,02	[µm]
	HF solution with water	26,04	24,61	[µm]
	HCl solution with H2SO4	61,56	47,4	[µm]
	Aqua regia	33,55	28,75	[µm]

TABLE 3

Results of percentage mass loss of scaffold for pristine titanium and Ti6Al4V alloy after etching process

		MATERIAL		Unit
		Ti6Al4V	Ti	
SOLUTION	HF solution with water	7,6	9,72	[%]
	HCl solution with H2SO4	30,9	50,6	[%]
	Aqua regia	1,8	3	[%]

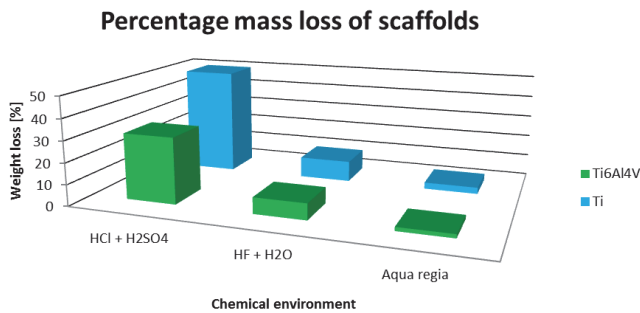


Fig. 20. Chart of percentage mass loss of scaffolds made of pristine Ti and Ti6Al4V alloy using etching in different types of acids

## 6. Summary

The investigations performed confirm the necessity to apply an etching process to reduce surface roughness of scaffolds made in the SLS/SLM process, both, such made of titanium alloy and Ti6Al4V alloy. Etching in different chemical mediums contributes to a reduced value of the average arithmetic profile deviation from the average line ( $R_a$ ), and also influences the mass of the fabricated objects. It was clearly pointed out that all the tested chemical mediums, i.e. (i) HF solution with water, (ii) HCl/H<sub>2</sub>SO<sub>4</sub> solution, (iii) aqua regia, are reacting much more strongly on pristine titanium, than on its Ti6Al4V alloy. The most beneficial value of the average arithmetic profile deviation from the average line ( $R_a$ ) for the both tested materials was attained when etching with a hydrochloric solution (HF), as confirmed by images from an electron scanning microscope and a confocal microscope. The mass loss examinations have allowed to conclude that the most appropriate chemical medium serving to reduce roughness ( $R_a$ ) with, at the same time, a small mass loss, is aqua regia, causing a much smaller mass loss for objects as compared to the other tested chemical mediums. Further investigations are now being carried out to confirm the efficiency of aqua regia as the best chemical reagent for scaffold etching, made of titanium or Ti6Al4V alloy, manufactured in the Selective Laser Sintering or Melting process.

## Acknowledgements

The works have been implemented within the framework of the BIOLASIN project entitled “Investigations of structure and properties of newly created porous biomimetic materials fabricated by selective laser sintering” headed by Prof. L.A. Dobrzański, funded by the Polish National Science Centre in the framework of the “Harmony 4” competitions. The project was awarded a subsidy under the decision DEC-2013/08/M/ST8/00818.

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