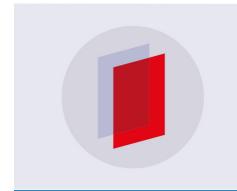# Main factors affecting the structure and properties of titanium and cobalt alloys manufactured by the 3D printing

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Main factors affecting the structure and properties of titanium and cobalt alloys manufactured by the 3D printing

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Abstract. This paper is short review the main factors affecting the structure and properties of the metals manufactured by additive technology (selective laser melting). A comparative analysis of the structure and properties of Ti6Al4V or CoCrMo alloys obtained by selective laser melting is presented. We describe the capabilities of laser melting method for producing materials with high density and high mechanical properties. The optimized process parameters for 3D printed medicine materials Ti6Al4V and CoCrMo with high density of are discussed.

1. Introduction

The materials, such as cobalt chromium (CoCrMo) alloy and titanium (Ti6Al4V) alloy are widely used in medicine manufacturing for stent coronary, surgical implants, surgical instruments, and dental purposes. For example, the metal stents must have excellent corrosion resistance, high elastic modulus, excellent biocompatibility and low residual stresses [1]. The dental and surgical cobalt chromium and titanium (Ti6Al4V) materials must have the high plasticity, high strength, low elastic modulus, also high biocompatibility and low residual stresses [2-5]. All these characteristics are present in the alloy of cobalt chromium and titanium. Development of techniques for additive manufacturing parts from titanium or cobalt chromium alloys are relevant at present for both scientific and industrial purposes. Methods of 3D printing are very promising, especially for medicine, because they allow one to obtain parts of complex designs and to take into account the personal characteristics of the human body. Additive technology is a novel surface engineering technique, which allows us to obtained alloys with high density (about 99.9%) similar to cast materials [6]. A number of characteristics are important in manufacturing of the parts with additive technologies (selective laser fusion, selective laser synthesis, electron beam fusion). These characteristics include the parameters of the used printer (for example, laser power), the quality and size of the powder, the distance between layers, substrate surface quality, substrate temperature, etc. All of them will affect the porosity, level of residual stresses and structure of the material, which, accordingly, determines the mechanical properties of the manufactured material. However, today we may say that 3D printing technology has her special possibilities and restrictions. Today many different researches devote to the problem of laser regime for control the properties of the 3D printed materials. The questions of determination the optimal regime of the 3D printer and factors, which may affect the high quality manufacturing, are the main and important aim for scientific investigators.

The report is a short review considering the main factors affecting the structure and properties of

titanium alloys Ti6Al4V and CoCrMo alloys, manufactured by selective laser melting (SLM).

2. Key parameters and physical processes of the selective laser melting

To obtain the good quality material it is need to understand the processes occurring in the material during 3D laser manufacturing. Some processes, such as absorption and transmission of laser energy, flow temperature and gradient in a molten pool, fast solidification because of the high cooling rate of the molten pool of the SLM sample (up to 108 K/s), cycling heating, and thermal deformation of the sample under laser manufacturing may be considered in this case [7]. All of these process lead to the high level of residual stresses in the 3D printed material that promote the crack initiation. SLM process uses a tiny focused spot with high energy density, and the laser beam moves fast. It is known that in the process of intensive heating and solidification of metal, compressive stresses, which exceed the yield strength of the material, are created. As a result, a residual compressive deformation arises in the material. After the removal of heat, this deformation causes tensile stresses in the material.

Common temperature deformation of the material after intensive heating may be described as follows [8]:

$$\varepsilon_t = \int_{t_m}^{t_1} a^*(t)dt,$$

where t1 is a temperature of the material after cooling, $a^*(t)$ is a coefficient of linear thermal expansion of the material at temperature t. Temperature stress of the material, which is associated with the thermal deformation, can be calculated as follows:

3. $\sigma = -E \cdot \varepsilon_t,$

where E is Young's modulus [8]. As can be seen, even with small changes in temperature, the thermal stresses in the material may be significant. For example, as it was shown in [8], for steel at t=100°C, E=200 GPa, $a^*(t)\approx 11\cdot 10^{-6}$ 1/°C, the calculated temperature stress (σ) was 220 MPa. In the case of the Ti6Al4V, at t=400°C, E=114 GPa, a^*(t)$\approx 10\cdot 10^{-6}$ 1/°C, the calculated temperature stress (σ) is 456 MPa. With a further temperature increase, the modulus of elasticity decreases, and the coefficient of linear thermal expansion increases [8]. Thus, during laser melting when the temperature in the 3D printed material may reaches 3000 K, significant residual tensile stresses can be expected. This suggestion was supported results obtained in SLM TI6Al4V alloy in [9].

The structural features of the SLM samples also point on the presence of high level of the residual internal stresses. As-built 3D printed alloys have a non-equilibrium state in comparison with the conventional cast materials. For example, the as-built Ti6Al4V SLM alloys have the HCP α′martensitic structure without any cubic BCC phase. Standard stress-relief annealing of these alloys does not lead to the equilibrium two-phase α (HCP)+β (BCC) structure [6]. SLM dental CoCrMo alloys exhibit the γ (FCC) metastable structure in comparison with the equilibrium two-phase ε (HCP)+γ (FCC) state of the conventional cast alloys [3, 4, 10]. A second Mo-rich phase was observed inside the inter-dendritic spaces in the as-build SLM CoCrMo alloy in [4]. For SLM CoCrMo alloys was found that the environment of stress-relief annealing directly affected both the nanostructure and hardness of the alloy [2]. As it was shown in [2], the procedure of the stress-relief annealing of the dental CoCrMo SLM alloys required the argon atmosphere and included the many steps. Sample should be heated to 1150°C over the course of 173 minutes, stabilized at this temperature for 232 minutes, cooled to 300°C in 593 minutes, then removed from the furnace, and left to cool at room temperature.

Twinning also points to the presence of the high local residual stresses in the materials. Tensile twins were observed in both SLM Ti6Al4V and CoCrMo alloys [6, 10].

3.1. Laser density and specific enthalpy

Unfortunately, there are not so much parameters that can be controlled during the 3D printing process, which allow us to obtain the materials with high density and good mechanical properties. First, these are parameters associated with the 3D printer's specifications, such as laser power, hatching space,

scanning speed, layer sickness. These parameters define a laser energy density, which is key factor that affects the properties of as-built 3D sample. The laser density affects the defects of the 3D sample. It was suggested that the spherical shape defects were associated with the gas bubbles formed during the rapid solidification of the SLM sample. These gas bubbles were generated when too high laser energy was applied to the molten pool [7, 11]. In the case of the lack of energy input during SLM process, the incomplete fusion holes may be observed [7]. Two different equations are suggested for calculation of the laser density. First equation (1) considers the specific energy density as relation of the laser power and the scanning speed (*V*) and beam (spot) diameter (*d*) [7], the second equation (2) includes the relation between laser power (*P*) and scanning speed (*V*), hatching space *(h)*, and layer sickness (*s*) [12]:

$$E_s = \frac{P}{V \cdot d},\tag{1}$$

$$E_d = \frac{P}{V \cdot h \cdot s}.\tag{2}$$

One more variant for describing the laser melting process using the thermo-dynamical parameters was suggested in [13]. In this case, the equation relates the melt-pool width and depth to the absorbed energy density (specific enthalpy ΔH) delivered by the laser into the powder bed:

$$\Delta H = \frac{A \cdot P}{\rho \cdot \sqrt{\pi \cdot D \cdot V \cdot d^3}},\tag{3}$$

where *A* is a function of absorptivity, *D* is a thermal diffusivity, and ρ is a density of the powder, *P* is a laser power, *V* is a laser scan speed, and *d* is a laser spot diameter. As can be seen, the powder parameters are also present in this equation, and it is important for getting of the quality material.

3.2. Powder quality

The formation of the defects is a critical issue in the SLM materials. Except density, the shape and size distribution of precursor powder granules also have an important meaning for producing the low porosity of the 3D printed samples. It was found in [11] that the small particles inclusion (about of 10 μm) in Ti-6Al-4V powder had an effect on extra laser energy absorption resulted by the multiple scattering of laser. The small powder particles are stress concentration the SLM Ti-6Al-4V sample and promote the crack initiation under the high-cycle fatigue test [11]. The formation of pores inside the SLM sample was detected in the case when the powder size distribution included powder particles that were larger than the gap between the coater arm and the coated material [14].

It is known that the powders for SLM process is mainly processed with gas atomization technology. The powder should have the spherical morphology, good flowability, high packing density. The origin of gas pores inside the powders is connected to the gas atomization process of the powder, where powder particles might contain argon [15]. In addition, if the packing density of metal powders is low, e.g., 50%, the gas present between the powder particles may dissolve in the molten pool [7].

Thus, the defects contained in the initial powders increases the probability of pore formation in SLM metals, which are the cause of the stress concentration and lead to the failure of the SLM sample under deformation. The ideal objective in SLM is to obtain 100% dense parts, i.e. zero porosity. Some authors suggest that the high porosity may be useful for medicine implants. However, as it was found that pore in SLM samples may be filled with gases. It is obviously may be more useful to design the part with predetermined pore sizes from the material with high density.

3.3. Parameters of the melting process

The next key parameters are connected with melting process; the laser scanning strategy and building direction can be attributed to them. Scanning strategy defines the methods of laser energy delivery to the surface of the designed sample. The right choice of the scanning strategy may allow one to provide better control of the temperature gradient and size of the melt-pool in the designed sample. The vertical distortion after each layer and residual stresses arising in the as-build SLM sample obtained with the chosen strategy are also should be taken into account. It is known that without high density it is

impossible to obtain the high strength. Different scan strategies have been suggested for the SLM processes to obtain the materials with high density. Effect of the scanning strategy on the density of the Ti6Al4V alloy was studied in [16]. Three scanning strategies were used, such as zigzag, unidirectional scanning, and cross-hatching. Zigzag scanning strategy consists on the alternating scan vectors. In unidirectional scanning strategy presents the one-directed scan vectors. In cross-hatching strategy consists on the alternating layers with unidirectional scan vectors and layers with rotate through 90 ° scanning direction. The authors of [16] found that cross-hatching scanning strategy allowed one to obtain the density of 99.9 % in as-build SLM Ti6Al4V alloy. Zigzag scanning strategy and another cross-hatching strategy for the CoCrMo alloys was suggested in [17]. This variant of the cross-hatching strategy consists on the alternating layers with unidirectional scan vectors and layers with rotate through 67 ° scanning direction. As it was found in [17], applying the zigzag strategy allowed one to form the directional microstructures with columnar grain growth, whereas the cross- hatching strategy promoted the arbitrary crystallization. Inter-layer stagger was suggested in [18] to enhance density of the CoCrMo SLM alloy. In this scanning strategy, the scanning lines of the scanning layer lying between the two consecutive scanning lines of the previous scanning layer was added to the orthogonal X-Y scanning.

Residual stress depends not only on material properties, process parameters, and scanning strategy, but also on the building geometry of the SLM samples. It is associated with the different orientation of layer structure, which is formed of the SLM samples. The orientation of building means the angle between longitudinal (horizontal) plane and vertical plane of the building platform. Change the building geometry has a strong influence on the mechanical properties due to the different orientation of the layered structure of the SLM sample to the axis of deformation.

3.4. Optimized parameters for SLM Ti6Al4V and CoCrMo alloys

There is a wide variety of literature data on the mechanical properties of the SLM Ti6Al4V and CoCrMo alloys. In this report, we try to present a short review the literature date collected according to suggested main factors. Tables 1 and 2 present the effect of the different values of the above-mentioned main factors for Ti6Al4V and CoCr alloys on their mechanical properties. It is known that without high density it is impossible to obtain high strength, while we should not forget about plasticity of our manufactured material. As can be seen from the tables, both as-build Ti6Al4V and CoCr SLM SLM alloys have a good potential to obtain the high density and high mechanical properties with suitable key-factors.

Table 1. The effect of the different values of main factors on mechanical properties of the as-build SLM Ti6Al4V alloy.

Laser density (J/mm^3)	Scanning strategy	Building geometry	Density (g/mm^3)	UTS (MPa)	E (GPa)	Elongation (%)	Ref.
Ti6Al4V ASTM F-136 grade 5	-	-	4.43	860	114	10	[19]
86.8	Zigzag with 90° rotation between each layer	-	100 %	1267	109.2	7.28	[20]
285	Multidirectional	-	99.79 %	1155	-	4.1	[21]
139	Zigzag alternating	Horizontal	99.06 %	831.5	97.5	1	[22]
139	Zigzag alternating	Vertical	99.06 %	749.2	84.9	1	[22]
55	Chessboard	-	99.81 %	1215	-	8.9	[23]
47.2	Zigzag with 90° rotation between each layer	Horizontal	99.9 %	1265	112	9.4	[6]

For Ti6Al4V the best results in density, elongation and elastic modulus, which are close to industrial reference (ASTM F-136), is found in [6]. As for SLM CoCrMo alloy, one can say that despite the many works devoted to the study of the mechanical properties of these materials, it is difficult to name the work where key-factors, high density and mechanical properties were indicated simultaneously. The lack of suitable data is a serious problem because it affects the repeatability and check of the results and greatly hampers the scientific research of these materials, especially in terms of using of the unique 3D printing capabilities to create complex shapes. However, it can be assumed that the best mechanical properties for this alloy were found in [24].

Table 2. The effect of the different values of main factors on mechanical properties of the as-build SLM CoCrMo alloy.

Laser density (J/mm^3)	Scanning strategy	Building geometry	Density (g/mm^3)	UTS (MPa)	E (GPa)	Elongation %	Ref.
ASTM F75 CoCr	-	-	8.3	655	220	□8	[19]
138.8	-	-	99.8 %	1050	-	14.5	[24]
53.6	-	-	95 %	1000	-	12	[24]
143	Chessboard	Horizontal	-	1281	-	12.8	[25]
143	/-/	45	-	1290	-	14.09	[25]
143	/-/	Vertical	-	1301	-	13.0	[25]
120	Chessboard	Vertical	98.2 %	874	-	-	[26]
36	Chessboard	Vertical	94.9 %	756	-	-	[26]
25.6	Island (contour), deployed relative to each other on 45	-	-	720	213	-	[27]
67	-	Vertical	-	1136.95	225	13.73	[28]

4. Conclusion
The following conclusions can be done from this study:
1) A short review considering the main factors affecting the structure and properties of the Ti6Al4V and CoCrMo alloys manufactured by the selective laser melting is presented.
2) Main factors affected the mechanical properties of the SLM alloys are chosen according the physical processes, which occur in the material during 3D laser manufacturing.
3) It was shown that mechanical properties of the SLM Ti6Al4V and CoCrMo alloys depend on main factors, such as laser density, powder quality, scanning strategy, and building geometry. The variants of optimized process parameters for 3D printed medicine materials Ti6Al4V and CoCrMo with high density of are suggested.

5. Acknowledgments

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