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

N Kazantseva\textsuperscript{1,2}

\textsuperscript{1}Institute of Metal Physics UD RAS, 18 Sofia Kovalevskaya Str., Ekaterinburg, 620219, Russia
\textsuperscript{2}Ural Federal University, 19 Mira Str., Ekaterinburg, 620002, Russia

kazantseva-11@mail.ru

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 \( t_1 \) 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:

\[ \sigma = -E \cdot \varepsilon_t, \]

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 \( t=100^\circ C \), \( E=200 \) GPa, \( a^*(t)=11 \times 10^{-6} \) 1/°C, the calculated temperature stress (\( \sigma \)) was 220 MPa. In the case of the Ti6Al4V, at \( t=400^\circ C \), \( E=114 \) GPa, \( a^*(t)=10 \times 10^{-6} \) 1/°C, the calculated temperature stress (\( \sigma \)) 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 \( \alpha' \)martensitic structure without any cubic BCC phase. Standard stress-relief annealing of these alloys does not lead to the equilibrium two-phase \( \alpha \) (HCP)+\( \beta \) (BCC) structure [6]. SLM dental CoCrMo alloys exhibit the \( \gamma \) (FCC) metastable structure in comparison with the equilibrium two-phase \( \varepsilon \) (HCP)+\( \gamma \) (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]:

\[
E_s = \frac{P}{V \cdot d},
\]

\[
E_d = \frac{P}{V \cdot h \cdot s}.
\]

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 \( \Delta H \)) delivered by the laser into the powder bed:

\[
\Delta H = \frac{A \cdot P}{\rho \cdot \sqrt{\pi \cdot D \cdot V \cdot d^2}},
\]

where \( A \) is a function of absorptivity, \( D \) is a thermal diffusivity, and \( \rho \) 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 \( \mu m \)) 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 $90^\circ$ 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 $67^\circ$ 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 data 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.

| 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     | Zigzag with $90^\circ$ rotation between each layer | - | - | 4.43 | 860 | 114 | 10 | [19] |
| 86.8                   |                  |                 |                  |           |         |               |     |
| 285                    | Multidirectional | - | - | 100 % | 1267 | 109.2 | 7.28 | [20] |
| 139                    | Zigzag alternating | Horizontal | - | 99.79 % | 1155 | - | 4.1 | [21] |
| 139                    | Zigzag alternating | Vertical | 99.06 % | 831.5 | 97.5 | 1 | [22] |
| 55                     | Chessboard      | Horizontal | - | 99.81 % | 749.2 | 84.9 | 1 | [23] |
| 47.2                   | Zigzag with $90^\circ$ 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/mm³) | Scanning strategy | Building geometry | Density (g/mm³) | UTS (MPa) | E (GPa) | Elongation % | Ref. |
| ASTM F75 | - | - | 8.3 | 655 | 220 | □8 | [19] |
| CoCr 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 Island (contour), deployed relative to each other on 45 | Vertical | 98.2 % | 874 | - | - | [26] |
| 36 | Chessboard Island | Vertical | 94.9 % | 756 | - | - | [26] |
| 25.6 | - | - | 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
This work was supported by Russian Found of Basic Research N 17-03-00084, State programs “Diagnostics” AAAA-A18-118020690196-3.

References
[1] Asnawi Omar Mohd, Baharudin BT-HT and Sulaiman S 2017 AIP Conference Proceedings 1901
Ayyıldız S, Soylu E H, İde S, Kılıç S, Sipahi C, Pişkin B and Suat Gökçe H 2013 J Adv. Prosthodont 5 471

Lee S.-H, Takahashi E, Nomura N and Chiba A 2005 Materials Transactions 46 1790

Al Jabbari Y S 2014 J. Adv Prosthodont 6 138

Sarria P, Torres Y, Gotor F J, Gutiérrez E, Rodríguez M, González R, Hernández L, Peon E, Guerra H and González J 2006 Key Engineering Materials 704 260

Krakhmalev P, Fredricsson G, Yadroitseva I, Kazantseva N, Du Plessis A and Yadroitsev I 2016 Physics Procedia 83 778

Bi Zhang, Yongtao Li and Qian Bai Chin 2017 J. Mech. Eng. 30 515

Birger I A 1963 Residual stresses (Moscow : Mashgiz) 478

Van Zyl I, Yadroitseva I, Yadroitsev I 2016 South African Journal of Industrial Engineering 27 134

Hae Ri Kim, Seong-Ho Jang, Young Kyung Kim, Jun Sik Son, Bong Ki Min, Kyo-Han Kim, Tae-Yub Kwon 2016 Materials 9 596

Haijun Gong et al. 2017 IOP Conf. Ser.: Mater. Sci. Eng. 272 012024

Ben Vandenbroucke and Kruth J-P 2007 Rapid Prototyping Journal 13 196

Ghouse S, Babu S, Van Arkel R J, Nai K and Hooper P A, Jefferis J R T 2017 Materials and Design 131 498

Mindt H-W, Desmaison O, Megahed M, Peralta A, and Neumann J 2017 Journal of Materials Engineering and Performance 1

Karlsson J, Sjögren T, Snis A, Engqvist H, Lausmaa J 2014 Mater. Sci. Eng. A 618 456

Thijs L, Verhaeghe F, Craeghs T, van Humbeeck J and Kruth J-P 2010 Acta Materialia 58 3303

Zhou X, Li K, Zhang D, Liu X, Ma J, Liu W and Shen Z 2015 Journal of Alloys and Compounds 631 153

Song C, Yang Y, Wang Y, Wang D, Yu J 2014 Int. J. Adv. Manuf. Technol. 75 445

https://www.astm.org/Standards/B265

Vrancken B, Thijs L, Kruth J P and van Humbeeck J 2012 Journal of Alloys and Compounds 541 177

Becker T H, Beck M and Scheffer C 2015 South African Journal of Industrial Engineering 26 1

Hernández D G 2014 Influencia Microestructural y Dimensional en el Desgaste de Prototipos de Prótesis de Cadera Metal-Metal Fabricados en Co-Cr-Mo-C (Tesis; Universidad Autónoma de Nuevo León FIME Techiko Lisboa, Portugal)

Dimitrov D, Becker T H, Yadroitsev I and Booyens G 2016 South African Journal of Industrial Engineering 27 3

Liverania E, Balbob A, Monticellib C, Leardinic A, Belvederec C and Fortunato A 2017 Procedia CIRP 65 25

E Girardin, G Barucca, P Mengucci, F Fiori, E Bassoli, A Gatto, L Iuliano and B Rutkowski 2016 Materials Today: Proceedings 3 889

Liverani E, Fortunato A, Leardini A, Belvedere C, Siegler S, Ceschini L and Ascani A 2016 Materials and Design 106 60

Dolgov N A, Dikova Ts, Dzhendov Dzh, Pavlova D and Simov M 2016 2016 Proc. II International scientific-technical conference "Innovations in engineering" XXIII 29

Mergulhão M V and Martins M D 2018 Journal of Biomaterials and Nanobiotechnology 9 89