Structure and properties of a cobalt-chromium-molybdenum alloy obtained by selective laser melting

A A Saprykin\textsuperscript{1,a}, Yu P Sharkeev\textsuperscript{1,2,b}, N A Saprykina\textsuperscript{1,c}, M A Khimich\textsuperscript{2,3,d} and E A Ibragimov\textsuperscript{1,e}

\textsuperscript{1}National Research Tomsk Polytechnic University, Tomsk, Russia
\textsuperscript{2}Institute of Strength Physics and Materials Science SB RAS
\textsuperscript{3}National Research Tomsk State University, Tomsk, Russia
\textsuperscript{a}sapraa@tpu.ru, \textsuperscript{b}sharkeev@ispms.tsc.ru, \textsuperscript{c}saprikina@tpu.ru, \textsuperscript{d}khimich@ispms.tsc.ru, \textsuperscript{e}egor83@list.ru

Abstract. Cobalt-based heat-resistant alloys have unique properties that are used in corrosive environments and at high temperatures. The addition of chromium improves resistance to hot corrosion, while molybdenum improves corrosion resistance and strength. When machining a workpiece of a heat-resistant alloy, up to half of the material goes into chips and goes to processing. Modern trends in the development of additive technologies are aimed at saving material, introducing new materials and improving the physical and mechanical characteristics of the resulting products. Selective laser melting (SLM) is one of the additive methods for obtaining bulk metal products and is one of the most promising directions in the development of science and technology in recent years. This paper describes the porosity (the average value was 14 ± 5\%), the structure and properties of alloy samples obtained by selective laser melting in the following modes: laser power - 100 W, scanning speed - 350 mm / s, thickness of the applied powder layer – 25 μm, scanning step – 100 μm, frequency of pulse-periodic laser action (modulations) - 2.5 kHz from a spherical powder of the CoCrMo alloy (66 wt% Co, 28 wt% Cr, 6 wt% Mo).

1. Introduction
Alloys of the Co-Cr-Mo system are widely known in the world for their high physical and mechanical properties, corrosion resistance and resistance to aggressive media and critical temperature conditions. Alloys are well studied in domestic and foreign literature. The cobalt structure exists in two crystalline modifications: a low-temperature ε-phase with a hexagonal close-packed lattice and a high-temperature γ-phase with a face-centered cubic lattice. Studies have shown that the value of the hardness of the alloy directly depends on the amount of the low-temperature phase. The laser melting method allows to reduce the time of exposure of the laser beam to the powder composition by increasing the power and speed of the laser movement. Due to the high thermal conductivity of the metal alloy, rapid crystallization and cooling occur, which contributes to an increase in the proportion of the ε-martensite phase in the alloy and an increase in the hardness and wear resistance of parts. Obtaining products from alloys of this system by selective laser melting makes it possible to form the structure and phase composition, and, consequently, a complex of physical and mechanical properties, which are impossible or very problematic to obtain using traditional methods of manufacturing alloys and products from them. Powder compositions used in selective laser melting must meet certain requirements: spherical shape of particles, particle size, phase and elemental composition, fluidity, flowability, etc. This paper describes the porosity (the average value was 14 ± 5\%), the structure and properties of alloy samples obtained by selective laser melting in the following modes: laser power - 100 W, scanning speed - 350 mm / s, thickness of the applied powder layer - 25 μm, scanning step - 100 μm, frequency of pulse-periodic laser action (modulations) - 2.5 kHz from a spherical powder of the CoCrMo alloy (66 wt% Co, 28 wt% Cr, 6 wt% Mo).

2. Results and discussion
The produced powder is particles of the required chemical composition (66 wt.% Co, 28 wt.% Cr, 6 wt.% Mo), particle size distribution with a particle size in the range of 20-70 μm, phase composition (stabilized high-temperature γ-phase) with spherical or spherical-like shape. Such a set of characteristics is obtained by spheroidization methods through melting and rapid crystallization of powder particles. In recent years, metal powders, including pure iron, stainless steel, tool steel, titanium alloys, cobalt-chromium alloys, nickel-based superalloys, alloys based on copper, aluminum, etc., have been used in additive technologies [1]. A part produced by laser melting layer-by-layer consists of cured tracks and combined layers. In the process of local melting of a metal powder by a laser beam, rapid crystallization and cooling, it is possible to obtain unique features of the microstructure inherent only to this method. A promising direction is the creation of a martensitic structure. All existing studies were carried out on samples obtained from commercially available Co28Cr6Mo alloy powder and on industrial commercial equipment. A large number of works are devoted to the determination of laser melting conditions for obtaining samples from CoCrMo alloy powder [2, 3]. An increase in the martensitic structure in samples of CoCrMo alloy powder obtained by selective laser melting after aging is described in [4]. The samples with the highest microhardness were obtained by aging at 900 °C for 10 hours. In these studies, a relationship was established between the heat treatment process, microstructure and microhardness. In articles [5], the preparation of an alloy in the process of laser melting from a powder mixture of a CoCrW and Cu alloy was investigated and the mechanical properties of the obtained samples were studied. Before laser melting, the two powders were uniformly mixed together for 30 minutes. Barucca et al. [6] studied the structure of Co24Cr5Mo samples prepared by selective laser melting and confirmed the phase transition from β (cubic face-centered lattice) to α (hexagonal close-packed lattice) and carbide formation by electron microscopy and found unexpectedly high values hardness exceeding the values of a sample of this alloy, made by traditional methods. In Russia, in STANKIN, A. Nazarov. [7] developed a technological process for the manufacture of complex-profile parts from a heat-resistant cobalt alloy by the method of selective laser melting. The relationships between the parameters of selective laser melting, the structure and phase composition of the heat-resistant cobalt alloy are determined. Large-scale research in the field of selective laser melting from a CoCrMo alloy is carried out at the Massachusetts Institute of Technology (Boston, USA) [8]. In Russia, the team of Professor I. Shishkovsky (Skolkovo) is engaged in selective laser sintering (melting) of products. [9] in cooperation with the National School of Engineering Saint-Etienne (France) and the "Laboratory of innovative additive technologies” MSTU "STANKIN”. Equipment for the manufacture of medical implants is produced by several companies in the world. Concept Laser GmbH (Germany) manufactures Mlab cusing and R Mlab cusing installations, which can work with titanium alloys, titanium powder and cobalt-chromium powders [10]. SLM Solutions GmbH (Germany) manufactures SLM® 500 HL units that can work with titanium and cobalt-chromium alloys [11]. The experiment on the formation of bulk samples was carried out on a VARISKAF-100MVS selective laser melting facility. The melting process of powder materials was carried out in a chamber filled with an inert Ar gas after preliminary evacuation. The samples were formed on a VT1-0 titanium substrate preheated to a temperature of 190-200 °C. Analysis of the literature data and the available experience of working with refractory metal powders made it possible to preliminarily estimate the ranges of variable parameters of the installation. The scanning scheme is line-by-line by areas, the direction of shading is mutually perpendicular from layer to layer. The experience of previous studies has shown that with the proposed strategy for the formation of a single layer, a decrease in the scan length is accompanied by a decrease in residual stresses [12, 13]. The samples obtained had the shape of a parallelepiped with a square base, the side of which was 10 mm. The height of the obtained samples reached 5 mm. The surface of all the obtained samples after the completion of the melting process had developed morphology, relief, and roughness. To assess the structure and phase composition, the obtained samples were subjected to mechanical grinding in sections parallel and perpendicular to the substrate, polishing with diamond pastes, and chemical etching in a HCl:H2O2 mixture in a 5:1 ratio for 15 s [14]. The volumetric porosity of the obtained samples was estimated by the metallographic method. The study of the microstructure and elemental composition was carried out by the methods of optical metallography, scanning electron microscopy, and energy dispersive microanalysis. To assess the phase composition, studies were carried out using X-ray diffraction methods. Specimens prepared from spherical powder had varying porosity. Its average value was 14 ± 5%. The pores were irregular in shape with rounded edges. Most of the pores in the volume of the sample are interconnected and the pores form open porosity, which affects the strength and toughness of the alloy of the formed products. In the longitudinal and cross sections after etching, closed gas pores were observed in the samples, in the vicinity of which there were areas of dark contrast. A similar picture was observed by the authors of [15], who investigated the γ → ε transformation in alloys of the CoCrMo system, initiated by an increase in the defectiveness of the material.
under multiple plastic deformation by rolling. In their work, they identify such areas of dark contrast as the ε-phase based on the low-temperature cobalt phase. In some areas, grains were observed whose shape was close to equiaxial, and the average size did not exceed 10 μm. Both open and closed porosity are observed in the raster images of the obtained sample in longitudinal and cross sections, Figure 1. The pores had an irregular shape. The closed pore size did not exceed 25 μm. In the vicinity of the pores, areas of dark contrast were observed. In individual images, areas of molten material were observed inside the pores. The study by the method of energy dispersive microanalysis showed a uniform distribution of the components of cobalt, chromium and molybdenum over the cross section of the sample. Analysis of the chemical composition over the entire cross-sectional area showed an integral ratio of the values of the concentrations of cobalt, chromium and molybdenum, corresponding to the declared alloy, i.e. 66 wt. % Co, 28 wt. % Cr, 6 wt. % Mo. The results of point microanalysis showed that the concentration of cobalt, chromium and molybdenum in certain areas of the surface, in the vicinity of the pores and in the areas of molten material inside the pores corresponds to 66, 28, and 6 wt. %, respectively. Oxygen is present in the alloy. Its mass fraction did not exceed 2 wt. % and indicates the formation of an oxide layer on the surface, which is formed during storage and transportation of samples. The elemental composition in dark and light areas is identical. The single-phase state of the studied samples is identified by X-ray diffraction methods, Figure 2. All reflections present in the profile correspond to reflections from the planes of the ε-phase. Broadened X-ray peaks indicate the small size of the coherent scattering regions, which indirectly indicates the small size of the structure elements, as well as a high level of internal residual stresses. The lattice parameters calculated from the profiles turned out to be equal: a = 0.2535 ± 0.0001 nm, c = 0.4114 ± 0.0002 nm, which exceeds the reference values of the ε-cobalt lattice parameters (a = 0.2507 nm, c = 0.40695 nm [16]). This difference in lattice parameters is a consequence of the deformation of the crystal lattice of the base, in this case, cobalt, due to the incorporation of molybdenum and chromium atoms into the crystal lattice, an increase in defectiveness, as well as thermal stresses that accompany the SLM process. A significant redistribution of intensities on the X-ray profiles of the alloy obtained should be noted. The predominant growth is observed in the crystallographic direction <002>. This direction is perpendicular to the plane of the substrate, parallel to the direction of growth of the samples, and is traditional for the samples obtained by SLS. Thus, the resulting alloy is a solid solution based on a hexagonal low-temperature phase of cobalt - ε, in which cobalt, chromium and molybdenum are uniformly distributed, with the predominant crystallographic growth direction being <002>. It should be noted that the ε-phase is thermodynamically stable in the alloy and increases its strength, workability at low temperatures, and plasticity [17].

Figure 1. SEM images of the polished surfaces of an SLM sample of a Co-Cr-Mo alloy made of a spherical powder in longitudinal (a) and transverse (b) sections.
The microhardness of the SLM samples obtained from the powder was studied in sections parallel and perpendicular to the substrate. Its value in the section parallel to the substrate was 4800 ± 400 MPa; perpendicular – 5600 ± 310 MPa. Such a difference in the values in the longitudinal and cross sections can be associated with the applied strategy of selective laser melting [18].

Conclusions

This article discusses the possibility of obtaining bulk samples from a spherical powder of the CoCrMo alloy (66 wt% Co, 28 wt% Cr, 6 wt% Mo) by selective laser melting. The results of the influence of the selective laser melting mode (laser radiation power – 100 W, scanning speed – 350 mm/s, thickness of the applied powder layer – 25 μm, scanning step – 100 μm, frequency of pulse-periodic laser action (modulations) - 2.5 kHz are presented.) on the porosity of the samples (the average value was 14 ± 5%), changes in the structure of the material, microhardness (in the section parallel to the substrate, 4800 ± 400 MPa; in the perpendicular section, 5600 ± 310 MPa).

Acknowledgments

«The reported study was funded by RFBR and Tomsk region according to the research project №19-48-700022»

References

[1] Zhou, X., Li, K., Zhang, D., Liu, X., Ma, J., Liu, W., Shen, Z., 2015. Textures formed in a CoCrMo alloy by selective laser melting. J. Alloys Compd. 631, 153–164. https://doi.org/10.1016/j.jallcom.2015.01.096

[2] Saprykin, A.A., Sharkeev, Y.P., Saprykina, N.A., Ibragimov, E.A., 2020. Surface formation mechanisms in selective laser melting of cobalt-chromium-molybdenum powder. Key Engineering Materials, 839 KEM, 73–78

[3] Saprykin, A.A., Sharkeev, Y.P., Saprykina, N.A., Ibragimov, E.A., The mechanism of forming coagulated particles in selective laser melting of cobalt-chromium-molybdenum powder. Key Engineering Materials, 2020, 839 KEM, 79–85

[4] Zhang, M., Yang, Y., Song, C., Bai, Y., Xiao, Z., 2018. An investigation into the aging behavior of CoCrMo alloys fabricated by selective laser melting. J. Alloys Compd. 750, 878–886. https://doi.org/10.1016/j.jallcom.2018.04.054

[5] Lu, Y., Ren, L., Xu, X., Yang, Y., Wu, S., Luo, J., Yang, M., Liu, L., Zhuang, D., Yang, K., Lin, J., 2018. Effect of Cu on microstructure, mechanical properties, corrosion resistance and cytotoxicity of CoCrW alloy fabricated by selective laser melting. J. Mech. Behav. Biomed. Mater. 81, 130–141. https://doi.org/10.1016/j.jmbbm.2018.02.026

[6] Barucca, G., Santeccchia, E., Majni, G., Girardin, E., Bassoli, E., Denti, L., Gatto, A., Iuliano, L., Moskalewicz, T., Mengucci, P., 2015. Structural characterization of biomedical Co-Cr-Mo components produced by direct metal laser sintering. Mater. Sci. Eng. C 48, 263–269. https://doi.org/10.1016/j.msec.2014.12.009
[7] Nazarov A. P. Development of the technological process for manufacturing complex-profile parts and heat-resistant cobalt alloy by selective laser melting: dis. candidate of technical Sciences, Moscow, 2013

[8] Benjamin M. Wua, Scott W. Borlandb, Russell A. Giordanob, Linda G. Cimac, Emanuel M. Sachsd, Michael J. Cima Solid free-form fabrication of drug delivery devices. Journal of Controlled Release Volume 40, Issues 1–2, June 1996, Pages 77–87.

[9] I. I. Zhuravleva, T. V. Rodchenko, A. L. Petrov, V. I. Shcherbakov, A. I. Snarev, and I. V. Shishkovsky Modeling and studying the properties of gradient filtering elements using the synthesized SLS method. Laser engineering and technology 2006 with 419-428

[10] I. V. Shishkovskii, I. A. Yadroitsev, I. Yu. Smurov Selective laser sintering/melting of nitinol–hydroxyapatite composite for medical applications. Powder Metallurgy and Metal Ceramics September 2011, Volume 50, Issue 5-6, pp 275-283.

[11] Nazarov A. P., Okunkova A. A. Typical samples of products obtained by selective laser sintering. Bulletin of the Saratov state technical University No. 1 (67) / volume 3 / 2012 p. 76-82

[12] Sharkeev Yu P, Eroshenko A Yu, Kovalevskaya Zh G, Saprykin A A, Ibragimov E A, Glukhov I A, Khimich M A, Uvarkin P V and Babakova E V 2016 Structural and Phase State of Ti–Nb Alloy at Selective Laser Melting of the Composite Powder Russian Physics Journal 59(3) pp 430-434

[13] Saprykin A A, Sharkeev Yu P, Ibragimov E A, Babakova E V, Kovalevskaya Zh G, Eroshenko A Yu, Khimich M A, Uvarkin P V, Glukhov I A 2016 Synthesizing conditions and structural-phase state of Ti-Nb alloy when selective laser melting ECCM 2016 - Proceeding of the 17th European Conference on Composite Materials

[14] F. Z. Hassani, M. Ketabchi, S. Bruschi, A. Ghiotti Effects of carbide precipitation on the microstructural and tribological properties of Co–Cr–Mo–C medical implants after thermal treatment. J. Mater. Sci. 2016. 51. 4495–4508. Doi: 10.1007/s10853-016- 9762-5.

[15] M. Mori, K. Yamanaka, S. Sato, S. Tsubaki, K. Satoh, M. Kumagai, M. Imafuku, T. Shobu, A. Chiba Tuning strain-induced γ-to-ε martensitic transformation of biomedical Co-Cr-Mo alloys by introducing parent phase lattice defects. Journal of the Mechanical Behavior of Biomedical Materials. 90. (2019). 523–529. Doi: https://doi.org/10.1016/j.jmbbm.2018.10.038

[16] https://www.webelements.com/cobalt/crystal_structure.html

[17] M. Béreš, C.C. Silva, P.W.C. Sarvezuk, L. Wu, L.H.M. Antunes, A.L. Jardini, A.L.M. Feitosa, J. Žilková, H.F.G. de Abreu, R.M. Filho Mechanical and phase transformation behavior of biomedical CoCr-Mo alloy fabricated by direct metal laser sintering. Materials Science & Engineering A. 714. (2018). 36–42. Doi: https://doi.org/10.1016/j.msea.2017.12.087

[18] Mechanical and phase transformation behaviour of biomedical Co-Cr-Mo alloy fabricated by direct metal laser sintering. M Béreš, CC Silva, PWC Sarvezuk, L Wu, LHM Antunes, AL Jardini, Materials Science and Engineering: A 714, 36–42, 2018. 9. 2018