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DOI: 10.31897/PMI.2020.2.191

UDC: 621.762.2

Chemical heterogeneity as a factor of improving the strength of steels manufactured by selective laser melting technology

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The aim of this paper was to establish the causes of the heterogeneity of the chemical composition of the metal obtained by the LC technology. The powdered raw material was made from a monolithic alloy, which was fused by the SLM, the initial raw material was a laboratory melting metal of a low-carbon chromium-manganese-nickel composition based on iron.

To determine the distribution pattern of alloying chemical elements in the resulting powder, electron-microscopic images of thin sections were combined with X-ray analysis data on the cross-sections of the powder particles. As a result, it was found that transition (Mn, Ni) and heavy (Mo) metals are uniformly distributed over the powder particle cross-sections, and the mass fraction of silicon (Si) is uneven: in the center of the particles, it is several times larger in some cases. The revealed feature in the distribution of silicon is supposedly due to the formation of various forms of SiO_4 upon the cooling of the formed particles.

The internal structure of the manufactured powder is represented by the martensitic structure of stack morphology. After laser fusion, etched thin sections revealed traces of segregation heterogeneity in the form of a grid with cells of ~ 200 μm. The boundaries of segregations and the fine-grained structure were the dominant mechanisms of steel hardening in the SLM process.

Under compression of the obtained samples, the yield strength was 720 MPa, and the greatest value of the deformation resistance reached 1050 MPa, which exceeds the performance of a monolithic material of the similar chemical composition. In the diagrams σ (ε) in the parabolic hardening section, randomly located extrema of local hardening are recorded, followed by a sharp load decrease. The appearance of the diagrams indicates an inhomogeneous internal structure of the samples.

Key words: additive technology; powder materials; fusion; hardening; chemical heterogeneity

Introduction The manufacture of complex-shaped products by selective laser melting technology (SLM[*]), fusing of layers of powdered materials, is of practical and scientific interest [4, 6, 9-11, 13, 14]. In experiments on the fusion of industrial powders with similar granularity (JSC "Polema", JSC "Höganäs") and with the chemical composition of common steel grades (07Kh16N4D4Б, 03Kh16N15M3, 12Kh18N10T and others [1, 2, 8, 12, 15]) they noted the improvement of strength of the final samples in comparison with the monolithic state of metal with the same chemical composition. One of the reasons for strength improvement was the chemical heterogeneity of the fused material. However, it remained unclear at what technological stage the chemical heterogeneity arose.

The goal of this paper was to establish the root causes of the heterogeneity of the chemical composition of the metal fused with SLM. To achieve this goal, it was necessary to produce powdered raw materials from a monolithic alloy of given chemical composition with its subsequent fusion by the SLM method in laboratory conditions.

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[*] In a number of works, the technology under consideration is treated as selective laser fusion (SLF).

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Methods. The initial raw material was the experimentally laboratory melted metal of low-carbon (C ~ 0.09 wt.%) chromium-manganese-nickel composition based on iron. The laboratory ingot and the produced powder have the following chemical composition (wt.%), respectively: Mn (0.38; 0.35), Si (0.26; 0.3), Cr (0.41; 0.45), Ni (1.93; 1.88), Mo (0.25; 0.24).

At all manufacturing stages and subsequent testing of samples, the chemical composition of the metal was controlled by the X-ray spectral analysis. According to averaged data, the chemical composition of the powder almost matched the chemical composition of the laboratory ingot.

The powder for selective laser melting was made on the HERMIGA 75/IV unit (Fig.1) by spraying the melt (atomization) at a temperature of 1650 °C in an argon atmosphere, followed by cooling at a rate from 10^5 to 10^8 °C/s.

The resulting powder was characterized by spherical particles with a size up to 200 μm. Then, the powder was screened to form the powder suitable for SLM (<80 μm); the fraction of suitable powder was 70 %. The SLM was carried out on the EOSINT M270 unit (Fig.2), which technical characteristics ensure the complete fusion of powders in successively applied layers of the manufactured raw materials.
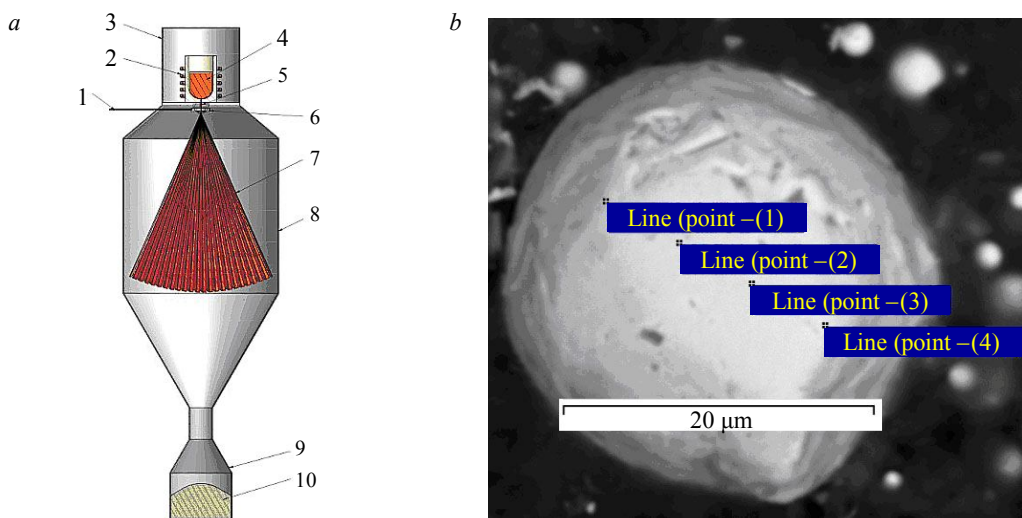

Fig.1. HERMIGA 75/IV unit for atomization of the melt (*a*) and representative powder particle with points for determining the chemical composition of the metal (*b*)

1 – nebulizer gas supply; 2 – inductor rings; 3 – induction furnace; 4 – melted metal; 5 – metal discharge pipe; 6 – atomizing nozzle; 7 – metal spray fan; 8 – spraying chamber; 9 – receiving container; 10 – metal powder
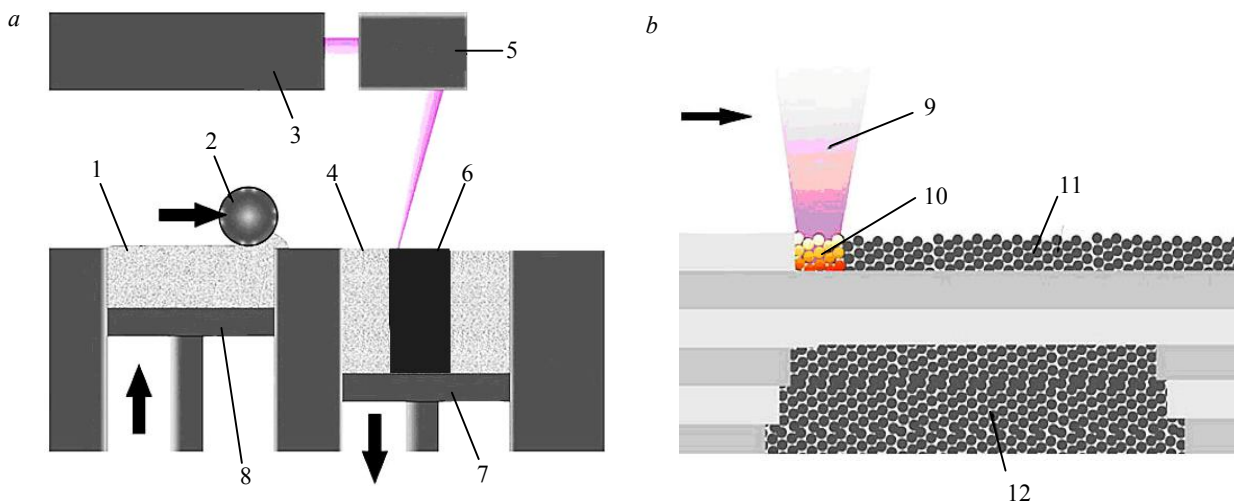

Fig.2. The SLM process scheme carried out at EOSINT M270 unit

1 – input powder; 2 – feed roll; 3 – laser; 4 – non-fused powder; 5 – scanning system; 6 – a model after fusion; 7 – control system; 8 – powder supply system; 9 – laser beam; 10 – SLM fusion zone; 11 – previous layer of the powder; 12 – SLM fusion material model

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The spherical shape of the particles indicated that the sprayed metal condensed according to the vapor → liquid scenario [3]. Depending on the cooling conditions, the liquid could crystallize into a crystal or remain in a supercooled (partially amorphous) state.

In the experiment, the cylinder samples with a diameter of 6 and a height of 10 mm were produced from the obtained powder. The samples were built by scanning with a laser beam with a specific energy of 0.2-0.3 J/mm of the construction area with the introduction of powder into the layers. The samples were created layer by layer.

The produced samples were tested in the chamber of Gleeble 3800 power simulator by mechanical compression at room temperature to a true strain $\varepsilon = 0.3$ with a strain rate of 10^{-3} s^{-1}. The compression test allowed to level the effect of possible non-melts and blow spaces on the strength of the samples.

The structure of the resulting SLM metal was studied by thin-section metallography using light (Axiovert 4MAT) and electron scanning (Teskan Vega 3) microscopes.

Discussion. To determine the distribution pattern of the alloying chemical elements in the manufactured powder, electron-microscopic images of thin sections were combined with the data of the X-ray spectral analysis on the sections of the powder particles. The distribution of alloying elements (Cx) was estimated in relative units (mass fractions) in relation to the basis iron: Cx/Fe.

It was found that transition (Mn, Ni) and heavy (Mo) metals on the cross-sections of powder particles are distributed uniformly regardless of the size of the probed area (Figs.3, 4). The mass fraction of silicon is distributed unevenly: in the center of the particles, the silicon content in several cases exceeds the values in the peripheral regions. This suggests that silicon, having an affinity for oxygen, at high temperatures actively diffuses toward the outer surface of the particles and interacts with the environment, forming oxides.

Under conditions of a high-temperature state, several forms of silicon-containing melts are known, which differ in the mutual arrangement of SiO$_4$ tetrahedra [7]: β-cristobalite (1710 °C), β-tridymite (1470 °C), β-quartz (870 °C), α-quartz (573 °C), etc., with macromolecular covalent bonds in the solid-state. It can be assumed that the revealed feature in the distribution of silicon is due to the formation of various forms of SiO$_4$ during cooling of the formed particles. Moreover, their internal structure can affect the crystallization kinetics and the liquid-solid interaction of the contacting powder particles in the laser exposure zone.

The noted fact can explain the excess of the improved strength of the alloy due to the concentration factor (Cx) in comparison with strain hardening [5]: $d\sigma/dCx > d\sigma/d\gamma$, where γ is the shear strain.
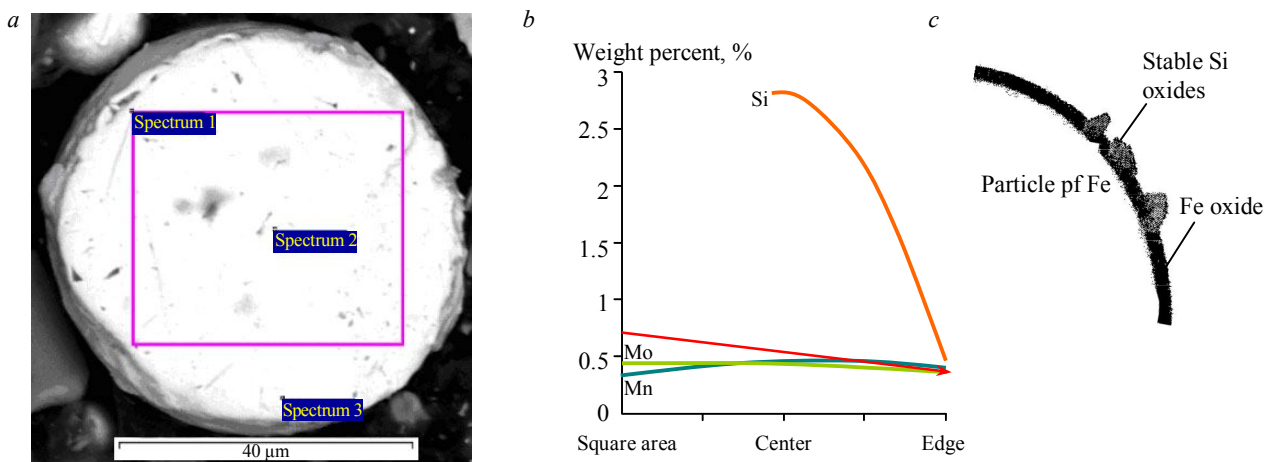

Fig.3. A section of powder with an indication of the square area and local points of X-ray spectral analysis (*a*), the distribution of Si, Mn, and Mo depending on the size and points of X-ray spectral analysis (*b*) and the arrangement of metal oxidation products obtained by the SLM method (*c*)

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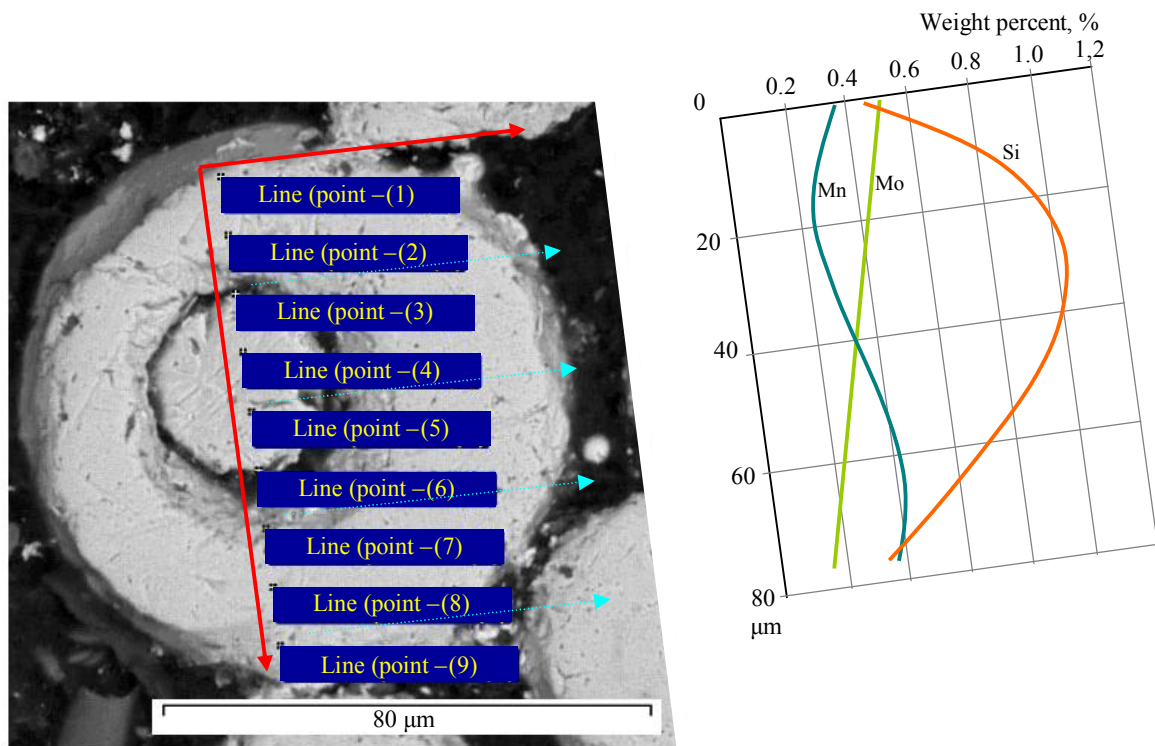
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Fig.4. On the cross section of a powder particle the distribution of Si, Mn, and Mo along the red line of local scanning (*a*), the coordinate reference is shown by dashed blue lines (*b*)
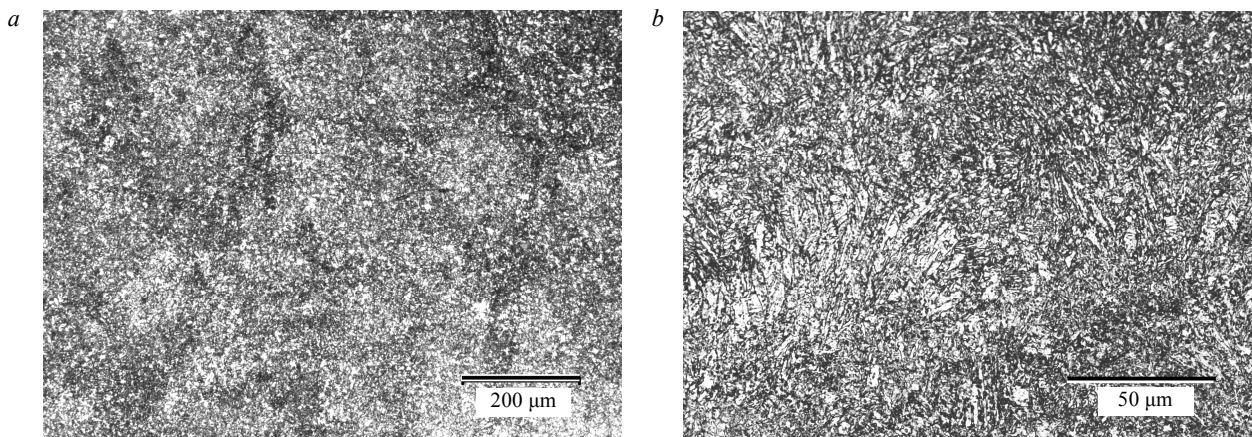

Fig.5. The structure of steel obtained by SLM method: segregation cells up to 200 μm in size (*a*) and unequal dendritic crystals of size ~ 5 × 50 μm and equiaxed grains of micrometric scale (*b*)

The internal structure of the manufactured powder is represented by the martensitic structure of stack morphology. After laser fusion, etched thin sections revealed traces of segregation heterogeneity in the form of a grid with cells of ~ 200 μm. Inside the cells, there are unequal (5 × 50 μm) crystals of a dendritic type and different orientations, as well as a grain mass of 3-5 μm in size (Fig.5). It must be assumed that the boundaries of segregations and the fine-grained structure were the dominant mechanisms of steel hardening in the SLM process.

The formulated proposition was confirmed by the results of mechanical tests. It was established (Fig.6) that, when compressing the obtained samples, the yield strength was 720 MPa, and the greatest value of the deformation resistance reached 1050 MPa, which exceeds the similar indices of a monolithic material of the similar chemical composition. The σ (ε) diagrams in the parabolic hardening section show randomly located extrema of local hardening, followed by a sharp load decrease. The shape of the diagrams verified the heterogeneous internal structure of the samples.
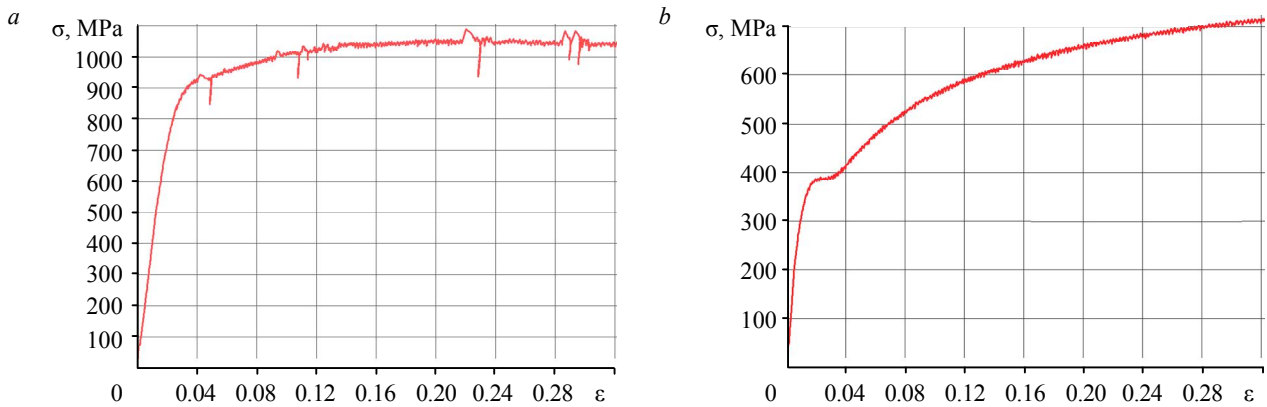
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Fig.6. Diagrams of plastic deformation resistance of steel samples in the following states: right after SLM (*a*);
after SLM and subsequent heat treatment at 980 °C for 300 s (*b*)

Annealing of the obtained samples at a temperature of 980 °C for 300 s in the structural state of a face-centered cube (FCC) followed by cooling at a rate of ~ 6 °C/s eliminated the structural inhomogeneity of the initial state, which caused a decrease in the strength characteristics of the metal by 1.5 times. In addition, at the level of $\sigma = 400$ MPa, a yield site appeared, that is typical of steels with a body-centered cube (BCC) structure, because of strain age effect.

Conclusions. Based on the results of the study we can conclude the following:

1. Chemical inhomogeneity of the powder produced by the spraying method arises at the stage of the atomization of the melt.

2. For the implementation of the process with the complete fusion of the powder layers, the particle size should not exceed the thickness of the applied layer, provided for by the technical documentation of the equipment used with a concentrated (laser or other) energy source.

3. For high-quality manufacturing of products using the SLM method, the technological and morphological parameters of the used powdered materials should be regulated.

4. During the implementation of the SLM process, the chemical heterogeneity of the powder raw materials can be aggravated by the diffusion of chemical components towards the outer surface of the particles, followed by the formation of oxides.

5. The chemical heterogeneity of the fused sample can be leveled by additional heat treatment at temperatures and times sufficient for the diffusion of segregates.

6. Compared to monolithic metal materials, samples of a similar chemical composition manufactured by the SLM method are characterized by increased strength characteristics due to chemical heterogeneity and ultrafine crystallization structure.

REFERENCES

1. Barakhtin B.K., Zhukov A.S., Deev A.A., Voznyuk A.V. The effect of the chemical composition of powdered raw materials on the strength of the material after selective laser melting. *Metallovedenie i termicheskaya obrabotka materialov*. 2018. N 6, p. 48-52 (in Russian).

2. Barakhtin B.K., Bobyr V.V., Voznyuk A.V., Deev A.A., Zhukov A.S., Kuznetsov P.A. Optimization of technological parameters and determination of the regimes of lasercusing of powder based on 316L steel. *Voprosy materialovedeniya*. 2017. N 2 (90), p. 146-151 (in Russian).

3. Palatnik L.S., Paptrov I.I. Oriented crystallization. Moscow: Metallurgiya, 1964, p. 408 (in Russian).

4. Perevertov V.P., Andronchev I.K., Abulkasimov M.M. Technologies for processing materials with concentrated energy flow. *Nadezhnost i kachestvo slozhnykh sistem*. 2015. N 3(11), p. 69-79 (in Russian).

5. Rudskoi A.I., Vargasov N.R., Barakhtin B.K. Thermoplastic deformation of metals. St. Petersburg: Izd-vo Politekhnicheskogo un-ta, 2018, p. 286 (in Russian).

6. Grigoryants A.G., Kolchanov D.S., Tretyakov R.S., Malov I.E. Selective laser melting of metal powders, growing thin-walled and mesh htructures. *Tekhnologiya mashinostroeniya*. 2015. N 10, p. 6-11 (in Russian).

7. Sienko M., Plein R., Khester R. Structural inorganic chemistry. Moscow: Mir, 1968, p. 344 (in Russian).

8. Kuznetsov P.A., Zisman A.A., Petrov S.N., Goncharov I.S. Structure and mechanical properties of 316L austenitic steel obtained by selective lasercusing. *Deformatsiya i razrushenie materialov*. 2016. N 4, p. 9-13 (in Russian).

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Chemical Heterogeneity as a factor of Improving the strength of steels…

DOI: 10.31897/PMI.2020.2.191

9. Shishkovskii I.V. High Resolution Additive Technology Basics. St. Petersburg: Piter, 2016, p. 400 (in Russian).

10. Hussein A., Hao L., Yan C., Everson R., Young P. Advanced lattice support structures for metal additive manufacturing. *Journal of Materials Processing Technology*. 2013. Vol. 213. Iss. 7, p. 1019-1026. DOI: 10.1016/j.matprotec.2013.01.020

11. Campanelli S.L., Contuzzi N., Angelastro A., Ludovico A.D. Capabilities and performances of the selective laser melting process. New Trends in Technologies: Devices, Computer, Communication and Industrial Systems. Croatia: InTech, 2010, p. 233-252. DOI: 10.5772/10432

12. Ganesh P., Giri R., Kaul R., Sankar P.R. Studies on pitting corrosion and sensitization in laser rapid manufactured specimens of type 316L stainless steel. *Materials and Design*. 2012. N 39, p. 509-521. DOI: 10.1016/j.matdes.2012.03.011

13. Sedlaka J., Rican D., Piska N., Rozkosny L. Study of materials produced by powder metallurgy using classical and modern additive laser technology. *Procedia Engineering*. 2015. Vol 100, p. 1232-1241. DOI: 10.1016/j.proeng.2015.01.488

14. Wang D., Yang Y., Liu R., Xiao D., Sun J. Study on the designing rules and processability of porous structure based on selective laser melting (SLM). *Journal of Materials Processing Technology*. 2013. Vol. 213. Iss. 10. P. 1734-1742. DOI: 10.1016/j.matprotec.2013.05.001

15. Zhukov A., Barakhtin B., Kuznetsov P. Study of strength characteristics of steel specimens after selective laser melting of powder materials 17-4PH, 316L, 321. *Physics Procedia*. 2017. Vol. 89. P. 179-186. DOI: 10.1016/j.phpro.2017.08.012

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