Crystallization and size effects in the technology of selective laser melting of metal powders

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Abstract. A phenomenological model of the formation of phase nuclei by the vapor condensation mechanism over the metal melting zone is formulated. A multifractal analysis of the structure of steels manufactured from powders of different chemical composition by additive technology is presented. It is shown that the solidification of the molten metal is determined by the technological scheme of the selective process.

1. Introduction
At present, the technology of selective laser melting (SLM) has become widespread, consisting in the layer-by-layer formation of three-dimensional objects according to their computer models [1-3]. The peculiarity of the SLM process is the presence and interaction of areas of solid and liquid phases during short-term exposure to a laser beam. Local melting acts and structural phase transformations implemented under thermodynamic nonequilibrium conditions are not well understood, although they are widespread in applications with transitional technological regimes.

The aim of the present work is to identify the mechanisms of strengthening the material after SLM, taking into account the data of multifractal analysis of structures of metal samples obtained from powders of different chemical composition.

2. Materials and experimental methods
In the experiments, we have used powders with the chemical composition of two grades. One of the powders correspond to stainless steel 17-4PH, and the other to lightly alloyed technical iron (Table 1).

The powder for our experiments has been manufactured on the HERMIGA 75/IV unit by melt spraying (atomization). The granulometric composition of the powder is determined on a Malvern Mastersizer 2000 unit using laser diffraction. A spherical shape and a particle size of up to 200 µm characterizes the resulting powder. Then, the fraction of the powder suitable for use in the SLM technology <80 µm is screened out, with the proportion of usable powder of 70%.

Table 1. Chemical composition of used powders

| Metal grades | Basic alloying elements, wt.% |
|--------------|-----------------------------|
|              | C  | Si  | Mn  | Cr  | Ni  | Mo  | Ti  |
| 17-4 PH      | 0.07 | 0.38 | 0.70 | 15.70 | 4.00 | —   | 0.10 |
| Fe           | 0.02 | 0.07 | 0.08 | —   | —   | —   | —   |
SLM has been carried out with the EOSINT M270 unit placed on the experimental site of the Nanocentre of NRC “Kurchatov Institute” – CRISM “Prometey” (figure 1). In this unit, a solid-state (Yb-fibre) laser is capable of continuously scanning the powder melt zone. In our aim, the powders are melted at 200 W and scanning speeds of 600, 650, 700, 750, 800 mm/s. Precision optics is represented by F-theta-lens and high-speed scanner, variable focus diameter is 100-500 μm. The thermal energy introduced into the reaction volume is sufficient to realize the method of SLM of powder particles. Layer thickness depends on material and amounts 40 μm.

![Figure 1. The scheme of SLM realized on the EOSint M270 unit.](image)

Structural studies have been performed by common metallography methods, using optical (Axio Observer) and scanning electron (FEI Tecnai) microscopy. Image processing includes multifractal analysis to detect structural features caused by the transience of melting and solidification under conditions of heterogeneous temperature fields.

Multifractal parametrization of half-tone images of structures is carried out according to their black-and-white (binary) mappings, which are mathematically considered in the form of statistical sets of different dimensions, according to [4]. The required parameters are calculated from the Dq spectrum of dimensions: the spatial dimension of D0, the measure of ordering δ, and the measure of periodicity K. Here q is the dimension of monofractal binary subsets in the interval of q from –40 to +40 that make up the binary display of the original halftone image. The spatial dimension D0 is sensitive to the size of the region of structural changes and is a quantitative estimate of the image characterizing the filling of the image field. The δ value is sensitive to symmetry breaking for the general configuration of the structure under study as a whole. The greater the value of δ (in absolute value), the more ordered the structure is, and the striving of δ to zero is a sign of chaos on the eve of a change in the state of aggregation. An increase in K values indicates an increase in the periodic component in the inspected mapping of structures. The results of the multifractal parametrization have a probabilistic statistical meaning [5], and the usefulness of the analysis is determined by the physical content of the problem.

3. Experimental results and discussion

By means of light and electron scanning microscopy, it has been established that spherical particles with magnitudes ranging from tenths of a micrometer to several micrometers are present in SLM samples. The correct geometric shape of the particles indicates that they are formed in a “free” (suspended) state without contact with other objects. According to [6], such a phenomenon is possible if at temperatures below temperature of melting the vapor condenses into a liquid (V → L). With rapid cooling, the liquid could remain in a supercooled amorphous state or crystallize (L → C). Metal
condensation by the mechanism of desublimation $V \rightarrow C$ or $V \rightarrow L$ is associated with cooling conditions. Depending on the temperature and vapor pressure, both mechanisms can be realized. Traces of the droplets formation in the form of luminous tracks of scattering particles can be seen on figure 2 and are observed by the authors in the acts of the SLM of all the powders used [7].

In places where the particles are subjected to intense laser heating, they melted. Where the energy of the laser beam is insufficient, the particles are kept in a state of crystallization of different degrees of completion. It can be assumed that the preserved particles of small sizes played the role of mechanisms, both hardening with secretions and activation of epitaxy processes in fusion microvolumes with a new deposited layer of powder. A wide range of states, from non-equilibrium to close to equilibrium, determines the range of properties of the materials obtained, as well as the conditions for oriented growth (epitaxy) of powder layers.

![Figure 2. Tracks of scattering particles from the melting zone (a) and the sedimentation pattern of the condensed powder (b).](image)

When considering images of structures, it has been fixed that the smallest particle size formed in the mechanisms $V \rightarrow C$ or $V \rightarrow L$ is determined to be $0.15 \pm 0.05 \mu m$. Similar in size, the allocation of the correct geometric shape identified in the SLM structures of different chemical composition, for example, in 316L steel [7-9]. Consequently, the technological effect under consideration is a general phenomenon of the SLM.

In the physical thermofluctuation theory of strength, it is accepted [10, 11] that acts of destruction with the formation of germinal microcracks of $0.15\pm0.05 \mu m$ are caused by the sublimation process with irreversible breaks of interatomic bonds. We interpret the observed and oppositely directed process of consolidation of steam into spherical particles with sizes of $0.15\pm0.05 \mu m$ as the result of the formation of physical objects by ordering interatomic bonds with allowance for the coordination environment of atoms. For iron with an interatomic distance of $\sim 0.3 \text{ nm}$, $~10^7$ atoms can take part in the formation of spherical particles of minimal size, which is sufficient to implement such a reaction from the standpoint of topology. Under conditions of rapid cooling and compression of a vapor cloud, the efficiency of the proposed scenario is determined by fluctuations in vapor density with the dominant contributions of the periodic component in the interaction potential. Since the final stage of the organization of interatomic bonds is accompanied by a decrease in volume, the observed phenomenon can be regarded as a first-order phase transition. Implemented in the nonequilibrium thermodynamic conditions of the liquid-solid interaction, the particles of the condensed state are the basis for the formation of new objects – grains and crystals. During their crystallization, the morphology and direction of growth, the stability of the crystal lattice, the possibility of relaxation by shifts, and the orderliness are determined by fluctuations of temperature and chemical composition in the melting zone, possible convection, impurities and other factors [8].
A review of the thin sections of the samples after SLM showed that the metal structure is represented by a cellular-dendritic structure of different morphology. The data obtained indicated the crystallization of the metal under different conditions of concentration hypothermia by self-assembly of structural primitives according to the scheme that can be represented by an equation:

$$F = \frac{\lambda_i}{\lambda_{i+1}}$$  \hspace{1cm} (1)

where $F$ is the self-similarity function, $\lambda_i$ and $\lambda_{i+1}$ are the previous and subsequent threshold scales of the primitive in a self-governing system.

For a cellular-dendritic ground state of the structure, the determining factor is the cooling rate of the melt pool as the laser beam leaves the melting zone. The manifestation of the dendritic component indicates the mechanism of atomic migration associated with the periodicity in the molten structure. The occurrence of periodicity is associated with an acceleration of the diffusion process and the presence of a temperature field gradient. The effectiveness of the proposed scenario is determined by fluctuations in the vapor density with the dominant contributions of the periodic component to the interaction potential. The identification of periodicity signs in the structure of the SLP material was carried out using multifractal parameterization of structural images.

We have selected images of grains revealed by chemical etching on thin sections of stainless steel and technical iron (figure 3) as examples of multifractal parametrization of structures. Images of grains have been processed by the same algorithm.

![Figure 3](image_url)

**Figure 3.** An example of a multifractal parametrization of the structure of 17-4PH steel ($a$) and SLM iron ($b$).
The results of the multifractal parametrization of SLM structures reveal that, despite the short exposure times of the laser beam, an ordered periodic structure, characteristic for crystallization, dominates in the volumes of the solid-liquid state of the metal.

The scatter of the values of $D_0$, $\delta$, and $K$ suggests that the grains and crystals are formed under different thermodynamic conditions and are characterized by different morphology of the structures. For example, in grains, one can find signs of a disordered or amorphous state and pores ($D_0$ and $\delta$ are small), a tendency to ordering (growth $\delta$) with simultaneous periodicity (decreasing scatter $K$) and decreasing porosity (increasing $D_0$). Near the values of $\delta < 0.05$, the scatter $K$ increases, indicating the approximation of the structural phase transformation by the oscillatory mechanism. The obtained data suggest that, despite the close values of the multifractal parameters, even within the same image, the transformations occurring in volumes less than 0.15 $\mu$m are accompanied by less extensive acts of structural changes.

Although the data of multifractal parametrization of binary mappings are only approximately identified with real structures, the authors find it expedient to implement these results, believing that the obtained (although indirect) data provide additional information about the structure of the observed objects. For example, an increase in $\delta$ is accompanied by an increase in $D_0$, which indicates that the observation section is filled with the crystallizing phase. On the other hand, a decrease in $\delta$ indicates chaos in the mixture of melt and crystals, which leads to a buildup of $K$ values and indicates the appearance of a periodic dendritic component in the images (figure 4).

![Figure 4. Results of multifractal parametrization of technical iron grains.](image)

4. Conclusions

Upon receipt of materials by selective laser melting, the nuclei of a new structure or phase are formed not only in the volumes between the liquid and solid phases, but still earlier above the melting point through desublimation of steam into a solid state. Under the conditions of liquid-solid interaction, the particles of the condensed state become both hardeners of the metal and the basis for the formation of new objects — grains and crystals. The stable particle size of the condensed state is defined as $0.15\pm0.05$ $\mu$m.

We have processed halftone images of grains using the statistical-geometric approximation method, and obtained multifractal processing data, which provide additional quantitative information about the structural changes that have occurred. The structure of the metal after SLM has signs of a self-organized structure. The result of structural changes is influenced by the cooling rate of the molten metal zone.

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References
[1] Brandt M et al 2016 Laser Additive Manufacturing. Materials, Design, Technologies and Applications (Sawston, Cambridge: Woodhead Publishing) p 498
[2] Shishkovsky I V 2016 Basics of high-resolution additive technology (St.-Petersburg: Piter Publ) p 400 (In Russ)
[3] Kuznetsov P, Zhukov A, Deev A et al 2018 Structure and Properties of the Bulk Standard Samples and Cellular Energy Absorbers (Rieka: IntechOpen) p 144
[4] Barakhtin B K, Chashnikov V F 2001 Mater. Sci. Iss. 4(28) 5
[5] Bozhokin S V, Parshin D A 2001 Fractals and multifractals (Izhevsk: R&C Dynamics Publ) p 128 (In Russ)
[6] Palatnik L S, Papirov I I 1964 Oriented crystallization (Moscow: Metallurgiya Publ) p 412 (In Russ)
[7] Zhukov A, Barakhtin B, Kuznetsov P 2017 Phys. Proced. 89 179
[8] Durand-Charre M 2004 Microstructure of Steels and Cast Irons (Berlin: Springer-Verlag) p 406
[9] Saeidi K et al 2015 Mater. Sci. Eng. A 625 221
[10] Barakhtin B K, Nemec A M 2006 Metals and Alloys. Analysis and Research. Physico-Analytical Methods for Studying Metals and Alloys. Non-Metallic Inclusions (St.-Petersburg: SPA “Professional” Pul) p 490 (In Russ)
[11] Le J-L, Bažant Z P, Bazant M Z 2011 J. Mechan. Phys. Solids 59(7) 1291