Structural studies of samples manufactured by selective laser melting of the Fe-based powder

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Abstract. In the structure of the samples manufactured by the additive method of selective laser melting (SLM) of the Fe-based powder, particles were detected with a minimum size of 0.15 ± 0.05 μm, which were interpreted as germ objects of solidification. The model of additive samples hardening by nanoparticles was proposed, which were formed in the process of desublimations (condensation of metal vapors + crystallization) in the sequence: Metastable state to Segregation to Cluster to Nano-object.

1. Introduction
The additive method of manufacturing parts of a complex form with selective laser melting (SLM) of the metal powder is in demand and intensively developing [1]. In the works of domestic and foreign scientists, data is repeatedly given [2,3], according to which, the strength of additive parts is higher in comparison with monolithic metal materials. Tests of SLM samples manufactured from powders of different chemical and particle size distribution, confirm the improvement of the mechanical properties complex with an increase in the heat input of the laser [4].

Table 1. Efficiency of hardening mechanisms in steels.

| Reinforcing factor                  | The influence of the concentration factors: G-1 (dσ/dc) | Deformation hardification: G-1 (dσ/δγ) |
|------------------------------------|--------------------------------------------------------|---------------------------------------|
| Atoms of implementation            | 5 – 10                                                 | low or negative                       |
| Atoms of substitution              | 0.1 – 0.7                                              | 0.01 – 0.5                            |
| Borders of grains, surface section | 0.5 – 1.0                                              | 0.5 – 1.0                             |
| Partition formation                | 0.05 – 0.1                                             | 0 – 1.0                               |
| Streaming the structure            | 0.05                                                   | 0.1 – 0.3                             |

* Note: Dσ / DC is an increase in strength to the increase in factor concentration; γ – shift deformation; G – shift module.

In earlier works [5-7], it was assumed that in SLM samples of complex doping systems, the increase in strength and resistance to the development of cracks was caused by heterogeneity in the chemical elements distribution, the concentrations of which after the melting could be locally changed several times. However, the mechanical properties of metals and alloys are determined by the work of several hardening mechanisms [8], whose contributions may be comparable or differ (table 1).
Therefore, it is seen interesting to study the mechanisms of strengthening the SLM samples manufactured from powder with the elementary chemical composition, on the example of the technically-pure iron powder.

The aim of the presented work is to study the structure characteristics of the SLM samples manufactured from the metal powder of the elementary chemical composition, on the example of the technical-pure iron powder, as well as the refinement of nature and the mechanisms of strengthening these samples.

2. Materials and experimental methods

Non-spherical Fe-based powder was produced by Severstal PJSC (Cherepovets) from cast iron in two stages. First, the melted cast iron was sprayed with water, and then the resulting powder was thermally prepared in a hydrogen atmosphere to remove carbon. With this approach, the resulting pores become non-spherical (including having a fragmentation form). The appearance of the powder is presented on the figure 1.

Additive samples in the form of the prisms 10x10x50 mm (figure 2) were made on the EOSINT M270 SLM unit in the nitrogen atmosphere. The thickness of the melting layer of Fe-based powder was 40 μm. Variating the parameters of the melting, the magnitude of the heat input was obtained (the ratio of the laser power and the scanning speed) from 0.2 to 0.35 W · s / mm.

![Figure 1. Fe-based powder.](image1)

![Figure 2. Additive samples.](image2)

According to the chemical analysis of the initial powder and the samples made using the Leco CS 230 analyzer, the content of light chemical elements is recorded: 0.0184 % carbon, 0.001 % nitrogen, 0.0062 % sulfur and 0.22 % oxygen. Their presence is explained by a large number of pores in powder. The results of x-ray analysis obtained using the TESCAN electronic raster microscope indicated the presence of silicon (0.07 ± 0.04 %) and manganese (0.08 ± 0.06 %). Small concentrations of impurity chemical elements made it possible to level the possible effect of chemical heterogeneity on the strength properties of SLM samples.

The strength of additive samples was estimated according to HB hardness measurements. On the shelves prepared in thin sections of the melted prisms, the metal structure was detected by chemical etching in a 4 % alcohol solution of nitric acid. The structure of the samples was studied by the metallography with light (Axiovert) and electronic raster (Tescan) microscopes. Image processing was performed using a computer and software, as well as a “Fractal” program that allowed from the Rényi spectrum to determine the Hausdorff dimension \( D_h \), the measures of the non-equilibrium \( \delta \) and the periodicity \( K \) in the structure. The values of dimension \( D_h \) indicated the filling of the observation space by the objects under study. The value \( \delta \) is sensitive to symmetry disorders for the overall configuration of the structure under study as a whole. The greater the value \( \delta \) (by module), the more ordered the structure, and the aspiration \( \delta \) to zero is a sign of disordering and chaos. An increase in the \( K \) values indicates the growth of the periodic component in the inspected mapping of structures. The results of multifractal analysis have a probabilistic statistical meaning.
3. Experimental results and discussion

Data on hardness measurements of the Fe-based additive samples does not contradict the known results of experiments with the SLM powders of alloyed steels [5-7]. Within the values under consideration, the hardness is linearly increasing with an increase in heat input (figure 3). This fact suggests that the hardening of SLM samples is due to the rapid heating and cooling processes of the powder, the structure of which could be located in a locally inhomogeneous state. The presence of an oxide shell in the form of captivity around the particles of iron (figure 4) indicates the oxidation of the metal with reagents that were present in the pores of the initial powder.

![Figure 3. The growth of HV hardness.](image1)

![Figure 4. The particles of the powder structure (inside the sample) surrounded by the oxide shell.](image2)

The data obtained indicate local kinetic processes that occurred in non-stationary heat fluxes in the zones of melting and crystallization. The etching of the grinding revealed an inhomogeneous structure and in separate particles of the correct geometric shape (figure 5).

![Figure 5. Examples of presence of extended and twisted channels of the meso and microplastic flow filled with unequal deformed grains in samples. Resolution 25 μm.](image3)

In working on the growth of single crystals from metal melts, which were performed under the leadership of A. V. Stepanov, theoretical calculations and experimentally proved the causal relationship of temperature conditions near the crystallizer and convection of thermal flows in growing crystals, followed by vortex distribution of the elastic stresses’ tensor components in volume of the metal crystallizing. In [9], it was established that the gradient thermal field is able to generate dislocations responsible for local microplastic deformation and structural stresses. The etching and detected in the structure of the iron samples traces of mass localized meso and microplastic flow in the form of extended and curved channels were indicated on the rotational component of the deformation. Metallographic studies have confirmed the theory on the local structural transformation processes with
the participation of torque stresses and the appearance in the zones of new energy states curvature with near-ordering. Since diffusion processes are capable of transferring the material medium at a distance of just a few nanometers, it can be argued that the recorded traces of the mass mezo- and microplastic flow are due to the action of heterogeneous (gradient) thermal fields.

The correct spherical shape of individual particles provides reason to assume that the crystallization of the molten metal occurred without contacting the EOSINT M270 unit platform or other metal particles, i.e. in a free state. It follows that melt drops are the result of condensation of metal vapors formed over a laser exposure area. Despite the high speed of the SLM, it is likely to be confirmed by the trajectories of deploying and settlement particles on the layers of powder and the EOSINT M270 unit platform (figure 6). Those drops that came to the sections that have not yet treated with a laser melted and merged with the melt. Small particles (< 1 μm), located on the sections within gradient heat flows after the laser scanning, are embedded in grains and subgrains according to crystallographic orientation and perform the function of the germ crystallization and the factor of additional hardening of the additive sample. Large particles (> 1 μm) retain their geometric shape in the oxide shell.

The proposed model of the process of the metal evaporation, condensation and crystallization is confirmed by the results of studies [10-12] for phase transformations in steels. An electron microscopic analysis of samples from Fe-based powder made it possible to establish the smallest particle size, crystallized from the condensate drops: 0.15 ± 0.05 μm (figure 7). In the physical thermoformation theory of strength [13] the sublimation with the formation of germinal microcracks with such a size is due to irreversible breaks of interatomic connections.

Figure 6. Drill particles when manufacturing a sample on the EOSINT M270 unit.

Figure 7. Small (0.15 ± 0.05 μm) spherical particles detected in the thin sections are shown by arrows.

In the case of steam condensation and the transition of the liquid state into solid, the return process should be assumed – desublimation with a phase transition of the first kind, where the total symmetry of the condensed liquid medium turns into a periodic symmetry of the solid. Then, on the basis of the data obtained, particles with dimensions 0.15 ± 0.05 μm can be interpreted as germ nano-references, characterized by the frequency of density and capable of increasing, that is provided by equation 1:

\[
dE_{r_0}/dr \leq 0
\]

Here \(E_{r_0}\) is the energy activation energy of the germ radius \(r\), \(r_0\) is the critical size of the germ.

Consequently, the process of desublimation implemented in thermodynamically non-equilibrium conditions is subject to the influence of concentration fluctuations in the sequence: "Metastable state to Segregation to Cluster to Nano-object". Within the critical volume \((4\pi r_0^3 / 3)\), due to intensive mixing of atoms, germ nano-objects can become a prototype of any crystalline structures. For iron with an
interatomic distance of ~ 0.3 nm in the formation of germinal nano-objects in a free state, up to $10^7$ atoms can take part. The number of interactive atoms is the necessary topological condition for the start of crystallization, which is accompanied by the near and long-scale ordering, the formation of crystallographic texture, loss of coherence, separation and consolidation, as well as other processes inherent in the consolidated state. Since at the final stage of desublimation, the crystallization of the liquid state is accompanied by a decrease in volume, the observed phenomenon should be considered as a phase transition of the first kind, which is implemented in non-equilibrium thermodynamic conditions to form clusters of a condensed state. At high temperatures, when $kT > \hbar \nu$, the process of desublimation can be represented by an evolutionary equation 2:

$$\frac{dN}{dt} \sim \alpha N_0[\rho(r), V(r)] e^{U/kT}$$  

(2)

Here $N_0$ is the number of atoms in the critical amount of radius $r$, $U$ is the energy formation energy, $k$ is the Boltzmann constant, $T$ is the temperature, $\hbar$ is the Planck constant, $\nu$ is the frequency of oscillations of atoms, $\rho(r)$ is the medium density, $V(r)$ is the potential of interatomic interaction, $\alpha$ is the geometric parameter ($\sim 1$), $t$ is the time.

According to equation 2, the likely changes in groups of interacting atoms are determined by their initial state in some volume. Before crystallization in the density of $\rho(r)$ condensate and the potential of interatomic interaction $V(r)$, the properties of the frequency characteristic of the solid body are spontaneously manifest. If the initial state is given at $t_0$, then there is a single solution for any $t > t_0$, which determine the completion of the process of converting atomic clusters into nanoscale and larger objects with neighboring and distant ordering, crystallographic texture, coherence loss, separation and consolidation, as well as other acts, characteristic of a solid body.

Figure 8. Results of the multifractal analysis.

In order to estimate the structural-topological state of additive samples, a multifractal analysis of the structures of the start of crystallization began. According to the theory, the value of $\delta$ tends to zero, and the phase transformation itself can be implemented according to the oscillatory scenario. At the same time, the enlargement of the growing phase or a new structural state must be accompanied by an increase in the size of the dimension. Multifractal analysis data showed the correspondence of the values of $D_0$, $\delta$ and $K$ with the theory (figure 8). For example, in arbitrary areas of the crystallized metal structure, the value of $D_0$ increased with increasing $\delta$, and the $K$ values found a decline trend. This meant that crystallization occurred under conditions of far from equilibrium ($D_0$ and $\delta$ small) with the most likely mechanism for the transformation of the oscillating form (the growth of the dispersion $K$).
4. Conclusions
During SLM of the Fe-based powder, the formation of metal vapors is possible, which in the free state are consistently condensed into the liquid and crystallized into particles of different sizes, followed by sedimentation on the layers of the melted powder.

Set size reaction volume to $0.15 \pm 0.05 \mu m$, within which a statistical ensemble of $\sim 10^7$ atoms can form germ nano-objects of solidification any crystalline structures, which, depending on the crystallographic orientation, can act as the nucleation phases and grains as the hardening fine inclusions.

Not only local concentration inhomogeneities, but also nanophases in the form of structural constructions from cluster blocks, combined on coherent and other borders of the section, are responsible for the strength properties of additive samples. A model was proposed of the metal hardening by nanoparticles, which formed in the process of desublimation (condensation of metal vapors in the crystallization process) in the sequence: Metastable state to Segregation to Cluster to Nano-object.

It can be concluded that in the SLM manufacture of parts, nano- and microstructured levels are basic. In non-stationary temperature conditions, the structural formation increases the role of the kinetic processes of the nonequilibrium type.

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