The structure and magnetic parameters of the Fe-Cr-Co additive alloy

A S Zhukov\textsuperscript{1}, D S Sozinov\textsuperscript{1}, E A Ushanova\textsuperscript{1} and I S Gavrikov\textsuperscript{2}

\textsuperscript{1}NRC "Kurchatov Institute" – CRISM "Prometei", Saint-Petersburg, 191015, Russia
\textsuperscript{2}NUST "MISIS", Moscow, 119049, Russia

E-mail: npk3@crism.ru

Abstract. The structure of Fe-Cr-Co magnetic material, manufactured by selective laser melting (SLM) on Russian SLM FACTORY unit from spherical powder of size less than 80 μm, was studied. The powder was produced by the melt atomization. At different speeds of scanning and laser power, samples were manufactured to study the structure, magnetic and mechanical parameters. By constructing hysteresis loops, data obtained indicating the growth of magnetic characteristics (B\textsubscript{r}, H\textsubscript{cb} and (BH)\textsubscript{max}) in SLM samples in comparison with similar, obtained by foundry technologies.

1. Introduction

In mechanical engineering, laser additive technologies are increasingly used. One of the technologies that has spread recently – selective laser melting of powder (SLM) [1-3]. In this technology, the construction of a monolithic material manufactured from metal powder occurs by consistently laying small volumes, their melt and crystallization where the focused laser beam is directed. The movement of the beam is controlled by a computer according to a 3D-model. The feature of technology is the speed of alternating acts of melting and crystallization of the powder mixture, as a result of which the structure of the composite in the form of a mixture of crystallites of different morphology is formed in the stack of exposure to the laser. Local melting acts and structural-phase transformations implemented under non-equilibrium thermodynamic conditions are not sufficiently studied, although widely distributed in various technological applications with transitional modes.

The interest of using SLM for magnetic materials is caused by the fact that with the transition to fine metal powders, the density of electrons in the valence zone and the conduction zone of materials changes dramatically [4-5]. This is reflected on the properties caused by the behavior of electrons, primarily magnetic.

The aim of the work was to approbate the SLM for the manufacture of permanent magnets from the Fe – 25 wt. % Cr – 15 wt. % Co hard magnetic alloy. It is necessary to obtain powders and manufacture samples with parameters close in magnitude to magnets of traditional manufacturing technology.

2. Materials and experimental methods

Fe – 25 wt. % Cr – 15 wt. % Co alloy relates to a group of precision hard magnetic materials. It is used for the manufacturing of permanent magnets. The basis of the alloy represents iron (Fe), the content of
which can vary in the range from 45 % to 64 %. Also present cobalt, chrome, impurities. The chemically composition of the powder obtained by atomizing on the Hermiga 75/3VI unit with induction heating of the crucible (figure 1) is presented in table. 1. The initial raw material for atomization was the ingots provided by JSC "S-magnet", Moscow, Russia. Spraying parameters are: at a temperature of ~ 1650 °C in an argon atmosphere, followed by cooling with rates from 10^5 to 10^8 °C / s. After spraying, the powders are made to the desired fraction of less than 80 μm satisfying the requirements of SLM.

**Table 1. Chemical composition of the powder.**

| Alloy             | Fe  | Cr  | Co  | Nb | V  | Ni | Ti | Cu |
|-------------------|-----|-----|-----|----|----|----|----|----|
| Fe – 25 wt. % Cr –| 56.0| 23.0| 16.5| 1.2| 1.2| 0.5| 0.2| 0.2|
| 15 wt. % Co       |     |     |     |    |    |    |    |    |

The manufacture of the necessary samples from the atomized powders was produced on the laboratory areas of Nanocentre NRC "Kurchatov Institute" – CRISM "Prometey" using the RussianSLM FACTORY unit with a solid-state iodine laser (figure 2). To select the best melting parameters, the laser power and the scanning speed ranged from 150 to 195 W and from 800 to 1000 mm / s so that the heat input is maintained constant.

Structural studies were performed on thin sections by metallography using the Axiovert light microscope and Tescan Lyra 3 raster electron microscope, equipped with an Oxford instruments Symmetry diffractometric analysis of reflected electrons with quantitative image processing.

Magnetic parameters with the definition of B_r, H_c and (BH)_{max} were obtained on hysteresographs and militeslameter.

3. Experimental results and discussion

It can be considered established that when using laser additive technologies, from metal powders, fine-grained composite material is obtained with micro and nanostructure objects [6]. According to triple isotherms, in Fe-Cr-Co composites (figure 3) complex structural and phase transitions initiated by concentration inhomogeneities are possible. The heterogeneity in the chromium distribution is noteworthy as one of the powerful carbido-forming elements that determine the strength and plastic properties by the formation of hardening particles. Sequential quasi-periodic processes of melting and solidification may be accompanied by dissolving carbide particles, forming dendritic cells of different sizes with repeated release of nanoparticles of variable stoichiometric composition. At each level of the structural hierarchy of nanoparticles, not compatible among themselves by crystallography, locally combine on the sections of epitaxial growth in the ensembles due to the coherence effects.

The stability of atomic clusters is determined by the type and strength of interatomic bonds, temperature and the nearest environment. Than the particle smaller and the temperature below, than its
quantum properties appear stronger. At high temperatures, the accumulation of clusters and the growth
time of the embryos are determined by the size of the reaction volume. Internal ordered space-
time formations due to the interaction of defects of the crystalline structure in a medium with nonlinear
properties in convective mixing conditions may indicate the instability. Under conditions, a non-
stationary mass transfer with chemical interaction is characterized by (in the dimensionless coordinate)
by equation 1:

$$\frac{\partial c}{\partial \tau} = \frac{\partial^2 c}{\partial x^2} - k f(c)$$

Here \(x = X / a\) (\(X\) is a coordinate, measured from the surface of the powder particle), \(a\) is the scale,
\(\tau = d \cdot T / a^2\), \(D\) is the diffusion coefficient, \(t\) – time.

Depending on the type of kinetics functions, the distribution of reagent concentrations within the
reaction volume may vary.

**Figure 3.** Isothermal sections of the triple system Fe-Cr-Co at temperatures of 900 °C and 700 °C.

Assessing the type of metallographic of the structures (figure 4), where the traces of leakage
inhomogeneities were recorded in the form of waves with alternating extremums, it can be assumed
that in non-equilibrium conditions, the non-stationary local mass transfer is implemented as an
autocatalytic reaction.

**Figure 4.** Typical structures of the Fe – 25 wt. % Cr – 15 wt. % Co SLM samples.

Experiments have shown that an increase in the laser power is accompanied by an improvement in
the metallurgical quality of the additive metal with a small amount of discrepancy. On the figure 4, the
traces of recrystallization in the form of alternating cellular and columnar structures are distinguished.
The identified features formally correspond to the reactive structures formed autocatalytic in
synergistic reactions.
Using morphological features [7] it was assumed that in the zone of the laser beam in the acts of melting and crystallization, the temperature of the powder ranged from 0.24 to 0.34 $T_{\text{main}} / T_{\text{melt}}$. The identified structures indicate micron-sized objects that do not correspond to the nanoscale range. Consequently, the issue of its formation should be attributed to the initial stages of the crystallization of the melt. Therefore, it is necessary to refer to the characteristics of the observed objects in a micrometric scale with consideration of the not the entire set of crystal atoms, and its small part – aggregates, clusters and imperfect crystals up to 5 μm.

Structural inhomogeneity in the form of objects of different morphology detected on the thin sections is a fundamental property of a nano-condition, the reason for which the quantum properties of the system and the appropriate structure of the structure are. Therefore, the control of the processes of the nano-range should be based on the spin nature of the electronic subsystem interaction, in which the movement of the magnetization vector has the form (equation 2):

$$\frac{dM}{dt} = \gamma M \times H$$  \hspace{1cm} (2)

Here $M$ is the magnetic moment vector of the volume unit, $H$ is a vector of a static magnetic field, $\gamma$ – the ratio of the magnetic moment by the time the amount of movement.

The size of the domains is not a substance constant, but it is determined by the properties of the sample. In terms of optimizing the structure, a possible model with a limitation of domain growth in the form of a logistics function corresponds to the Malthus evolutionary equation 3:

$$\frac{dX}{dt} = X - X^2 - kY$$  \hspace{1cm} (3)

Here $X$ is the magnetization due to the distribution of spins, $Y$ is the size of single-domain particles. $k < 1$.

Under the action of the external field, the increase in the resulting magnetic moment is due to an increase in the volume of domains with the rotation of the magnetization vectors in the direction of the external field [8]. But in materials consisting of small grains ($< 1 \mu m$), the formation of a domain structure is unprofitable. Therefore, it is assumed that in the SLM manufacturing of magnets in short-term acts of melting and crystallization, the formation of particles is due to their substitution – clusters. The formation of clusters is an unstable physical process in the thermodynamic sense.

According to preliminary estimates in the used method, the heating rate of the powder to melt is determined in $10^4$ °C / s in the laser focusing zone, and the cooling rate is based on the recurring heating cycles at $10^2$ °C / s, regardless of variation of the operation modes of the Russian SLM FACTORY unit on the injected laser power and scanning speed. In fast acts of melting and crystallization, electronic shells $s$, $p$ and others with a suitable state of phases of wave functions (figure 5) can take part by not only the diffusion of atoms as a whole, but also with the participation of electronic shells from collectivized electrons with a periodic lattice field and valence due to spin splitting. For example, overlapping orbitals $s$, $p$ or $d$ of the external electronic shells responsible for the formation of magnetic properties. Therefore, according to indirect features, it can be assumed that the beginning of crystallization is concentrated in a vapor cloud during the desublimation on the surface of the laser beam focus [9].

**Figure 5.** Options for self-organizing consolidation of molecular orbitals $1s$ or $2p$ with different signs (arrows and signs) phases of wave functions.
Magnetic measurements showed (figure 6, table 2) that SLM allows to manufacture a magnet whose parameters are not inferior to the samples obtained by the traditional foundry.

Figure 6. Dependencies residual induction $B_r$, coercive force $H_{cb}$, maximum energy product $(BH)_{max}$ from a laser power for two samples manufactured at 700 mm / s scanning speeds and values for foundry samples.
Table 2. Magnetic properties of the Fe – 25 wt. % Cr – 15 wt. % Co SLM samples.

| Sample   | Br, T | Hcb, kA / m | (BH)max, kJ / m³ |
|----------|-------|-------------|------------------|
| SLM      | 1.14  | 45.7        | 32.2             |
| foundry  | 1.29  | 41.9        | 39.3             |

4. Conclusions

By the selective laser melting of hard magnetic metal powders of the Fe-Cr-Co alloy, it is possible to manufacture magnets with properties that are not inferior to the material of traditional foundry technology.

Structural heterogeneity in the form of objects of different morphology, detected on the thin sections, is the fundamental property of additive samples.

In rapid acts of heating and crystallization, electronic shells s, p and others can take part, and the overlaps of the orbitals s, p or d of external electronic shells responsibly for the magnetic properties formation.

References

[1] Brandt M et al. 2016 Laser Additive Manufacturing. Materials, Design, Technologies and Applications (Sawston, Cambridge: Woodhead Publishing) p 498
[2] Froes F, Boyer R 2019 Additive Manufacturing for the Aerospace Industry (Amsterdam: Elsevier) p 482
[3] Zhang J, Jung Y-G 2018 Additive Manufacturing: Materials, Processes, Quantifications and Applications (Oxford: Butterworth-Heinemann) p 362
[4] Korznikova G F 2015 Physical Mesomechanics 18 issue 2 89-94
[5] Omar M A 1994 Elementary Solid State Physics: Principles and Applications (Boston: Addison-Wesley) p 600
[6] Zhukov A, Barakhtin B, Bobyr V and Kuznetsova P 2019 IOP Conference Series: Earth and Environmental Science 272 № 022233
[7] Barahtin B K, Sedletsky R V 2016 Interuniversity Collection of TsySU scientific works "Physical and chemical aspects of studying clusters, nanostructures and nanomaterials" 8 43-49
[8] Grigorovich V K 1970 Electronic structure and thermodynamics of iron alloys (Moscow: Nauka) p 292
[9] Zhukov A S, Bahatytin B K, Kuznetsov P A 2018 Fundamental problems of modern materials science 15 issue 2 169-175

Acknowledgments

Experimental studies were carried out on the equipment of the Core shared research facilities "Composition, structure and properties of structural and functional materials" of the NRC «Kurchatov Institute» - CRISM "Prometey" with the financial support of the state represented by the Ministry of Education and Science of the Russian Federation under agreement No. 13.CKP.21.0014. The unique identifier is RF----2296.61321X0014.