Directed changing properties of amorphous and nanostructured metal alloys with help of nanosecond laser impulses

I. V. Ushakov, *Dr. Eng., Prof., Head of Physics Dept.*[1]*, e-mail: ushakoviv@mail.ru*
I. S. Safronov, *Cand. Eng., Senior Lecturer, Physics Dept.*[1]

[1]*National University of Science and Technology "MISiS", Moscow, Russia*

One of the most important problems of materials science is the ability to control the physical and mechanical properties of materials that differ in structure. Forming a specific structure on the surface is a time-consuming process, especially for non-standard alloys. Such materials include amorphous and nanostructured metal alloys. In practice, their use is possible after heat treatment. Additional processing often leads to the destruction of the nanostructure. The laser impulse has a number of features, including a complex effect on the surface layers of the material. The wide variable possibilities of laser processing provide the basis for the possibility of forming the mechanical properties of amorphous-nanocrystalline metal alloys. Spot irradiation with high-energy beams can preserve the unique physical properties of the samples as a whole and improve the strength characteristics. The directed change in the properties of an amorphous-nanocrystalline metal alloy by local processing with a nanosecond laser impulse is an urgent research task.
Key words: amorphous-nanocrystalline cobalt- and iron-based alloy, microhardness, laser processing, viscosity of microfracture, crack formation.
DOI: 10.17580/cisisr.2021.02.14

Introduction

Amorphous and amorphous-nanocrystalline metal alloys have a great potential for practical use. The unique properties of such alloys are in demand in metallurgy, mechanical engineering, aviation, nuclear engineering, etc. [1–3]. Such materials are used in various fields of technical electronics, are part of structural composites, corrosion-resistant equipment elements, and so on.

The practical use of amorphous alloys is expanding. Unfortunately, a significant part of the new amorphous alloys, especially bulk amorphous alloys, has a high cost. In this regard, amorphous iron-based alloys are of particular interest, since in addition to good performance properties [4], such alloys are relatively cheap. The creation of new methods for forming the properties of amorphous iron-based alloys will expand the scope of their practical use.

Common and standardized methods for optimizing the properties of conventional metal alloys are constantly being improved, but they can rarely be applied to amorphous-nanocrystalline structures [5–9]. The attempt to apply standard processing methods leads either to the mechanical destruction of such materials, or to the destruction of their structural state.

As a rule, in amorphous nanocrystalline materials, the plastic characteristics significantly decrease with an increase in the microhardness index H_V. For example, in the process of thermostatic, the material passes into the nanocrystalline/crystalline state, and the main factor affecting the reduction of the plastic characteristic is a decrease in the proportion of the amorphous phase and formation of nanocrystals [1–3, 10]. Superhard amorphous-nanocrystalline materials are usually brittle. Additional processing by classical methods of influencing the structure of the material dramatically reduces the useful properties, and in some cases provokes a complete transfer of the sample to the crystalline state.

Modern technologies for the production are actively introducing methods of high-energy surface treatment of parts. These include the impact of the laser impulse, electricity plasma methods, etc [5, 11–13]. With the optimal selection of laser exposure modes, it is possible to create a thin layer on the surface with a certain change in the structural state of the material. It is usually accompanied by an increase in the mechanical characteristics of the sample as a whole. Experimental data confirm the possibility of the formation of certain properties in local areas under the influence of a given number of laser impulses, lasting several nanoseconds. Laser processing can affect not only the properties of amorphous-nanocrystalline metal alloys, but also to be effective for metals and alloys based on iron, cobalt, etc [11, 14].

Thus, the study of the possibility of controlling the physical properties of amorphous-nanocrystalline metal alloys by laser treatment of nanosecond duration is the goal of this work.

Laser treatment of steel and metal alloys in metallurgy

The laser treatment is the most effective and high-quality method of cutting steel and metal alloys in metallurgy and mechanical engineering (**Fig. 1**). The laser cuts well any metals with various coefficients of heat conductivity. The high energy power of the laser beam ensures that the steel melts in the cutting area [14]. Advantages of laser treatment of steel: there is no mechanical deformation of the steel billet completely, since the thermal impact zone is very limited; the high accuracy and speed of treatment; the edge in the laser cutting zone of steel is very smooth, without influxes and burrs. The most demanding laser technologies in metallurgy and mechanical engineering are: the direct laser sintering,

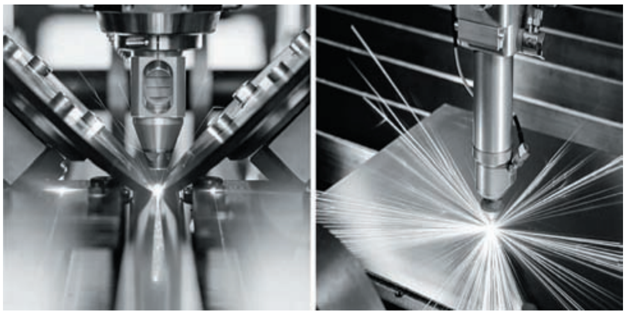

Fig. 1. Laser welding of the steel pipe's ends (left) and laser cutting of steel sheet (right)

the laser and laser-mechanical bending, the laser cutting, the laser drilling and the laser welding. With help of the laser beam we can cover surfaces and change the properties of steels and metal alloys.

The technology of *direct laser sintering* of metals allows you to make samples of steel and metal parts of any geometric shape. Using the laser beam, you can uniformly fuse the metal powder on the surface of the steel billet or along its contour.

At *laser bending* steel, the laser beam heats the treatment area of the steel sheet. Under the influence of the appearing thermomechanical stresses, the steel sheet bends. At *laser-mechanical bending*, the bending place of the steel sheet is first heated by the laser beam, and then mechanical bending is performed, which allows us to get a larger bending angle at smaller radius of curvature.

The technology of *laser cutting* of steel allows us by using a laser beam to perform thermal cutting of steel sheets, pipes and profiles. The *laser drilling* of steel is carried out without removing chips. In the zone of laser influence, the steel is ionized, turns into plasma and evaporates. The *laser welding* of steel is used to connect steel workpieces and details. It is differed by great depth and high speed. As a result, we obtain the thin and high-quality weld.

Experimental procedure

Studies on the formation of certain mechanical characteristics were carried out using an amorphous-nanocrystalline metal alloy. This material was obtained from an amorphous metal alloy 82K3HSR with cobalt and iron. The amorphous alloy was a thin film (thickness 30 μm), from which rectangular samples of 25×30 mm were cut. The prepared samples were transferred to the amorphous-nanocrystalline state by thermostatic, after which they were applying in a polymer substrate with a metal base. The substrate material is a polyester putty with a micro-glass fiber additive, which has the necessary physical and chemical characteristics and mechanical strength (microhardness 3.6×10^8 Pa).

Laser treatment of thin film surface was performed on the ELS–01 unit. Pumping energy of single impulse was 50–100 mJ with a wavelength of 1064 nm. Exposure time of laser impulse is 15–20 nanoseconds. The reflow regions were formed in the form of a band from sequentially superimposed rounded regions with a step between their boundaries of 40–50 μm (sample velocity 10^{-2} m/s) with a width of 450–500 μm at an impulse repetition frequency of 50 Hz.

Mechanical characteristics were determined using a Vickers pyramid on a modernized PMT–3 microhardness tester. The reference point was considered to be the center of the reflow zone — a straight line dividing the reflow strip into two equal parts. To assess the viscosity of micro-destruction the load on the indenter was carried out with a force of up to 3 N.

Experimental results

Experimental studies of samples of amorphous-nanocrystalline metal alloy were based on the method of determining the microhardness and viscosity of micro-fracture. The mechanical characteristics were evaluated using well-known and generally accepted mathematical calculations [15–21]. In accordance with the obtained data, a graph of the dependence of the microhardness on the distance to the center of the reflow zone was plotted. The selected temperature range of furnace annealing of 803–993 K was divided into groups according to the known data of X-ray images of this metal alloy [10]. X-ray images of the temperature range include several structural-phase transitions. The initial amorphous metal alloy is converted to the amorphous-nanocrystalline state at temperature of more than 550 K. The second metastable phase is observed at temperatures of 825–840 K. The third metastable phase corresponds to the temperatures of 850–940 K. Most of the material undergoes changes, which can be traced by an increase in the crystal peaks on X-ray images [10]. A further increase in the temperature exposure, above 970 K, leads to an almost complete transfer of the amorphous matrix to the crystalline state. As the destruction of the amorphous-nanocrystalline structure of the material is in a great measure loses its unique properties.

Fig. 2 shows the obtained experimental data on the dependence of microhardness on the distance to the center of the laser reflow zone for furnace annealing temperatures of 803–993 K. Changes in microhardness, depending on the distance to the axis of the laser reflow area, occur quite smoothly for samples annealed at temperatures of 803–838 K. The microhardness inside the fused zone decreases slightly in relation to the initial sample, then increases in the border area (the fourth group of points) and does not change as it moves away from the border of the laser exposure zone.

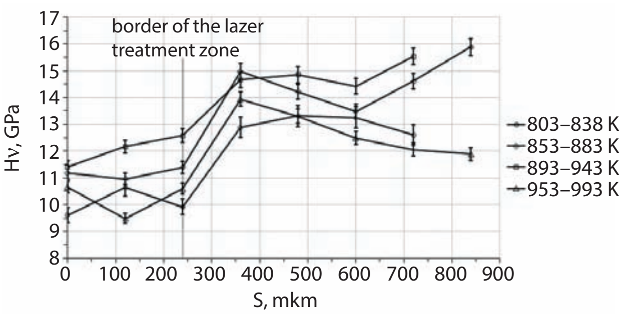

Fig. 2. The nature of the change in the microhardness of samples of an amorphous-nanocrystalline metal alloy depending on the distance to the center of the laser processing band at a load on the indenter of 0.98 N

The microhardness inside the processing zone and on the initial material differs on average by 2–2.5 GPa. In the two dependences, the peak value of microhardness is observed in the boundary region of laser processing and approaches the maximum value (Fig. 2). Inside the reflow band, the microhardness decreases by 4 GPa, compared to the initial material. Such changes can be determined by the processes of recrystallization or repeat surface amorphization of the material as a result of laser processing. The temperature range of furnace annealing 853–883 K is characterized by the predominance of the amorphous phase.

The combined effect of a nanosecond laser impulse can lead to a number of effects. The pressure of the laser plasma leads to the hardening of the boundary zone due to the displacement of the melted material from the irradiation area and its deposition on a solid nanocrystalline material. As a result, a composite is formed: a plastic surface layer and a solid nanocrystalline substrate. At a distance of 600 μm from the center of the reflow zone, a slight decrease in microhardness is observed, which is associated with the recrystallization of the heated material.

The annealing temperature group 893–943 K corresponds to the third metastable phase of an amorphous-nanocrystalline metal alloy. As can be seen from Fig. 2, a smooth increase in microhardness is observed on the fused region (the second and third points of dependence).

For better understanding the nature of changes in the mechanical characteristics of samples under mechanical loading, an additional parameter was introduced — the parameter viscosity of micro-fracture. Common techniques applicable to classical metal alloys cannot be fully applied to thin films of an amorphous-nanocrystalline metal alloy. The determination of this parameter will allow us to determine the possibility of increasing the microhardness and reducing the brittleness of destruction of an amorphous-nanocrystalline sample. This technique is based on the study of the nature of material destruction when loading local areas with a Vickers pyramid. Microcracks when penetration the indenter takes place, in most cases form symmetrical shapes in the form of nested squares on the brittle material. The absence of cracks indicates a high viscosity. On the base of analysis of distances between parallel micro-cracks it is possible to calculate viscosity of micro-fracture [11, 16]. At the milli- and micro-level, the strength depends on both the microhardness and the micro-fracture toughness. To estimate the viscosity of micro-fracture, a load of 2.94 N was used, which led to more than 80 % of the cases of crack formation. The nature of the change in the viscosity of micro-fracture must be compared with the dependence of the microhardness for the same loads. **Fig. 3** shows the dependence of the microhardness on the distance to the center of the reflow zone with a load of 2.94 N.

In the center of the reflow zone, there is a slight decrease in the microhardness of the material (Fig. 3) for temperatures of 803–883 K and 953–993 K. As you move away from the laser exposure boundary, the hardness practically does not change. Starting from a distance of 360 microns, the hardness parameters are similar for all furnace annealing temperatures with minor differences. The minimum values that are typical for an amorphous material or a material that has passed into a crystalline state are also noted. This feature manifests itself in the temperature range of 893–943 K. The microhardness decreases within the reflow zone to the border areas.

The viscosity of micro-fracture was calculated, combined into temperature groups, averaged, and a graph of the dependence was plotted (**Fig. 4**). The exponential dependences on the graph show changes in the parameter viscosity of micro-fracture ε. In general, the fracture pattern is similar for the temperature range 803–838 K. Significant differences in the parameter viscosity of micro-fracture begin at an annealing temperature above 863 K. The following dependence is typical for the furnace annealing temperature range of 853–883 K. A high parameter viscosity of micro-fracture is characteristic of the central part of the laser processing band, and then decreases to the initial level of the untreated sample. The plastic characteristic ε on the initial sample is the same for all temperature ranges of furnace annealing. This confirms high brittleness of the material as a result of the extensive destruction formation of micro and macro-regions in the indenter's indentation zone.

The first two points (the fused region) are of primary importance on the graph of the temperature range 853–883 K (Fig. 4), where high microhardness values are maintained without reducing the plastic characteristic. An increase in the viscosity of micro-fracture can be defined as an increase in the energy intensity of the destruction of a material under mechanical action. In some cases, at annealing temperatures that are within the

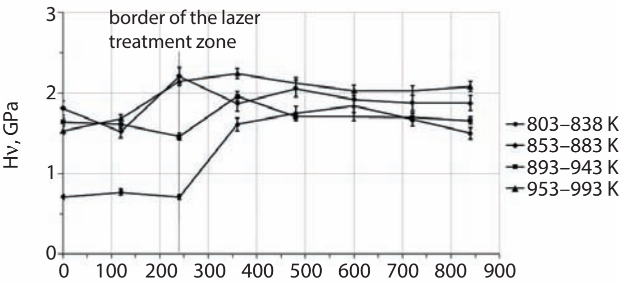

Fig. 3. The character of the change in the microhardness of samples of an amorphous-nanocrystalline metal alloy as a function of the distance to the center of the laser processing band under the load on the indenter of 2.94 N

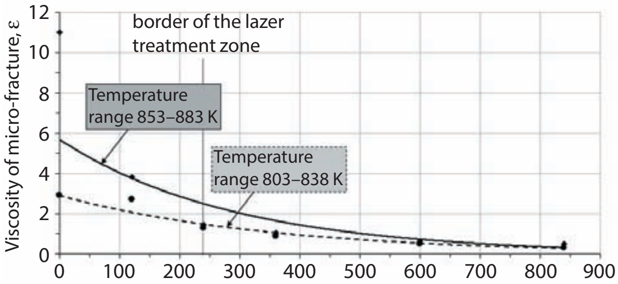

Fig. 4. The exponential dependence of the viscosity of micro-fracture on the distance to the center of the laser processing zone of samples annealed in the temperature range of 803–838 K and 853–883 K

range of phase transitions, the microhardness increases in the center of the laser exposure band. This indicates the possibility of a simultaneous increase in the microhardness and viscosity of micro-fracture even at high loads on the indenter (2.94 N or more). The optimal selection of the processing modes of temperature control and laser exposure to local areas will increase the mechanical characteristics of the material as a whole.

In the case of similar plastic properties of a thin film of an amorphous-nanocrystalline metal alloy, it is possible to use common mathematical methods of calculations and modeling [14–21]. The dependences of the viscosity of micro-fracture on the distance to the center of the reflow zone shown in Fig. 4 are typical for one-sided processing of the material. However, there is a possibility of simultaneous improvement of mechanical characteristics during two-way processing of samples, as was discussed in some papers [11]. According to the data of X-ray diffraction analysis, as a result of laser processing, there is no change in the structural state. Such processing can significantly increase the required parameters while maintaining the unique physical properties of the amorphous-nanocrystalline metal alloy [11–13, 22].

Of great importance in determining the mechanical properties of the material is the nature of the fracture and the formation of cracks on the surface of the sample (**Fig. 5**). The region of an amorphous nanocrystalline metal alloy with a thickness of 30 microns is brittle when indented by the Vickers pyramid.

The Fig. 5 shows the characteristic micro-pattern of destruction, which is typical for a thin and brittle sample. The fracture micro-pattern is a system of cracks oriented along the faces of the indenter. There are also ring and trunk cracks there, which in most cases lead to the destruction of macroscopic sections of the sample. Microfractures crossing the laser-treated zone boundary were not observed; their development was inhibited at the boundary of the melted region. There are practically no shear strain lines in these areas.

Inside the fused strip, on an amorphous-nanocrystalline metal alloy, the damage is minimal or absent. Around the print from the indenter is the formation of lines of shear deformation. Cracks form only at maximum loads (3–4 N) and most of them are inhibited at the initial stages of development. Based on the experimental results obtained, based on the graphical dependences of the mechanical characteristics of the samples, it can be concluded that it is possible to maintain the microhardness at an acceptable level with an increase in plasticity in the areas treated with a nanosecond laser impulse.

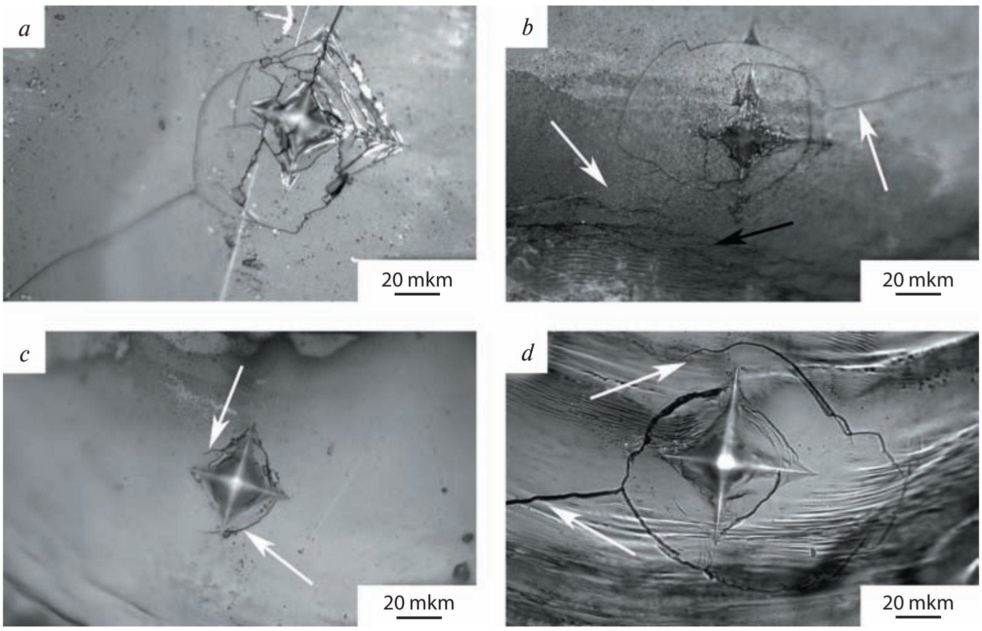

Fig. 5. Micro-pictures of the destruction of local areas after loading a Vickers pyramid on the samples annealed in temperature range 803–993 K: *a*) the initial area, not subjected to laser impulse; *b*) border region (the black arrow marks the boundary of the reflow, and the white arrow marks the developed crack along the boundary); *c*) the center of the melted zone (annealing temperature range 853–893 K, the arrows indicate the region braking cracks); *d*) the center of the melted zone (annealing temperature range 803–838 K, the arrow marks the circular and main crack)

The local treated areas retain the amorphous-nanocrystalline state as a whole without changes, which makes it possible to use the material for its intended purpose without problems [14]. Thus, it is possible to optimize the physical and mechanical characteristics of an amorphous-nanocrystalline metal alloy with subsequent treatment by nanosecond laser impulses.

Conclusions

1. The presented method of processing is effective for thin films of amorphous-nanocrystalline metal alloy. The processed material is able to withstand significant mechanical loads without macro-destruction. The main advantage of the method of laser modification of the sample surface is the preservation of the structure of the metal alloy in the amorphous-nanocrystalline state.

2. On samples corresponding to the central part of the metastable amorphous-nanocrystalline phase, a simultaneous increase in the microhardness and the viscosity of micro-fracture was determined. Thus, it is possible the effective control of the material properties under nanoseconds laser impulse processing.

3. The method of selective laser processing has been successfully tested for various amorphous-nanocrystalline structures. The prospects for further development of this method are related to the development of technologies for

its application to amorphous metal alloys with a different chemical composition. This is especially important for amorphous alloys based on iron, which is a common and cheap chemical element.

This work was carried out with financial support by International Information Nobel Centre.

REFERENCES

1. Gusev A. I., Rempel A. A. Nanocrystalline materials. Fizmatlit. 2001. 224 p.
2. Gleiter H. Nanostructured materials: Basic concepts and microstructure. *Acta Materialia*. 2000. Vol. 48. No. 1. pp. 1–29.
3. Andrievsky R. A., Glezer A. M. Size effects in nanocrystalline materials. II. Mechanical and physical properties. *The Physics of Metals and Metallography*. 2000. Vol. 89. No. 1. pp. 91–112.
4. Boriskin O. I., Nuzhdin G. A., Vvedenskii V. Yu. Properties of Fe-based amorphous alloy. *Chernye Metally*. 2021. No. 5. pp. 39–42.
5. Shulov V. A., Gromov A. N., Teryaev D. A., Perlovich Yu. A., Isaenkova M. G., Fesenko V. A. Texture formation in the surface layer of VT6 alloy targets irradiated by intense pulsed electron beams. *Inorganic Materials: Applied Research*. 2017. Vol. 8. No. 3. pp. 387–391.
6. Brandt M. Laser additive manufacturing: Materials, design, technologies and applications. Woodhead Publishing. 2016. 498 p.
7. Andrievsky R. A., Ragulya A. V. Nanostructured materials. Akademiya. 2005. 192 p.
8. Shinkin V. N. Failure of large-diameter steel pipe with rolling scabs. *Steel in Translation*. 2017. Vol. 47. No. 6. pp. 363–368.
9. Ryzhonkov D. I., Levina V. V., Dzidziguri E. L. Nanomaterials. BINOM. 2012. 365 p.
10. Kalabushkin A. E., Ushakov I. V., Polikarpov V. M., Titovets Yu. F. Revealing of qualitative correlation between mechanical properties and structure of amorphous-nanocrystalline metallicalloy 82K3XCP by microindentation on substrates and X-ray powder diffraction. *Proceedings of SPIE — Nanodesign, Technology and Computer Simulations*. 2007. Vol. 6597. 65970P. pp. 1–6.
11. Safronov I., Ushakov A. Effect of simultaneous improvement of plasticity and microhardness of an amorphous-nanocrystalline material based on Co, as a result of laser processing of nanosecond duration. *Materials Today: Proceedings*. 2021. Vol. 38. No. 4. pp. 1516–1520.
12. Boriskin O. I., Blagoveshchenskiy D. I., Vvedenskiy V. Yu., Nuzhdin G. A. Cobalt-base amorphous alloy production quality management. *Chernye Metally*. 2019. No. 1. pp. 60–63.
13. Nolte S., Schrempel F., Dausinger F. Ultrashort pulse laser technology: Laser sources and applications. Springer. 2016. 376 p.
14. Ushakov I., Simonov Yu. Formation of surface properties of VT18u titanium alloy by laser pulse treatment. *Materials Today: Proceedings*. 2019. Vol. 19. No. 5. pp. 2051–2055.
15. Shinkin V. N. Simplified calculation of the bending torques of steel sheet and the roller reaction in a straightening machine. *Steel in Translation*. 2017. Vol. 47. No. 10. pp. 639–644.
16. Ushakov I. V., Polikarpov V. M. Mechanical tests of thin strips of metal glass with indentors of various geometric shapes. *Diagnostics of Materials*. 2007. Vol. 69. No. 7. pp. 43–47.
17. Shinkin V. N. Direct and inverse non-linear approximation of hardening zone of steel. *Chernye Metally*. 2019. No. 3. pp. 32–37.
18. Khalyapin V., Sazonov S. Extremely short pulses in anisotropic medium. Lambert Academic Publishing. 2011. 112 p.
19. Shinkin V. N. Arithmetical method of calculation of power parameters of 2N-roller straightening machine under flattening of steel sheet. *CIS Iron and Steel Review*. 2017. Vol. 14. pp. 22–27.
20. Jonsson B., Hogmark S. Hardness measurements of thin films. *Thin Solid Films*. 1984. Vol. 114. No. 3. pp. 257–269.
21. Shinkin V. N. Springback coefficient of round steel beam under elastoplastic torsion. *CIS Iron and Steel Review*. 2018. Vol. 15. pp. 23–27.
22. Shulika O., Sukhoivanov I. Advanced lasers: Laser physics and technology for applied and fundamental science. Springer. 2015. 238 p.