Journal of Chemical Technology and Metallurgy, 51, 4, 2016, 427-436

RESEARCH ON OBTAINING OF COMPOSITE MATERIALS BASED ON ALUMINUM MATRIX

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Received 24 November 2015
Accepted 27 April 2016

ABSTRACT

The processing of aluminum alloys (silumins) by ligatures containing various carbon modifications (in the form of microcrystalline graphite, nanocarbon additives in the form of fullerenes, fullerene soot, fullerene niello) based on casting-deformation technology of the manufacturing of products was studied. The elemental and phase composition, structural state and mechanical and tribological properties of the initial components of the charge in the Al-C and Al-Si-C alloys after mechanical activation by severe plastic deformation (extrusion) of the charge and cast aluminum workpieces were studied. The processes of structure formation of the alloys in the system Al-C and Al-Si-C when they are received and thermomechanically loaded are gradually studied. The formation of superhard carbon phases in ligatures, where instead of microcrystalline graphite was used nanocarbon additives is of particular interest. Using spectroscopy of combined light scattering amorphous phase, similar to glassy carbon, was revealed. In the ligatures were identified also carbides of aluminum Al_4C_3 and/or silicon SiC during annealing (800ºC, 30 minutes). The structural state of the alloys obtained after activation of the charge (mechanical activation in dispersive devices and intensive plastic deformation) determines the prospects of their use in the composites characterized by high anti-friction, plastic and strength properties.

Keywords: *fullerene niello, fullerene soot, casting, deformation, Al alloy.*

INTRODUCTION

In today world there is trend toward increasing research in the field of development and wide application of metal-matrix composite materials. The cheapest and most reliable are materials based on aluminum alloys subjected to modification and reinforcement by dispersed refractory particles. Among the distinctive properties of such materials are high-friction and strength properties, heat resistance, hardness, low density, which provide substantial weight reduction and reduce material consumption of the product while increasing reliability and increasing their lifetime.

The need to create new composite aluminum material (CAM) and technologies of their production is explained by the necessity of fabrication of competitive products as well as with the gradual depletion of natural raw materials. In this respect, the components of the CAM must be available and cheap. From this perspective, the composition of the surface of the earth crust contains up to 50 % SiO_2, 30 % Al_2O_3 and 10 % Fe. For this reason mankind in recent years, more intensively develops the production of Al_2O_3 for producing of aluminum and materials based on it.

Lately the fillers of considerable practical interest are nanostructured carbon materials: fullerenes, nanotubes, graphene, nanodiamonds, onions [1, 2]. This is because carbon nanomaterials, in very small concentrations contribute to the improvement of physico-mechanical characteristics and tribological properties of aluminum materials [3].

The most widespread such forms of carbon are fullerenes. They are chemical compounds which molecules consist only of carbon with an even number of atoms and have the form of hollow spheres. It should be noted the ability of fullerenes under the action of temperature and pressure to change its nature, which allows their use as reinforcing fillers and modifiers. A good illustrations are the widely known metal composite materials containing particles of hard and elastic carbon obtained from fullerenes under pressure [4, 5]. It is known that when heated to 1100 - 1500°C in the mixture of powders of metals and fullerenes at moderate pressures (3 - 5 GPa) occurs consolidation of the powder and synthesis of hard carbon particles from the crystallites of fullerenes and their conglomerates [6]. Composite materials with a metal base containing 5 - 10 % solid carbon phase, can combine the specific properties of the metal matrix (e.g., mechanical properties, corrosion and oxidation resistance, thermal and electrical conductivity) and the unique wear resistance of the hard and elastic carbon particles [7 - 9].

The use of graphite in antifriction alloys based on aluminum gave new impetus to the development and implementation of technologies aimed at the replacement of scarce and expensive bronzes used in friction pairs. Despite the progress achieved in this field, it is necessary to note the main disadvantages of such materials: high gas saturation of alloy, low strength and wear resistance of the resulting products, and impossibility of using this method for obtaining products of complex design.

Therefore, the goal of the present research is to improve the wear resistance and strength of articles made of silumin by grinding the material structure and its stabilization during subsequent plastic deformation and heat treatment.

In accordance with the research objective in this work the possibility of replacing expensive fullerene by cheaper fullerene material was evaluated. In order to obtain the composite materials a casting-deformation technology (technology-in-suit), is used comprising mixing the powder components of the charge, mechanical activation of the mixture, extruding the charge with the obtained ligatures and producing composite materials based on aluminum matrix during casting.

The samples were prepared from aluminum powders with particle size of the main fraction 5 - 100 μm or crushed chips alloy AK9 and different nanocarbon materials in composition Al - 10 mass % C in the original mixture.

The carbon materials used are:

- fullerene-containing soot;
- fullerenes C_{60};
- fullerene niello, all production of Institute Ioffe, St. Petersburg;
- carbon microparticles of size 3, 4, 9 μm, production of ASBURY GRAPHITE MILLS, INC., USA.

For production of composite materials alloy AL 25 is used.

The melt was prepared in an induction furnace ISV 0,004. The ligatures containing 10 mass % carbon was introduced into the melt AC at a temperature of 750 - 780°C, while the melting alloy was kept for 3 - 5 min. The ligature in the aluminum melt was calculated from the condition 1 mass % carbon composite. The temperature was controlled by a multichannel detector RMT 39D, connected to the PC.

The technology of producing ligatures included: mechanical activation processing of the source materials in the planetary mill, compacting in rigid molds and hot extrusion. Mechanically activated powders were formed in tablets at P = 450 MPa. Next, the tablets were extruded at a temperature of 450 - 500°C with a drawing ratio ≥ 10 and received a ligature in the form of rods. Mechanical activation treatment was carried out for 30-40 minutes at frequency of rotation of the Central shaft 400 - 600 rpm and ratio of the mass of grinding bodies to the mass download of 20:1.

Study of the initial components of the charge

Aluminium powder. The samples were prepared from powders of aluminum with particle size of the main fraction 5 - 100 μm. Topographic images of the original powder of aluminium is shown in Fig. 1.

Fullerene soot. The results of observation of fullerene soot in a scanning electron microscope is shown in Fig. 2. The powder consists of the dispersed soot particles and large particles of fullerenes.

The results of study on the phase and elemental compositions show that the investigated fullerene soot consists basically of amorphous carbon, contains around 8% of fullerenes and also small amounts of oxygen, no impurities.

Fullerene niello. The powder consists of small size particles (3 - 5 μm) and conglomerates of larger particles (Fig. 3a).

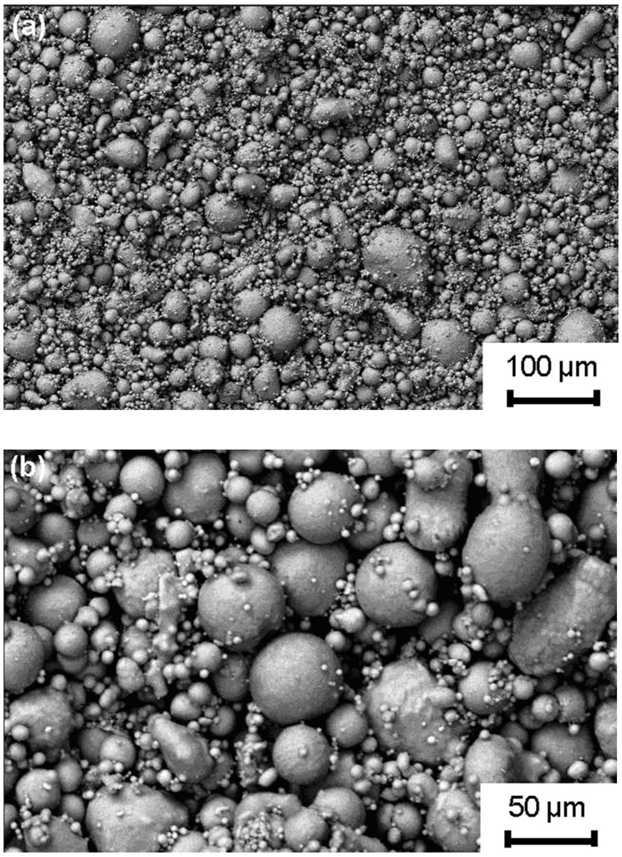

Fig. 1. Topographic images of the original aluminum powder.

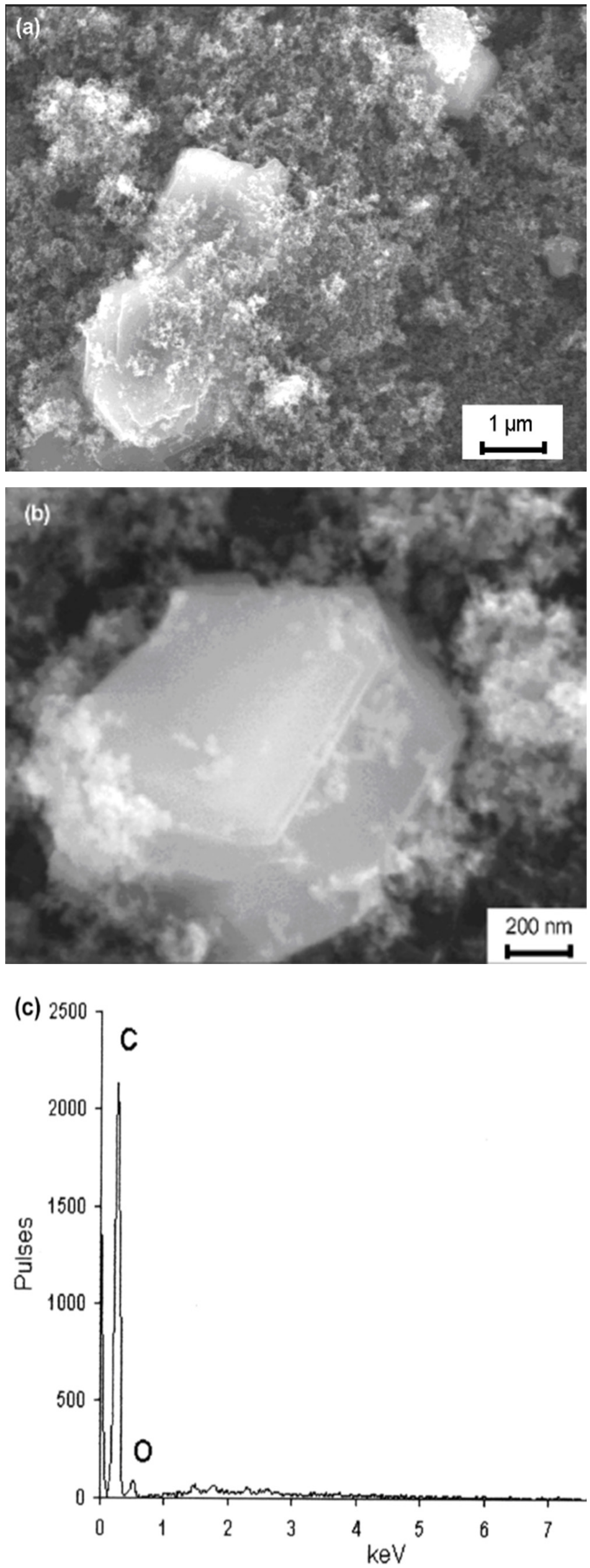

Fig. 2. Fine structure (a, b) and diagram of fullerene soot (c).

It is shown that the fullerene niello is 100 % black carbon and impurities are not detected (Fig. 3b).

Gusev [10] has reported that fullerene niello is a black fine powder with particle size of 40 - 50 nm, established by scanning electron microscopy (Fig. 3c).

Microcrystalline carbon. The results of the study of microcrystalline carbon powders of different dispersion showed that the carbon particles have both kinds of plates typical for hexagonal crystal structure and micro-particles of spherical shape. Fig. 4 shows the topographic images of the microcrystalline carbon.

Study of the charge after mechanical activation

The studies have shown that in the charge of the system Al-C after mechanical activation there are processes of plastic deformation of the initial powder components and changes of the elemental and phase composition. The topographic images of the charge powders with different carbon additives are similar. Fig. 5 shows topographic images of the powder charge Al + 10 % fullerene soot.

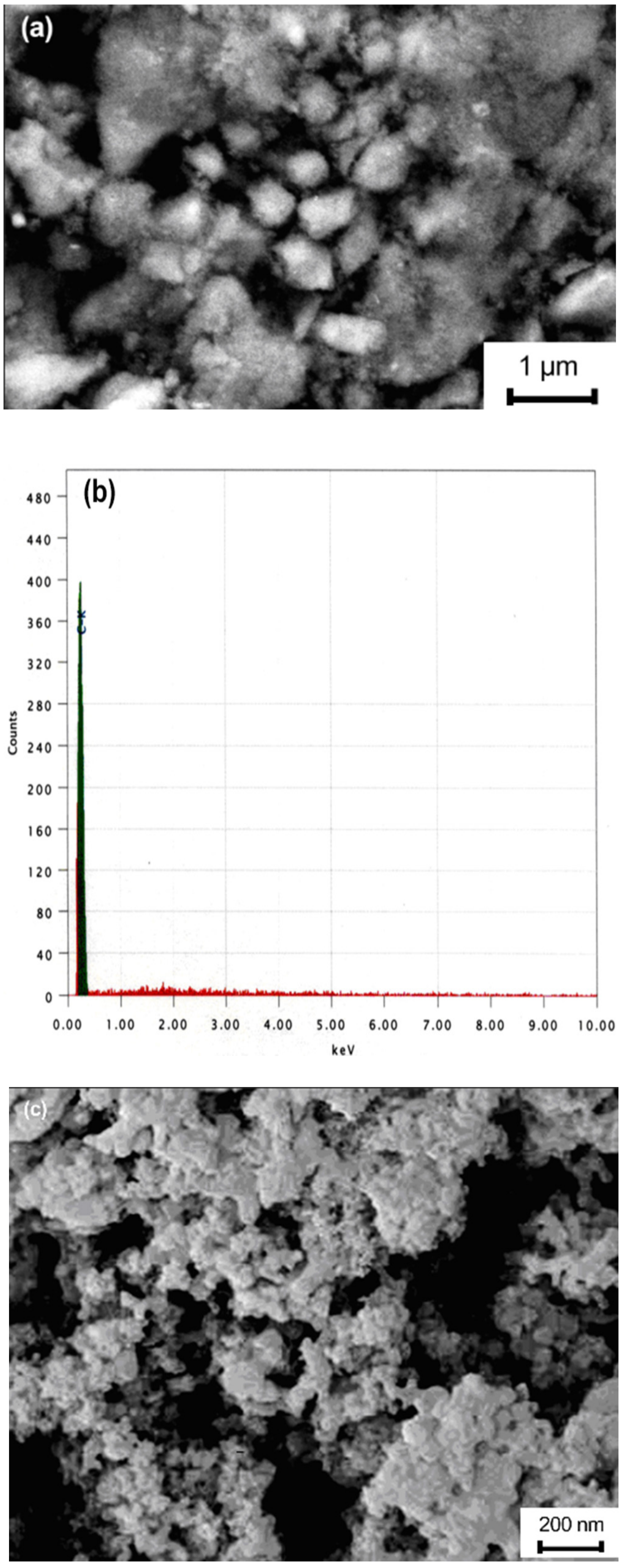

Fig. 3. Fine structure and results of EDX analysis of the powder of fullerene niello: (a) image of the area of EDX analysis; b) graph of Counts-keV; c) image of the particles in SEM.

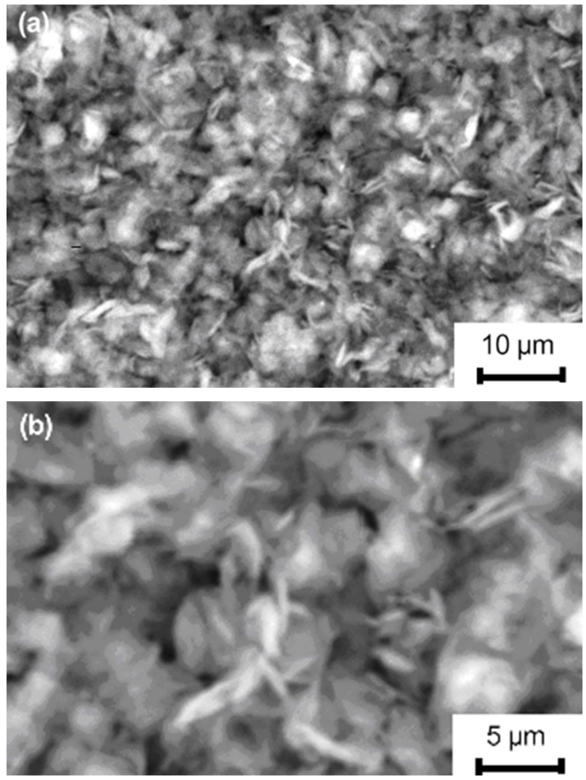

Fig. 4. Topographic images of microcrystalline powder of carbon.

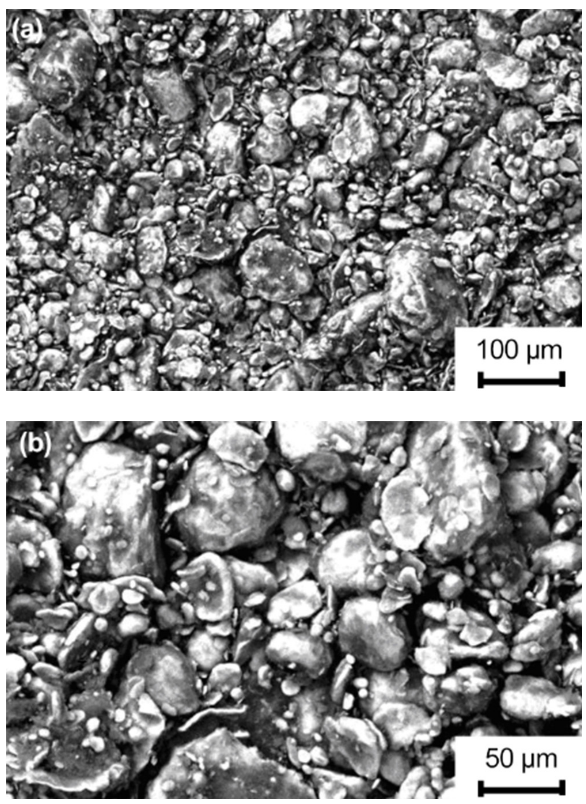

Fig. 5. Topographic images of powder charge Al + 10 % fullerene soot.

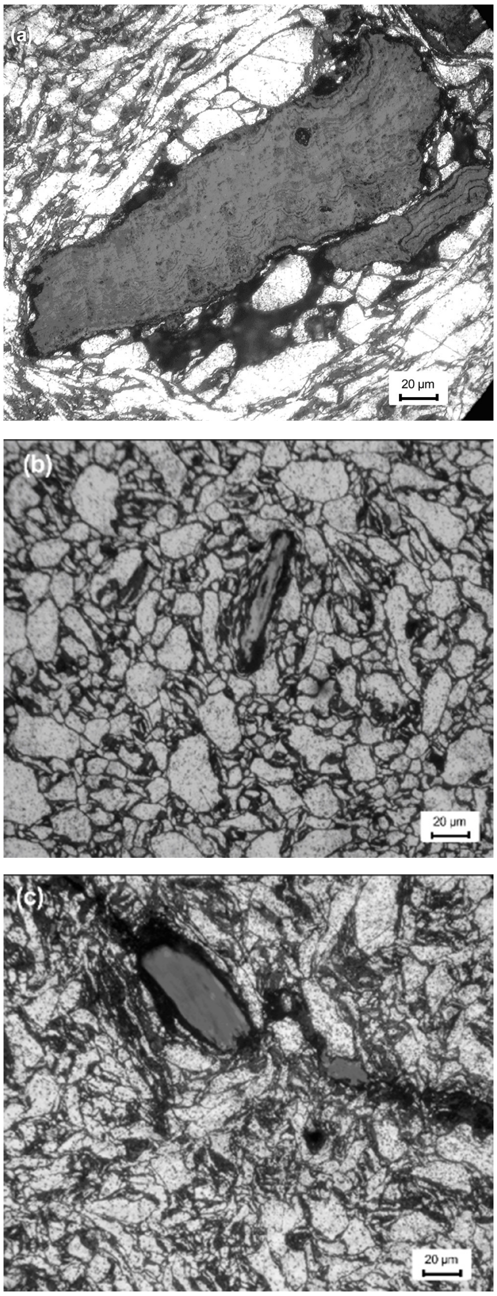

Fig. 6. The microstructure of the ligature sample Al-C: a) Al + 10% fullerene niello; b) Al + 10 % fullerenes C_{60}; c) Al + 10% fullerene soot.

Study of the compositions of Al-C after extrusion of the charge

The structural state obtained by extrusion of ligatures was studied. Unusual for Al-C alloys superhard grey particles of various modifications were revealed in the samples (Fig. 6). The measurements of microhardness of the phases detected the effect of restoring the imprint of the indenter, indicating its very high elastic

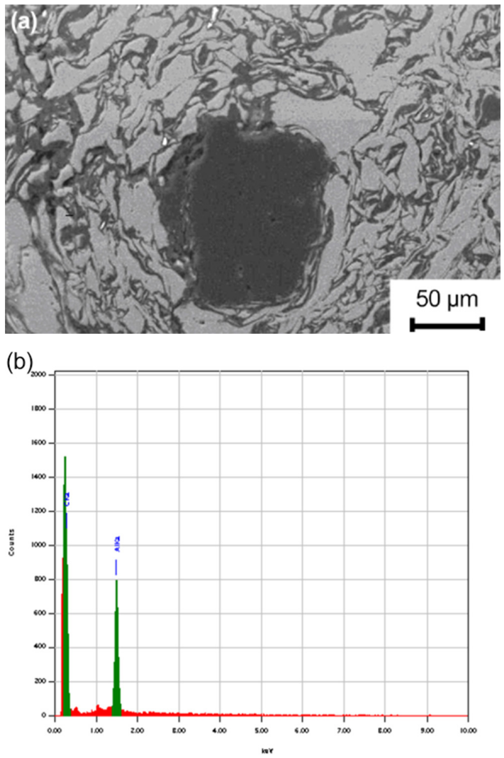

Fig. 7. Fine structure and results of micro-X-ray spectral analysis.

properties. Micro-X-ray spectral analysis EDX showed that this superhard phase is carbon (Fig. 7).

In the microstructure of several samples (especially in the series with fullerene niello) particles of gray phase with wavy surface (globular relief), without any traces of grinding and polishing (Fig. 6a), having a very high microhardness (the prints of the indenter on the image are not visible), were observed This behavior of the phase indicates that their hardness is close to the hardness of diamond.

All manufactured samples with nanocarbon additives contain this phase (Fig. 6). The analysis showed that the size, shape and number of the super hard pure carbon phase with high elasticity are various in the ligatures of different compositions.

The analysis of the results of the study of the structural state of the samples Al-microcrystalline carbon after extrusion of the charge showed an uniform distribution of the carbon component (black and grey inclusions) in an aluminum matrix (Fig. 8). While the small size of the carbon inclusions do not allow measurement of microhardness, which makes it impossible to identify them as superhard carbon phases obtained in the case of nanocarbon additives.

Table 1. Results of EDX analysis of ligatures Al + 10 % fullerene niello.

Element	(keV)	mass %	error %	At %	K
C	0.277	85.64	0.89	93.05	70.5855
Al	1.486	14.36	0.49	6.95	29.4145
Total		100.00		100.00	

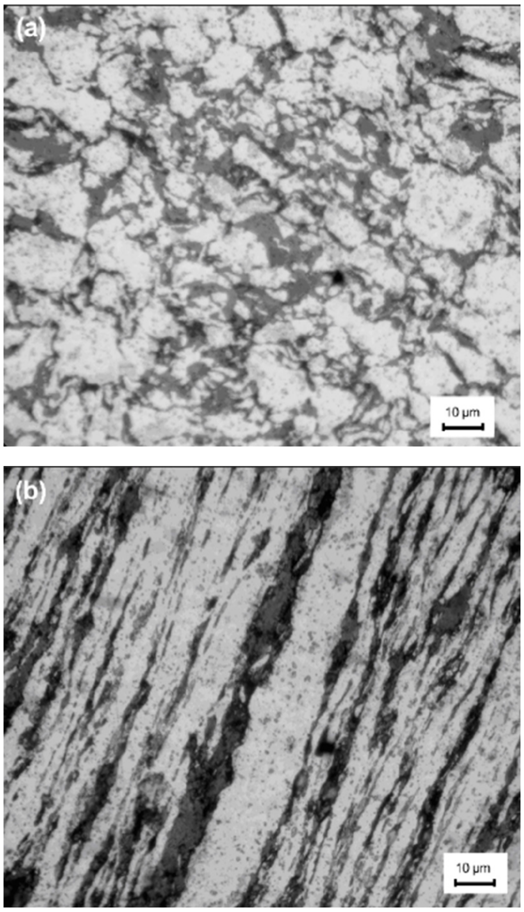

Fig. 8. The microstructure of the ligature sample Al + 10 % microcrystalline carbon: a) cross section; b) longitudinal section.

Study of aluminum alloys obtained by casting AL 25 alloy and ligatures Al-C

The research was carried out using light and scanning electron microscopy, X-ray diffraction and microprobe analyses, measurements of microhardness of the alloys obtained by casting using AL 25 alloy as the base and ligatures Al-C, added to the melt in quantity of 10 % of the total weight of the alloy.

The results of the study of the microstructure are shown in Figs. 9 - 13. The analysis of these studies showed that all composites of Al-C have modified structure of the metal substrate with distributed carbon structural component. As it is seen from the figures, there are significant differences in the amount, structure and distribution of carbon inclusions in the volume of the alloys obtained with different modifications of the carbon materials. In this case, all the samples of the composites obtained using microcrystalline carbon with different dispersion have similar structure and distribution of the carbon phases: the greatest, in comparison with the other samples, is the number of carbon inclusions, close to spherical with low volume of the dispersed allocation (Fig. 10).

On the other hand, the samples of the composites obtained using nanocarbon materials (fullerenes, fullerene soot and niello) also have similar structure and distribution of carbon phases essentially smaller, compared with the samples obtained using microcrystalline carbon (Figs. 11 - 13). During overheating of the melt at 120 - 180°C above the liquidus temperature there is a complete absorption of the ligature and uniform distribution of the components throughout the volume of the melt. This interval of overheating of the melt also contributes to the solubility of the gases, which reduces the gas-saturation of the alloy. Overheating of the melt at a higher temperature (e.g. 200°C) leads to exposure of dispersed particles of carbonaceous material on the surface of the melt. Overheating at lower temperature (e.g. 100°C) does not ensure complete dissolution of the ligature and optimal homogeneity of the melt, which affects the properties of the workpiece.

Thus, the obtained results define basic possibility of introducing in the structure of the aluminum alloy ultrafine carbonaceous raw materials for modifications.

The data, obtained in the measurement of microhardness of all samples of the composites Al-C, show low hardness and hardness characteristic of graphite inclusions. In the structure was not observed carbon inclusions with high hardness obtained in the ligatures after extrusion.

As shown above, all composites of the system Al-C have modified structure of the metal substrate with a dispersion-distributed inclusions of intermetallic compounds (Figs. 9 - 13). According to the results of microchemical analysis identified two types of intermetallic compounds of different composition: intermetallic compounds with a high content of Fe and Mn (Fig. 14a) and intermetallic compounds with a high

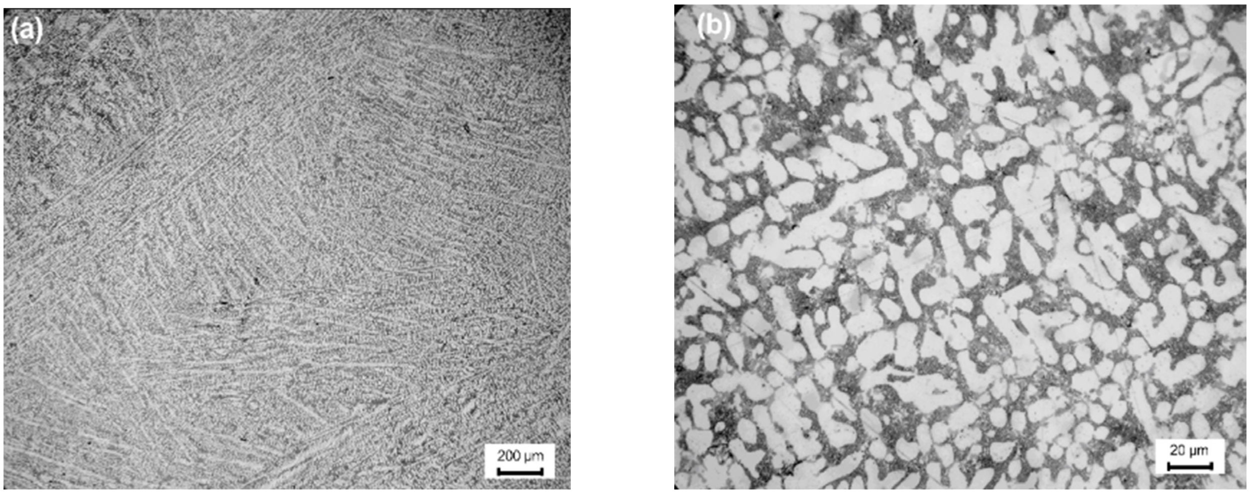

Fig. 9. The original microstructure of the alloy AL 25 after etching.

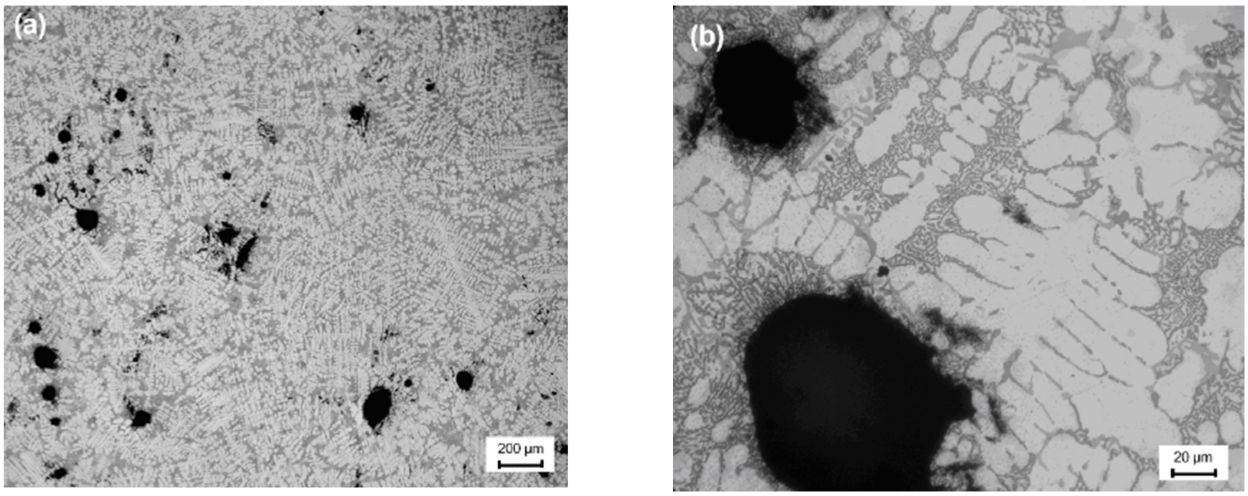

Fig. 10. The microstructure of the composite sample obtained with the use of microcrystalline carbon after etching.

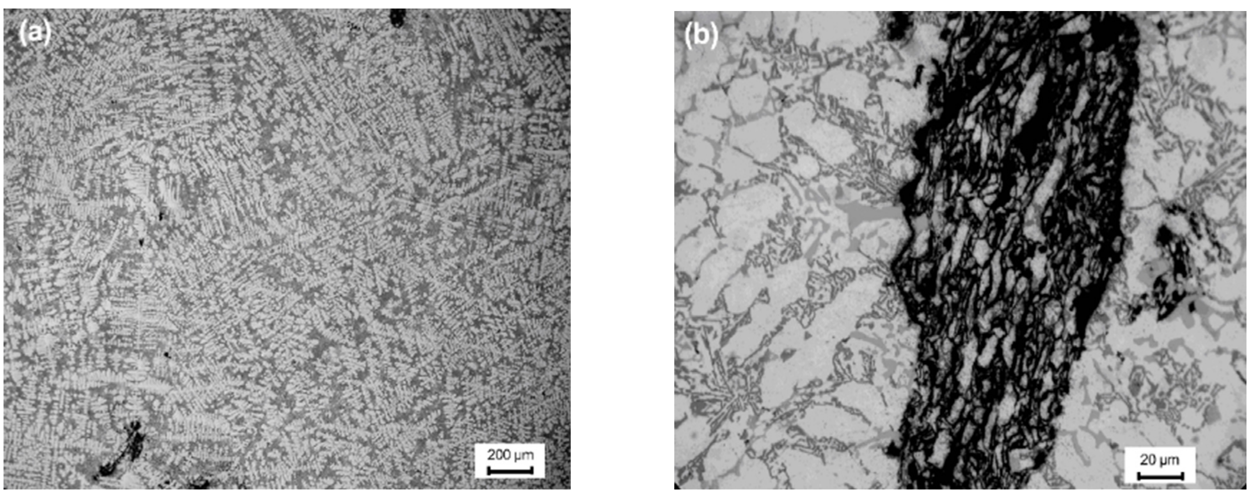

Fig. 11. The microstructure of the composite sample obtained using C_{60} after etching.

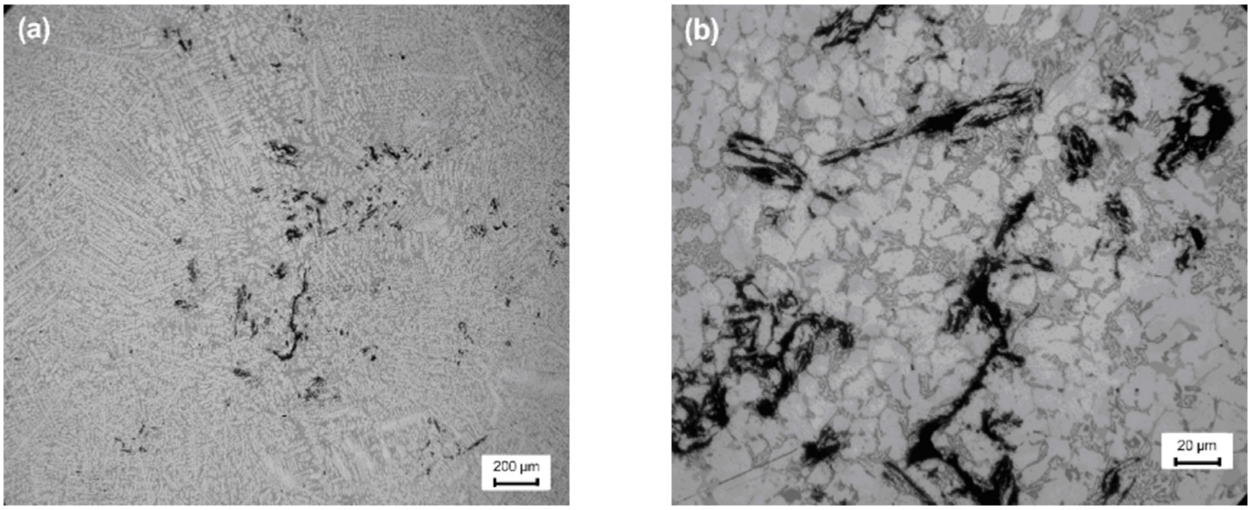

Fig. 12. The microstructure of the composite sample obtained with the use of fullerene soot after etching.

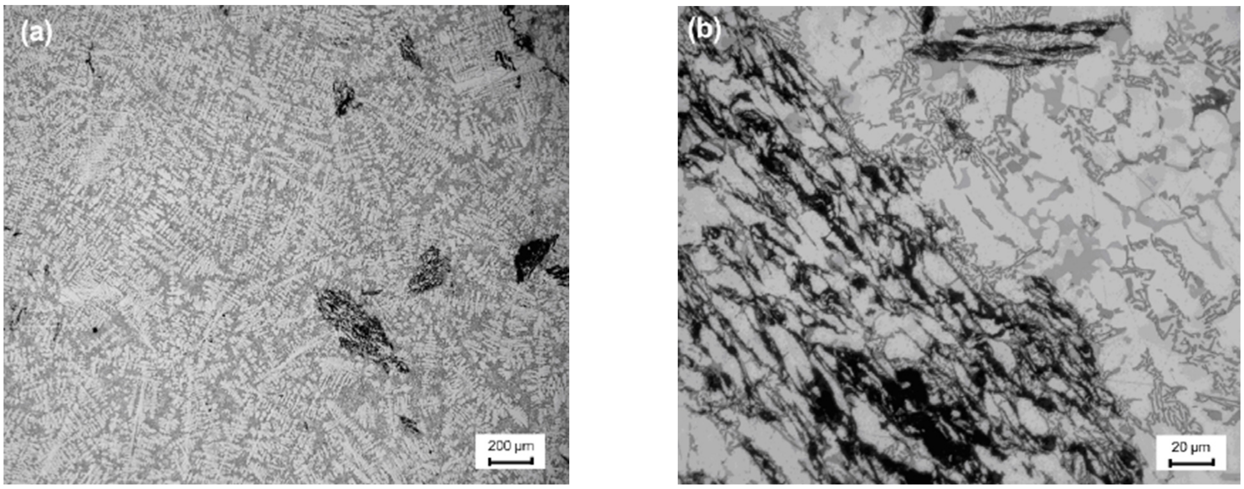

Fig. 13. The microstructure of the composite sample obtained with the use of fullerene niello after etching.

content of Cu and Ni (Fig. 14b). As show the results of studies of microhardness, the intermetallic compounds are characterized by significantly higher microhardness compared to the basis. Determining the true values of microhardness of the intermetallic compounds is difficult due to the small size inclusions. However, the obtained hardness values are of the level of 7000 - 8000 MPa (Fig. 15a), with hardness of the basics 1000 - 1300 MPa (Fig. 15b). It can be concluded that the dispersed distribution of the above-mentioned intermetallic compounds has a hardening effect on the structure of the composites Al-C.

CONCLUSIONS

The processing of aluminum alloys (silumins) by ligatures containing various carbon modifications (in the form of microcrystalline graphite, nanocarbon additives in the form of fullerenes, fullerene soot, fullerene niello) based on casting-deformation technology of manufacturing of products, developed by scientists of the Republic of Kazakhstan and the Republic of Belarus in the framework of the state budget-funded theme on the program “Grant financing of scientific research in the Republic of Kazakhstan for 2013-2015” was studied. The elemental and phase composition, structural state and mechanical and tribological properties of the initial components of the charge in the Al-C and Al-Si-C alloys after mechanical activation alloys by severe plastic deformation (extrusion) of the charge and cast aluminum workpieces were studied.

The processes of structure formation of the alloys in the system Al-C and Al-Si-C when they are received

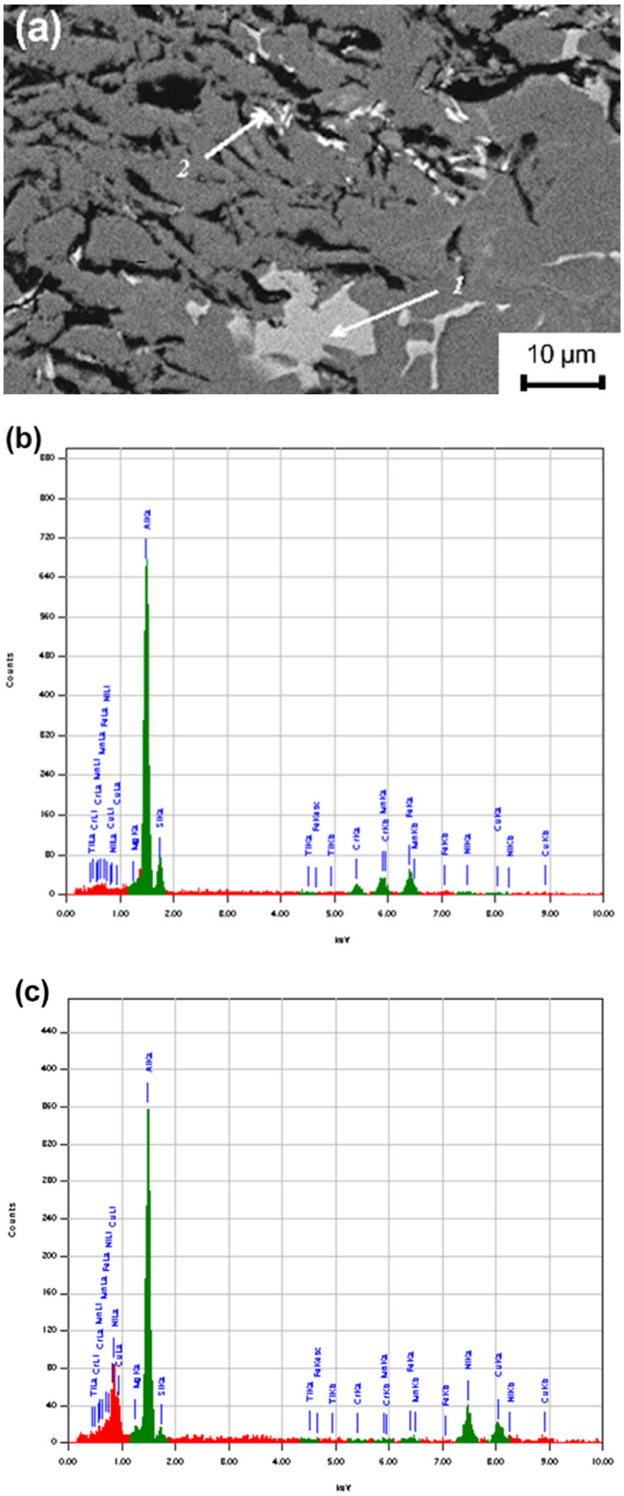

Fig. 14 – Fine structure and results of micro-x-ray spectral analysis EDX of the composite sample obtained using fullerene niello: a) image of the area of EDX analysis; b) results of micro-X-ray spectral analysis EDX at zone 1; c) results of micro-x-ray spectral analysis EDX at zone 2.

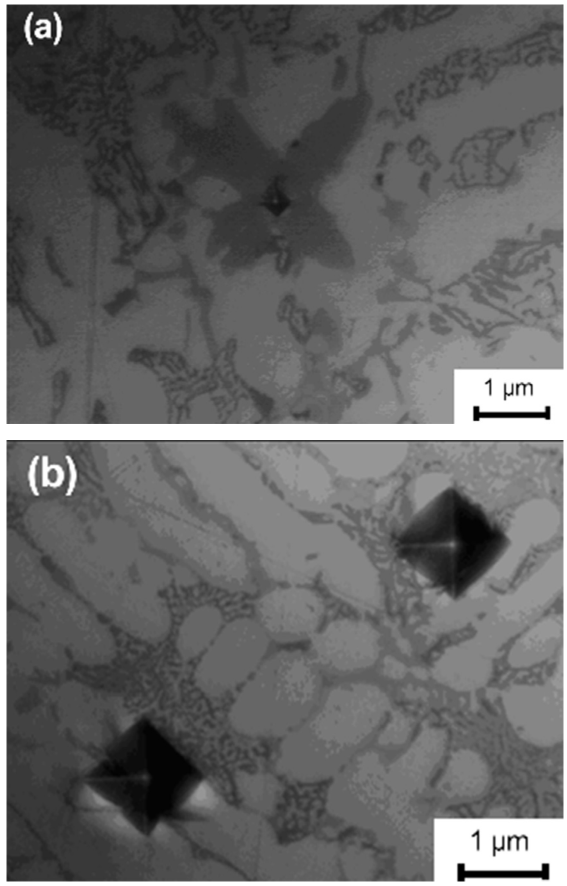

Fig. 15. Microstructure of the alloy specimen obtained using ultrafine raw materials, with imprints of the indenter: a) Hm = 8310 MPa; b) Hm = 1080 MPa, Hm = 1200 MPa.

and thermomechanically loaded are gradually studied. The formation of superhard carbon phases in ligatures, where instead of microcrystalline graphite was used nanocarbon additives is of particular interest. Using spectroscopy of combined light scattering amorphous phase, similar to glassy carbon was revealed. In the ligatures were identified also carbides of aluminum Al_4C_3 and/or silicon SiC during annealing (800ºC, 30 minutes). The structural state of the alloys obtained after activation of the charge (mechanical activation in dispersive devices and intensive plastic deformation) determines the prospects of their use in the composites characterized by high anti-friction, plastic and strength properties.

The results did not reveal fundamental differences in the structure formation of aluminum composites produced using expensive fullerenes in comparison with the composites produced using relatively cheap nanocarbon materials (fullerene soot, fullerene niello).

Table 2. Results of EDX analysis at zone 1.

Element	(keV)	mass %	error %	At%	K
Mg	1.253	0.29	0.12	0.38	0.2305
Al	1.486	59.94	0.11	71.18	56.7050
Si	1.739	9.66	0.20	11.02	5.6332
Cr	5.411	4.18	0.26	2.57	5.2930
Mn	5.894	9.83	0.31	5.73	12.0902
Fe	6.398	13.36	0.32	7.67	16.7313
Ni	7.471	1.50	0.50	0.82	1.8505
Cu	8.040	1.24	0.65	0.63	1.4663
Total		100.00		100.00	

Table 3. Results of EDX analysis at zone 2.

Element	(keV)	mass %	error %	At%	K
Mg	1.253	1.62	0.20	2.37	0.9491
Al	1.486	53.24	0.17	70.01	38.9922
Si	1.739	1.75	0.25	2.21	0.9872
Cr K	5.411	0.23	0.29	0.16	0.3208
Mn	5.894	0.09	0.33	0.06	0.1277
Fe	6.398	1.33	0.32	0.84	1.9762
Ni	7.471	22.92	0.54	13.85	31.7825
Cu	8.040	18.81	0.70	10.50	24.8643
Total		100.00		100.00	

REFERENCES

1. I.A. Yevdokimov, G.I. Pivovarov, V.D. Blank, V.V. Aksenenkov, A.N. Kirichenko, V.E. Vaganov, Metalcarbon composite material based on aluminum, Chemistry and Chemical Technology, 54, 7, 2011, 58-62, (in Russian).
2. S.N. Kolokol'cev, Carbon materials. Properties, technologies, applications, Dolgoprudnyj, Izdatel'skij Dom «Intellekt», 2012, (in Russian).
3. S.V. Mishenko, Carbon nanomaterials. Production, properties, applications, Moscow, Mashinostroenie, 2008, (in Russian).
4. O.P. Chernogorova, E.I. Drozdova, V.M. Blinov, N.A. Bul'enkov, Structure and properties of hyperelastic carbon particles reinforcing the wear resistant composite materials obtained by mixture of iron powders and fullerenes under pressure, Rossijskie nanotehnologii, 5-6, 2008, 150-157, (in Russian).
5. I.A. Yevdokimov, A.V. Panfilov, V.E. Vaganov, A.A. Panfilov. Isotropic aluminum-matrix composites with nanocarbon materials, 6th International Conference «Carbon: Fundamental Science Problems, Materials Science, Technology», Troitsk, 2009, 123, (in Russian).
6. R.A. Wood, M.H. Lewis, G. West, S.M. Bennington, M.G. Cain, N. Kitamura, Transmission electron microscopy, electron diffraction and hardness studies of high-pressure and high-temperature treated C_{60}, J. Phys.: Condens. Matter, 12, 2000, 283-293.
7. O.P. Chernogorova, E.I. Drozdova, Wear resistance of metallic composite materials containing diamond-like carbon particles in their volume, Metals, 3, 2003, 97-104, (in Russian).
8. S. Lezhnev, D. Kuis, A. Volochko, A. Shegidevich, N. Svidunovich, et al., Cast Aluminum Composite Obtained by Using Ultrafine Carbon Raw Materials, J. Material. Sci. Eng., 4, 2015, 166.
9. D.V. Kuis, S.N. Lezhnev, G.P. Okatova, N.A. Svidunovich, V.S. Urbanovich, P.V. Rudak, I.L. Tobolich, A.O. Tolkushkin, Amorphous-Nanocrystalline Composite Based On Nanocarbon, Obtained By Sintering Under High Pressure, Proceedings of the 2015 International Conference on Computer, Intelligent Computing and Education Technology (CICET 2015), Guilin, China, 2015, 731-735.
10. A.I. Gusev, Nanomaterials, nanostructures, nanotechnology, Moscow, PHYSMATLIT, 2009, (in Russian).