

V. KOVTUN\*, V. PASOVETS\*, T. PIECZONKA\*\*

## INVESTIGATION OF STRUCTURE AND PHYSICO-MECHANICAL PROPERTIES OF COMPOSITE MATERIALS BASED ON COPPER – CARBON NANOPARTICLES POWDER SYSTEMS

## BADANIE STRUKTURY I WŁAŚCIWOŚCI FIZYKO-MECHANICZNYCH SPIEKANYCH MATERIAŁÓW KOMPOZYTOWYCH MIEDŹ-NANOCZĄSTKI WĘGLA

Physico-mechanical and structural properties of electrocontact sintered copper matrix- carbon nanoparticles composite powder materials are presented. Scanning electron microscopy revealed the influence of preliminary mechanical activation of the powder system on distribution of carbon nanoparticles in the metal matrix. Mechanical activation ensures mechanical bonding of nanoparticles to the surface of metal particles, thus giving a possibility for manufacture of a composite with high physico-mechanical properties.

*Keywords:* powder metallurgy, electrocontact sintering, physico-mechanical properties, carbon nanoparticles, composite powder materials, triboengineering characteristics, mechanical activation

Materiały kompozytowe o osnowie miedzi zawierające nanocząstki węgla wytwarzano metodą spiekania elektrostrykowego. Spieki poddano badaniom właściwości fizyko-mechanicznych oraz badaniom strukturalnym. Obserwacje przełomów za pomocą mikroskopu skaningowego wykazały korzystny wpływ mechanicznej aktywacji mieszanki proszków na rozmieszczenie nanocząstek węgla w osnowie metalowej. Aktywacja prowadzona w wysokoenergetycznym młynie wibracyjnym doprowadza do mechanicznego połączenia nanocząstek węgla z powierzchnią cząstek miedzi, dzięki czemu możliwe jest wytworzenie spiekanej kompozytu o wysokich właściwościach fizyko-mechanicznych.

### 1. Introduction

Industrial development requires the application of novel composite materials that display high strength properties and wear resistance [1, 2]. It is well known that metal matrix composites containing dispersed carbides, oxides as well as diamond and graphite particles are used to manufacture the triboengineering components [3-5]. There are, however, some limitations related to the micron-sized particles used for such applications. The use of nanoparticles instead of coarser ones seems to be more effective in terms of composites' properties [6]. The powder systems containing nanodispersed particles belong to a new generation of composite materials.

Antifrictional composites with high triboengineering and physico-mechanical characteristics may be produced by impregnation of powder matrix by carbon nanostructures [7-9]. The use of macrolevel carbon nanotubes (CNT) and onion carbon nanostructures (OCN) as antifrictional and reinforcing fillers makes composite materials suitable, in particular, for dry friction applications [10]. Such properties of CNT like high specific surface, the dimensions commensurable with the forces of intermolecular interactions, along with high strength, thermal and electric conductivity are of great importance in

this case [11,12]. It is worth to note that composite materials containing different nanosized particles are intensively investigated worldwide at present.

The manufacture of composite materials by incorporation of carbon nanostructures in the molten metal matrix meets serious difficulties. From one hand the carbon nanoparticles tend to agglomerate in a free state [13, 14], from the other hand – the most metals used as matrix form carbides at elevated temperature [15]. Furthermore, the surface of carbon nanostructures is perfectly wetted by the matrix metal whose surface energy is within 100-200 mN/m [16]. The problem of wetting of carbon nanostructures with the surface energy surpassing 200 mN/m was solved in 1996 by oxidation of carbon nanostructures [17]. It is worth to add, however, that chemical surface functionalization of carbon nanostructures affects inevitably their mechanical properties. It is estimated that the oxidation of carbon nanostructures degrades their properties by 15-20%.

In view of above, the powder metallurgy route seems to be the most promising way to obtain metal-carbon nanostructures composites with homogenous distribution of carbon nanoparticles. In particular, the short-term technique of sintering, like electrocontact sintering, may be advantageous for these pur-

\* STATE EDUCATIONAL ESTABLISHMENT "GOMEL ENGINEERING INSTITUTE" OF THE MINISTRY FOR EMERGENCY SITUATIONS OF THE REPUBLIC OF BELARUS, GOMEL, BELARUS

\*\* AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, AL. A. MICKIEWICZA 30, 30-059 KRAKÓW, POLAND

poses. Electrocontact sintering is characterised by high-rate internal heating and a sharp temperature gradient, under which the hereditary structure of the material is preserved. Powder particles tend to bond via the diffusion-free setting and welding (in the solid, solid-liquid and liquid phases) and based on diffusion processes. The share of these processes is determined by the maximal temperature, pressing force, time of current flow and other technological parameters [18].

In spite of a great number of publications, the questions of combining micron-sized and nanodispersed powder components have not lost their actuality till now. The problem consists in obtaining a powder system having a uniform distribution of carbon nanostructures (initially present in the form of agglomerates) over the whole volume of the matrix and their strong bonding inside the metallic matrix of the composite material. The main purpose of the current work is to make a progress in this field by mechanical activation of the starting materials.

## 2. Mechanical activation of powder systems

Mechanical activation of the initial components of powder systems is believed to be a promising method used in powder metallurgy to control the structure development of composite materials. Particularly, to hamper agglomeration of carbon nanostructures [18], to ensure their uniform distribution in the matrix, and to increase the activity of metal component are subjected to mechanical activation.

The mechanical activation leads to enlarged specific area of metal particles and modification of their surface structure, generates the plastic strains that result in multiplying the structural defects which, in turn, facilitates interactions between the components. The intensive plastic strain may cause the significant structural and phase transformations of the material. One of the commonly encountered outcome of the intensive plastic strain is the shift of the phase transition to the lower temperature which is usually accompanied by a reduced time required for the following thermal treatment (e.g. sintering). Generally, the mechanical activation alters the free surface energy of the substance, decreasing thereby the energy potential of physico-mechanical processes [19].

The mechanical activation takes place if the rate of defect accumulation in the particles surpasses that of their disappearance [20]. This may be performed in a so-called energy-intensive equipment where, typically, the high frequency is combined with locally high mechanical forces. The examples of such equipment are centrifugal, planetary and jet-type mills, attritors or other disintegrators.

The efficiency of mechanical activation corresponds to the amount of the energy accumulated by the unit mass of the material treated in a unit of time of the activation action. This parameter depends on several factors, among which are the activator type, mechanoactivation medium, size and mass ratios of the working bodies and powder and as well as the characteristics of the treated material. The desired effect from mechanoactivation can be optimised, as a rule, through a laborious matching of treatment conditions, i.e. empirically. These conditions are very specific for any single system.

The activated powder is characterised by a uniform distribution of the components and by the presence of fragmented particles with a large number of cleavage facets, cracks and other defects. During mechanical activation the surface oxide films covering powder particles are broken and at least partly removed [21]. Typically, the specific surface of the powder significantly increases. All of these features are beneficial for the bonds formation between carbon nanostructures and metal particles occurring during consolidation.

## 3. Materials and experimental procedure

The composite materials were produced using copper powder PMS-V grade (State Standard GOST 4960-75), 50-100  $\mu\text{m}$  in size, CNT (Fig. 1a), OCN (Fig. 1b) and a combined carbon nanostructural filler (CCNF). CCNF is a bi-component nanopowder obtained by benzene pyrolysis, consisting of  $\sim 20\%$  CNT and  $\sim 80\%$  of OCN. CCNF content in the investigated powder systems was varied from 0.01 till 0.1 mass% with a 0.01% single step.

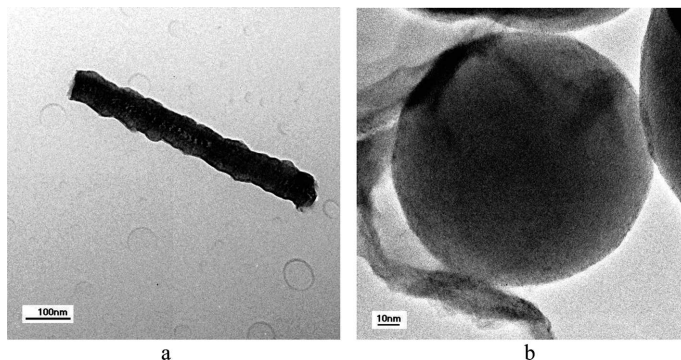


Fig. 1. Carbon nanostructures: a – carbon nanotube; b – onion carbon nanostructure

Mechanoactivation of the powder was carried out using an originally developed pilot mechanical activator. Its distinguishing feature is an intensive vibration effect accompanied by impaction and rolling of the working bodies. To produce the copper-CCNF composite materials the activated powder was consolidated by electrocontact sintering.

The structure and phase composition of composites were studied by a scanning electron microscopy using the standard procedures. Archimedes method was chosen to measure porosity. Brinell hardness and compressive strength limit of sintered composites were controlled.

Triboengineering tests using the shaft-on-partial-insert friction geometry were carried out in a dry regime on a friction machine SMT-2 for 8 h under 1 MPa loading, at 1 m/s as sliding velocity and at ambient temperature. The counterbody material was steel 45 of 44 HRC and  $R_a = 0.3\text{-}0.4 \mu\text{m}$ . The run-in was performed at 100 kPa load till a complete contact over the whole friction surface was formed. The friction coefficient and the wear rate were determined for a stationary friction mode. The values of tribological characteristics are averaged over three measurements.

For comparison, compacts of copper-graphite composites were made produced from the same copper powder and the natural graphite fine powder (UF-4 grade). The graphite

content varied from 1 up to 25 mass%. The copper-graphite powder mixtures were consolidated using the same processing applied for copper-CCNF composites and their tribological properties were also investigated.

#### 4. Results and discussion

There are two important phenomena taking place during mechanical activation of the copper-CCNF powder system: the disintegration of agglomerates of carbon nanostructures and formation of mechanical bonds between nanoparticles and microparticles. It is well known that electrolytic copper powder is characterised by the dendritic particles with rough surface (Figures 2 and 3) and thus its high specific surface is beneficial for the mechanical joints formation, both between copper-copper particles and as well between copper-carbon nanopowder particles. Because of the hits of mechanical activator on the treated particles, the carbon nanostructures may be joined between the metal particles or just on the dendrites' surface, which is documented by Figure 4.

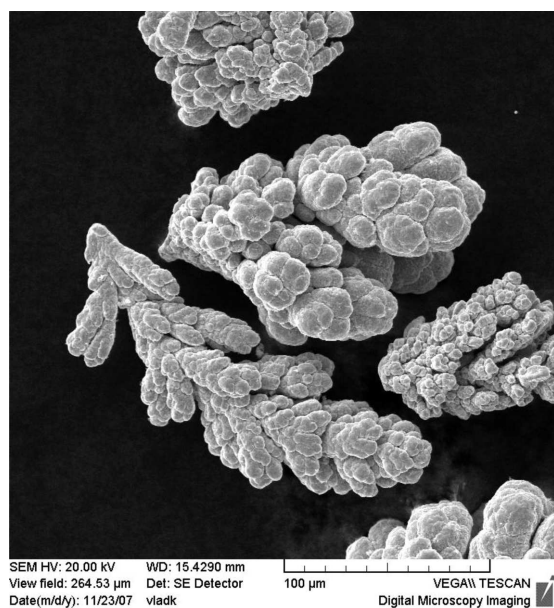


Fig. 2. SEM micrograph of the copper particles in a secondary electrons mode

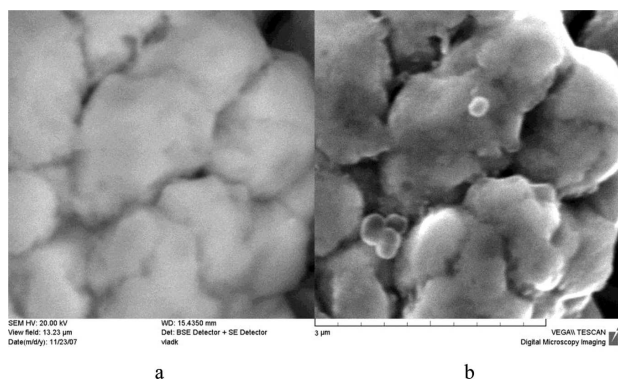


Fig. 3. Fracture surface of the copper particle in a non-activated powder system copper-carbon nanostructures: a – in a BSE mode; b – in secondary electrons mode

Figure 3 shows a fracture of the sintered composite material copper-CCNF produced without any preliminary mechanical activation of the components. For better identification of the carbon nanostructures the fracture was observed using both BSE (Fig. 3a) and secondary electrons (Fig. 3b) modes [22, 23]. As it is seen there are no carbon nanostructures joined to the surface of copper particles, which suggests that all CCNF particles are freely located within the spaces between copper particles. Typically, this is not the desirable structure of the composite material.

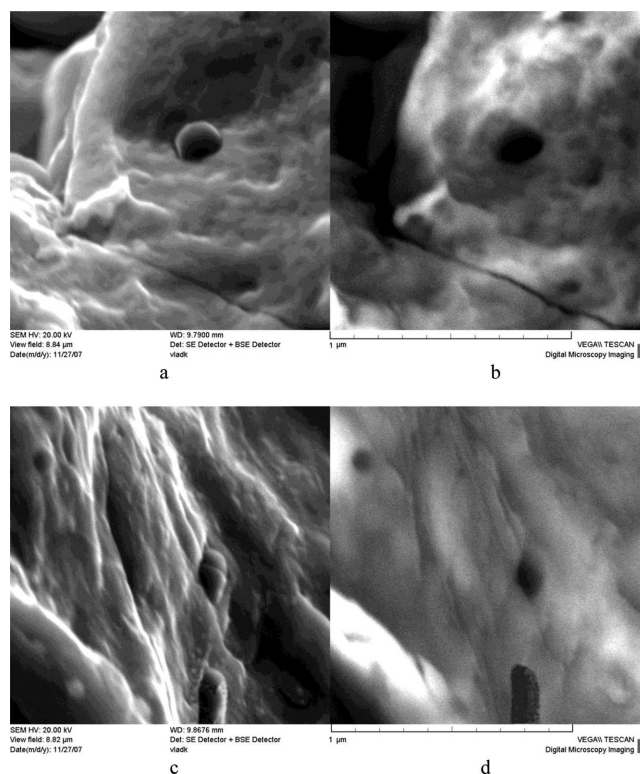


Fig. 4. Fracture surface of the copper particle in activated powder system copper-carbon nanostructures: a, c – in secondary electrons mode; b, d – in BSE mode

Mechanical activation of the powder is a crucial procedure affecting the properties of sintered composites. In general, the longer the powder is activated the more copper-carbon bonds are formed and thus the more uniform distribution of components may be expected. It is known, however, that prolonged time of mechanical activation may also result in the formation of agglomerates. Therefore, the time of mechanical activation should be optimised for any specific system. In case of investigated copper-CCNF composites the optimal time of mechanical treatment is about 60 min (Table 1). Sintered compacts produced from powder prepared in this way show the best properties, i.e. at the lowest porosity the best mechanical properties were obtained.

Tribological properties of the investigated antifriction composites were controlled on compacts manufactured from powders activated for 60 minutes. The results of triboengineering tests are presented in Table 2. It is evident that with increasing CCNF content from 0.01 up to 0.1 mass% the friction coefficient decreases monotonously.



TABLE 1  
 The effect of mechanical activation time on sintered properties of copper – 0.05 mass% CCFN composites

Mechanical activation time (min)	Porosity (%)	Hardness (HB)	Compressive strength limit (MPa)
20	6...7	90...95	226...230
40	4...5	100...105	244...248
60	3...4	110...115	260...264
80	5...6	95...100	220...223
100	6...7	90...95	215...220

TABLE 2  
 Friction coefficient and wear rate for sintered composite materials copper-carbon nanostructures

Concentration of combined carbon nanostructured filler in composite material (mass%)	Friction coefficient	Wear rate ( $\mu\text{m}/\text{km}$ )
0.01	0.42	0.48
0.02	0.35	0.29
0.03	0.3	0.2
0.04	0.28	0.16
0.05	0.24	0.12
0.06	0.2	0.09
0.07	0.17	0.06
0.08	0.14	0.12
0.09	0.105	0.26
0.1	0.095	0.42

However, the relationship “wear rate vs. CCFN content” shows the extremum character being is the lowest for material containing 0.07 mass% of CCFN. This can be explained by the reduction of the metal-metal joints at higher nanoparticles contents.

TABLE 3  
 Friction coefficient and wear rate for sintered composite materials copper-graphite

Graphite content in composite material, (mass%)	Friction coefficient	Wear rate ( $\mu\text{m}/\text{km}$ )
1	0.52	0.49
5	0.42	0.29
8	0.33	0.18
10	0.29	0.12
15	0.25	0.3
25	0.205	0.58

Tribological properties of copper-graphite composites were shown in Table 3. The tendency is similar as for copper-CCFN materials, i.e. the higher the graphite content the lower the friction coefficient and there is an optimal solid lubricant content ensuring the lowest wear rate. It should be noted, however, that natural graphite fine powder used in these

experiments is significantly less effective in terms of affecting the tribological properties of sintered materials than CCFN powder addition: 25 mass% of graphite is necessary to produce material of the same friction coefficient as 0.06 mass% of CCFN does. Considering the wear rate, in turn, at about 10 times lower CCFN content the more wear resistance material is produced than that containing graphite.

Figure 5a shows a representative 3D microstructure of the sintered copper – 0.07% CCFN composite observed by AFM. This fragment consists of five copper particles found in contact with each other. To recognise the carbon nanostructures location the same fragment was analysed using phase contrast procedure whose result is shown in Figure 5b. As it is documented the carbon nanostructures are located mainly between the particles of the copper matrix. However, the negligible amount of CCFN particles can also be seen on the surface of copper particles (Fig. 6).

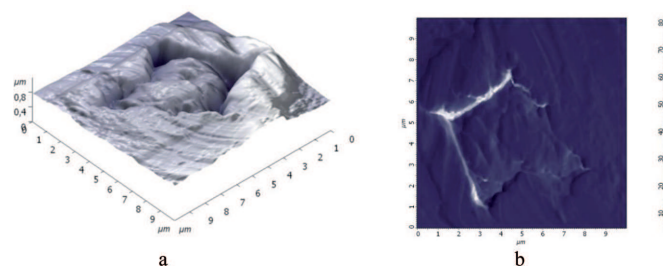


Fig. 5. AFM micrograph of the sintered copper – 0.07% CCFN composite: a – 3D image; b – phase contrast image

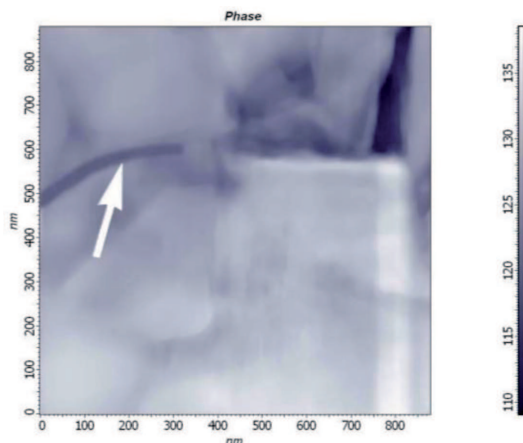


Fig. 6. Phase contrast image of the sintered copper – 0.07% CCFN composite with a CNT (shown by arrow) joined to the copper surface

At 0.06-0.07 mass% of CCFN content the most carbon nanoparticles are located between the metallurgically joined copper powder particles. At this content of CCFN the development of sintering necks formation is only in a limited scale impeded by the their presence. Therefore, from one hand the material shows the acceptable strength and from the other – the carbon nanoparticles being lubricant can not be easy removed from the friction zone. Thus, at the specified and experimentally proved CCFN content the sintered copper – CCFN composites show the best tribological properties.

## 5. Conclusions

The investigations proved the beneficial effect of preliminary mechanical activation of the copper – CCNF powder system: both on the distribution of carbon nanostructures in the sintered metal matrix composite and on the sintered properties. The optimal conditions of mechanical activation of initial powder mixture and its consolidation were established. The significantly higher effectiveness of carbon nanoparticles in comparison with graphite particles on tribological properties of sintered composites was clearly documented. As optimal CCNF content in the copper matrix 0.07 mass % was fixed. At this composition the sintered material shows the highest mechanical strength, low friction coefficient and the lowest wear rate. Thus, the combination of high triboengineering characteristics with perfect heat and electric conductivity makes the investigated composites especially useful for both dry friction and electric movable contacts applications.

## REFERENCES

- [1] D.M. Karpinos, L.I. Tuchinsky, and L.R. Vishnyakov, Novel Composite Materials, Kiev, Vishcha Shkola, 1977.
- [2] V.A. Belyi, Problems in Developing Composite Materials and Control of Their Frictional Properties, *J. Friction and Wear* **3**, 389-395 (1982).
- [3] N.M. Rusin, A.P. Savitsky, A.A. Bataev, Graphite Effect on Triboengineering Properties of Sintered Alloys of Al-Ti System, *J. Friction and Wear* **19**, 5, 628-632 (1998).
- [4] V.A. Vereshchagin, V.V. Zhuravlev, Composite Diamond-Containing Materials and Coatings, Minsk, Nauka i Tekhnika, 1981.
- [5] Catalogue of Diamond Goods Produced in Republic Belarus, Ed. By P.A. Vityaz', A.F. Iliyushenko, E.V. Zvonarev, Minsk, Tonpik, 2005.
- [6] T. Cabioch, E. Thune, J.P. Rivière, et al., Structure and Properties of Carbon Onion Layers Deposited onto Various Substrates, *J. Appl. Phys.* **91**, 3, 1560-1567 (2002).
- [7] S.R. Cohen, Y. Feldman, H. Cohen, et al., Nanotribology of Novel Metal Dichalcogenide, *J. Appl. Surf. Sci.*, 603-607 (1999).
- [8] X.H. Chen, J.C. Peng, X.Q. Li, et al., Tribological Behavior of Carbon Nanotubes-Reinforced Nickel Matrix Composite Coatings, *J. Mater. Sci. Lett.* **20**, 22, 2057-2060 (2001).
- [9] M. Damnjanovic, T. Vukovic, and I. Milosevic, Super-Slippery Carbon Nanotubes. Symmetry Breaking Breaks Friction, *Eur. Phys. J.* **25**, 2, 131-134 (2002).
- [10] V.A. Kovtun, V.N. Pasovets, Carbon Nanostructures: Properties and Promises for Using in Powder Composite Materials of Triboengineering Purposes, *J. Friction and Wear* **27**, 2, 206-215 (2006).
- [11] N. Kobayasi, Introduction into nanotechnology, Tran. From Japanese, Ed. By Prof. Patrikeeva L.N., Moscow, BINOM, Knowledge Laboratory, 2005.
- [12] M. Ratner, D. Ratner, Nanotechnology: Simple Explanation to a Next Genius Idea, Transl. From English, Moscow, Publ. House Williams, 2004.
- [13] A.D. Pomogailo, A.S. Rozenberg, I.E. Uflyand, Metal nanoparticles in Polymers, Moscow, Khimiya, 2000.
- [14] Nanomaterials: Synthesis, Properties and Applications, Ed. by A.S. Edelstein, C. Cammarata, Institute of Physics, Bristol and Philadelphia, 1996.
- [15] L.S. Pinchuk, V.A. Struk, N.K. Myshkin, A.I. Sviridenok, Materials science and Structural Materials, Ed. By Acad. Belyi V.A., Minsk, Vysheishaya Shkola, 1989.
- [16] E. Dujardin, T. W. Ebbesen, H. Hiura, K. Tanigaki, Capillarity and Wetting of Carbon Nanotubes, *Science* **265**, 1850-1856 (1994).
- [17] T.W. Ebbesen, H. Hiura, M.E. Bisher, et al., Decoration of Carbon Nanotubes, *Advanced Materials* **8**, 155-167 (1996).
- [18] A.I. Raichenko, Bases of Sintering Process of Powders by Passing Electric Current, Moscow, Metallurgiya, 1987.
- [19] L.S. Vasiliev, I.L. Lomaev, On Probable Mechanisms of Evolution of Nanostructures at Intensive Plastic Deformation of Metals and Alloys, *FMM* **101**, 4, 417-424 (2006).
- [20] S.F. Lomaeva, On the Mechanisms of Formation of Dispersity and Structural-Phase Composition in Iron-based Systems at Mechanical Activation, Deformation and Failure of Materials, **3**, 9-15 (2005).
- [21] A.A. Stefanovich, P.A. Vityaz, B.B. Khina, Structural-Phase Transformations and Mass-Transfer in Mechanically Alloyed Compositions, *Powder Metallurgy*, **23**, 85-90 (2000).
- [22] J. Goldstein, D. Newberry, P. Achlin, et al., Scanning Electron Microscopy and X-ray Analyzer, Moscow, Mir, 1984.
- [23] F.A. Gimelfarb, and S.L. Shvartsman, Contemporary Methods of Control of Composite Materials, Moscow, Metallurgiya, 1979.