METAL MATRIX CARBON CONSISTING NANOCOMPOSITES

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Abstract: Structure, physical and mechanical properties and technological approaches to development of metal matrix composite materials based on copper and aluminum matrix and carbon nanostructures were studied in this work. Comprehensive researches of prototypes of nanocomposites made by powder metallurgy were carried out. The analysis of the interaction of carbon nanoparticles with metal atoms on the basis of quantum-chemical calculations was made.

KEYWORDS: NANOCOMPOSITE, CARBON NANOSTRUCTURES, CARBON NANOTUBES, FULLERENES, QUANTUM-CHEMICAL MODELING, DFT.

1. Introduction

One way to solve the problem of improving the physical and mechanical properties of metallic materials is the creation of composites that are formed from the structurally heterogeneous substances by various methods, including powder metallurgy. Nanocomposites, the size of the structural elements of which (at least one component) is not greater than 100 nm, are of special interest. In this dimensional area reinforcing particles acquire the special structure and exercise unique mechanical, electronic and thermal properties. These objects include carbon nanostructures discovered in the last decade – fullerenes, nanotubes, astral, nanodiamonds [1-5].

Making of metal matrix composite materials begins with the preparation of the initial components. There are various technological methods of processing of metal powders: ultrasonic treatment, mechanical activation in high-energy mills, other high-energy impact. The choice of method effect on the original powder material is determined by its physical and mechanical properties, phase and granulometric structure.

A significant problem in creating nanocomposites is the even distribution of nanoparticles in the volume of material [6-8]. This problem is common for composites based on metals, polymers and other materials. It is caused to a tendency of nanoparticles to agglomerate and depends strongly on the structure of nanoparticles and the type of matrix material.

The most widespread method of homogeneous distribution of carbon nanoparticles in the metal matrix is a mixing of powders in a planetary ball mill [8-10]. This process is greatly complicated by the plasticity of metals. The distribution chemically inert nanostructures in the metal matrix is especially problematic. In particular, such structures are carbon nanotubes (CNT), grapheme and etc. Because of the tendency of particles to agglomerate its introduction in the metal through the melt is also problematic [11]. To solve this problem the nanostructures, before adding to the composite material, are subjected to a special chemical treatment – functionalization, which increases the energy of particle interaction with the matrix and promotes homogeneity of particle distribution.

The use of functionalized nanoparticles makes it possible substantially to change the properties of the final composite material.

This paper presents the results of researches of metal matrix carbonaceous nanocomposites based on copper and aluminum. The choice of materials is due to their wide application in various branches of engineering, aviation and electronics.

2. Background and necessaries for solving the problem

To optimize the method of producing powder compositions with a uniform distribution of strengthening phases in the volume of blank the following methods of mixing and mechanical activation were used: a grinding in a planetary disperser by steel and glass balls at different speeds and processing time; in a y-shaped mixer with hard-alloy refiner objects; manual method. Mechanical activation (MA) and mixing were carried out in a protective atmosphere by dry and wet method in different protective mediums. For the processing of aluminum powders grinding agent – stearic acid – was used. According to [12-14], in the process of MA metal particles are coated with a thin layer of stearic acid that prevents recrystallization and cold welding of metal particles. Copper powder PCS-1 and mechanically pure aluminum AD0 were used as starting powders. Multiwalled carbon nanotubes and nanofibers, fullerenes were used as nanomodifier. In the producing of aluminum matrix composites superdispersed nanodiamonds (SND), onions (OLC) and graphite were used.

X-ray diffractions of powders were made on diffractometer ARL XTRA (Thermo Electron Corporation), Cu Kα-radiation. High-resolution electron microscopy (HREM) researching was performed on the facility JEM-2010 at an accelerating voltage of 200 kV. Raman spectra was obtained on a spectrometer TRIAX 552 (Jobin Yvon) and detector CCD Spec-10, 2KBUV (2048x512) (Princeton Instruments), with cut filters system to suppress the excitation laser lines. Lasers STABILITE 2017 are the source of the exciting laser light. The spectral resolution is 1 cm⁻¹, the laser excitation spectrum is 514 nm, the spatial resolution is 2 microns.

Mechanically activated aluminium powders were sintered in the forms «piston – cylinder» type under the pressure of approx. 0,8 GPa, at the temperature of
280-300 °C and isothermal curing time of 5 min.

For the preparation of copper powder method, combining two processes simultaneously: dispersion and functionalization, was used [15]. Carbon material was introduced into the electrolyte and subjected to electrolysis at a current density of 0.3 A/m² for 60 min. After that the mixture was settled. The upper layer of electrolyte was poured out and the residue was washed with distilled water. The resulting suspension was separated from the sediment and was used when it is further mixed with copper powder. PCS-1 powder was treated for 30 min in a planetary mill. The mixture was dried at a temperature above 100 °C until full dry. The resulting mixture of copper and CNM was compressed with a force of 3 000 kg/sm², part of the samples after sintering was calibrated with a force of 7 000 kg/sm².

The density of compact samples was determined by hydrostatic weighing, the microhardness was measured on a PMT-3 according to State Standart 9450-76. Ultimate compression strength was determined for samples with a diameter 5.0 mm and a height of 6-7 mm on a universal tension testing machine Instron 5982.

Quantum-chemical researching was conducted by the Kohn-Sham method [16] using the exchange-correlation density functional O3LYP with the basis set 6-31G (d), which has worked well in the calculation of the energy of thermocyclic reactions [17] and the software package PC GAMESS [18].

3. Results and discussion

By X-ray and electron microscopic analysis it was revealed that as a result of mechanical activation there is a decrease of coherent scattering regions (CSR) from the initial 250-350 nm to 40-70 nm, the most intense decrease of CSR is observed during the first 20 minutes of treatment. It should be noted that the dependence of the size of the CSR on the processing time for various carbon nanostructures is the same, and has no specific features (Fig. 1).

![Figure 1](image)

The addition of stearic acid in an amount of 1% to the original powder leads to an additional reduction of CSR for 15-20%. Electron microscopy researching suggests that CSR structurally corresponds to the areas within the grain, separated by low-angle boundaries, which are formed during deformation of mechanically activated powders of copper and aluminum and the subsequent pressing and sintering (Fig. 2).

It is important to note that the initial preparation of powders also exert influence on the formation of subgrain structure. During mechanical activation and sintering part of CNS is undergoing the destruction. The resulting carbon nanomaterial (undamaged CNS, made graphene structure, amorphous carbon, C₆₀ fragments, etc.) forms covers around the nanoparticles of aluminum matrix (Fig. 3a), which are a kind of barrier to cold welding and recrystallization of metal nanoparticles.

According to the local spectral analysis it can be concluded that there are several phases in the structure of mechanically activated powders: pure aluminum, metal carbon clusters, amorphous carbon, aluminum oxide and carbide (Fig. 3b). Consequently the mechanical activation is accompanied by partial destruction of CNS and its chemical interaction with the matrix. The result of mechanical activation is the formation of new phases around the metal particles. Obviously during subsequent deformation and heat treatments such structures influence on the formation of grain boundaries and carbide substantially. By the method of local microanalysis it is also determined that the samples with the addition of stearic acid have heightened content of oxygen and carbon, especially in near-surface layers of individual metal particles.

Physical and mechanical, chemical, structural and other characteristics of CNS, used in this work, ONS cause its individual contribution to the final physical and mechanical properties of the resulting nanocomposites.

In Fig. 4 it is shown the values of conventional yield strength of aluminium matrix nanocomposites. The highest value of conventional yield strength corresponds to the nanocomposite aluminum-fullerene C₆₀.

According to the results of mechanical tests of nanocomposites based on copper there are the following examples, which have the best complex of mechanical properties:

The initial powder was obtained by mixing CNT, treated by film extraction, with copper powder. The mechanical characteristics of the sample: σₚ – 215 MPa; δ₀₂ – 113 MPa; δ – 41,8%; ψ – 38%.

The initial powder was obtained by wet mixing C₆₀ (concentration – 0,1 %) with copper powder in toluene. The mechanical characteristics of the sample: σₚ – 215 MPa; δ₀₂ – 105 MPa; δ – 48%; ψ – 65,7%.

It should be noted that on the scanning and transmission electron micrographs it is very difficult to detect the presence of carbon nanomaterials. Apparently carbon nanomaterials during the interaction with copper in the process of compacting and subsequent sintering tend to form copper covers on its surface, which are then compacted and completely cover up the surface of the carbon nanostructures. Another way to indirectly confirm the presence of carbon nanostructures is related to the conduct of local microanalysis.
In Fig. 5, in the selected area (spectrum 2 and 3) of micrograph there is a spread nanoscale structure. The research of the chemical composition of the material shows an increase of carbon content in the location of this structure relative to the average composition. It allows making the assumption about the presence of carbon nanomaterial in this structure.

Current researching of various systems trends an increase of theoretical researches with mathematical modeling methods. Computer researches of the electronic structure of composite metal matrix materials with the addition of carbon nanostructures have been performed in papers [19-21].

The results of paper [22] are the reason of researches the role of oxygen in the formation of bonds between CNT and the metal atoms. To explain the mechanism of bonding and the role of oxygen in metal matrix composites based on CNT theoretical researches of the electronic structure of copper-based composites was carried out in this paper. The influence of functionalization of single-layer carbon nanotubes by oxygen groups on the electronic structure and parameters of the bonds of copper-based composites based was made.

The analysis of results suggests that using CNT, surface of which is first modified by oxygen functional groups, for creation of composite cuprum matrix materials is very effective. Comparison of simulation results showed that carboxylation of CNT surface, which promotes the formation of Cu-C bonds, is the most effective. The interaction increased because of the inclusion an exchange mechanism between the electrons of Cu and C atoms in the presence of oxygen. This effect is confirmed by experimental researching that prove the significant role of oxygen.
on the surface between Cu and CNT [19].

In paper [21] the adsorption of fullerene molecules on the surface of the Cu (111) cluster is researched. It was carried out with the mathematical modeling by DFT in the local density approximation (LDA). Consequently there are conclusions about the nature of formed bonds. In the paper it is said that since the bond \( \text{C}_{60} \) and Cu (111) is accompanied by charge transfer, for which the electron correlation has the essential role, theoretical calculations of the bonds parameters are difficult. The chosen DFT approach does not allow taking full account of electron correlation and the use of more accurate models cannot be due to the large number of particles. Because of the difficult symmetry reliable experimental results are difficult to obtain for this complex. Therefore, theoretical researches were carried out in conjunction with experimental researches and conclusions about the reliability of the results were made by a good agreement between theory and experiment.

<table>
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<th>Spectrum</th>
<th>B stat</th>
<th>C</th>
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<th>Fe</th>
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<td>0.64</td>
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<td>0.83</td>
<td>84.51</td>
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Figure 5 – Tubular structure and chemical composition in the volume of compacted sample

The calculation results showed that the energy of each bond formed between \( \text{C}_{60} \) and Cu (111) is close to the value of 2.3 eV. Thus, without prior modification the energy of interaction Cu with \( \text{C}_{60} \) molecule is much higher than with CNT. According to the paper [21] the binding energy of single-layer CNT with an atom of copper without prior modification of the surface was about 0.5 eV, and after covalent functionalization by the carboxyl groups – about 2.5 eV. Therefore, it can be concluded that there is a sufficiently high chemical activity of fullerene, which does not require chemical pretreatment when added to copper.

There are other papers in which similar researches are performed for different metals. The interaction \( \text{C}_{60} \) with inert substrates (graphite, \( \text{SiO}_2 \), etc.) are characterized by the formation of a weak van der Waals bond. The interaction \( \text{C}_{60} \) with the metal substrate is characterized by the formation of ionic bonds of medium strength (Au, Ag, Cu), or a strong covalent bond, typical for Ni, Pt. The mechanisms of interaction monolayer of fullerenes with substrates Al (111) and (110) are of particular interest. According to the paper [23], this relation has medium strengths, which are covalent. There is unexpected fact that the bonds formed \( \text{C}_{60} \) with the substrate Al (111) are stronger than with Al (110). Initially it was supposed that since Al (110) has a greater number of open covers, its reactivity is higher, and thus bond \( \text{C}_{60} \) with Al (110) must be higher than that with Al (111). This fact is explained by the interaction 6 atoms of the fullerene hexagon facing to the substrate with 6 atoms of Al (111). In the case of Al (110) there is no such interaction because of the lower symmetry. Further researches have confirmed that the strength of the interaction \( \text{C}_{60} \) with metal substrates (111) depends on the symmetry and relative orientation of \( \text{C}_{60} \) and the substrate [24].

To understand the mechanisms of interaction carbon nanoparticles with an aluminum matrix quantum-chemical calculations of the interaction an atom of aluminum with the CNS and its fragments have been performed.

In terms of \( \text{C}_{60} \) it is shown that the possibility of formation of polar covalent \( \pi \)-bonds due to the overlap of valence 2p orbitals of carbon atoms with 3p orbital of an aluminum atom. Optimization of the complex showed the possibility of formation of one of the three equilibrium configurations (Fig. 6). One of these configurations corresponds to the location of aluminum atom on the axial between two hexagons of \( \text{C}_{60} \) (Fig. 6a), while the other – the location of aluminum atom in the center over the pentagonal face (Fig. 6b), and the third – the location of aluminum atom in the center over the hexagonal face of \( \text{C}_{60} \) (Fig. 6c).

Comparison of total energies of complexes indicates a preference for the configuration shown in Fig. 6a, which contradicts the experimental data in the paper [23]. The experimental results show that when depositing of a monolayer of fullerenes on an aluminum substrate, configuration presented at Fig. 6c is stable. This discrepancy of results can be explained by the fact that in the experiment the interaction fullerene with an aluminum substrate was considered. At the same time due to the higher symmetry of the hexagonal face at once six aluminum atoms come into the interaction with the carbon atoms, which leads to a decrease of the total energy of the system.
In equilibrium state the Al atom forms multiple covalent polar \( \pi \)-bond with the 23th and 22th carbon atoms (numbering according to Fig. 7a). The lengths of these bonds is about 2.5 Å. The interaction energy of Al-C\textsubscript{60} is about 0.97 eV (92 kJ/mol). The bonding under normal conditions leads to a decrease of the Gibbs energy: \( \Delta G = G_2 - G_1 \approx -85 \text{ kJ/mol} \). As the temperature increases, \( \Delta G \) decreases monotonically. It means a possible reaction in the conditions of milling and sintering powders. The enthalpy of formation of the complex Al-C\textsubscript{60} is negative and about -82 kJ/mol, i.e. complex formation reaction is exothermic.

In Fig. 7a the visualization of the highest occupied molecular spin-orbital (HOMO) of the complex Al-C\textsubscript{60} is shown. Parts of the orbitals with different characters are shown in different colors. The atoms are numbered according to Fig. 6b. Fig. 7a shows that the valence \( p \)-orbital of the aluminum atom, which participates in the formation of covalent polar bonds with the 10th and 8th carbon atoms, is making a significant contribution in the HOMO. The formation of bonds is accompanied by a modification of nonpolar \( \pi \)-bonds between the 10th and 9th, as well as between the 8th and 26th atoms, and by the redistribution of electron density from the less electronegative aluminum atom (electronegativity is 1.6) to the more electronegative carbon atoms (electronegativity is 2.6). Atomic charges calculated by Levdiniu are marked in Fig. 7b (using atomic units).

4. Conclusions
- The fullerenes has the greatest impact on increasing of conventional yield strength of NCM, than flaked graphite, carbon nanotubes, onions and superdispersed nanodiamonds are following.
- In the chosen conditions of mechanical activation flake graphite is reduced to nano-sized state and represents the clusters consisting of 7-10 graphene layers.
- The quantum-chemical modeling shows that aluminum atoms and carbon nanostructures are forming metalcarbon complexes with covalent bonds.
- In the process of mechanical activation part of the carbon nanostructures are undergoing destruction.
- The use of stearic acid as a grinding agent in the mechanical activation is reducing the size of CSR by 15-20 % and the sizes of aggregates by 20-30 %, which may be due to the formation of covalent bonds Al-C with the presence of oxygen.

References
Figure 7 – Model of the electronic structure of the complex Al-C60: 
a) visualization of the HOMO orbital; b) the atomic charges in atomic units, calculated by Levdinu


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