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Single-stage synthesis of a mixture of WC_{1-x} nanoparticles and a hybrid nanomaterial based on multi-wall carbon nanotubes with WC_{1-x} nanocoatings

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By the method of chemical vapor deposition of tungsten hexacarbonyl at atmospheric pressure in an argon flow has been used to obtain promising fillers for aluminum matrix composite materials in the form of a mixture of nanoparticles of non-stoichiometric cubic tungsten carbide (WC_{1-x}) and hybrid nanomaterials based on multi-walled carbon nanotubes decorated with nonstoichiometric cubic tungsten carbide. The influence of chemical vapor deposition (CVD) parameters on the morphology of samples was studied and the optimal synthesis conditions were selected. The structure and composition of the synthesized materials were studied by electron microscopy and X-ray phase analysis.

Keywords: multiwall carbon nanotubes, tungsten carbide, coatings, nanoparticles.

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The production of novel aluminum matrix composite materials (AMCMs) based on aluminum and its alloys with their high strength and enhanced performance parameters is a highly relevant task. The hardness, strength, and wear resistance of AMCMs are known to increase as a result of dispersion strengthening of aluminum with different ceramic fillers. Various nanoparticles (NPs), such as SiC [1], B_4C [2], and Al_2O_3 [3], have already been tested as fillers for AMCMs. Powder metallurgy techniques were used to inject and disperse NPs within the bulk of produced AMCMs. An improvement of physical and mechanical properties of AMCMs was noted. Considerable progress has been made in recent years in the production of AMCMs reinforced with multi-walled carbon nanotubes (MWCNTs). This was made possible by the studies of aluminum–MWCNT interaction processes, methods for MWCNT processing that is performed to achieve better dispersion, MWCNT breakdown in the course of processing, chemical reactions with the aluminum matrix on the MWCNT surface, and other processes [4]. At elevated temperatures, MWCNTs react chemically with aluminum, producing aluminum carbide (Al_4C_3) [5]. This has a negative effect on the physical and mechanical properties of AMCMs [6]. However, the authors of [6] have noted that nanodisperse Al_4C_3 exerts almost zero influence on the mechanical properties of a composite, while larger micrometer-sized grains impair its mechanical qualities considerably. It was proposed to suppress the adverse interaction of MWCNT surfaces with aluminum by applying metallic or ceramic coatings, which are wetted easily by aluminum, to them. It was demonstrated in [7] that copper NPs on a MWCNT surface may act as a protective interface and inhibit the reactions of growth of aluminum carbide, stabilizing its size within the nanometer range. Hybrid nanomaterials based on MWCNTs with SiC [8] and TiC [9,10] coatings have also been proposed to be used as reinforcing additives. A method for synthesis of a hybrid material based on MWCNTs with a non-stoichiometric tungsten carbide coating (WC_{1-x}/MWCNT) has been developed in our earlier study [11]. Synthesis was performed under a forevacuum pressure with tungsten hexacarbonyl $W(CO)_6$ (THC) used as a precursor. This hybrid material has been tested as a reinforcing filler in AMCMs [12,13]. It was found that the WC_{1-x} coating on a MWCNT surface subjected to high-temperature annealing at a temperature above 525°C reacts with the aluminum matrix, producing a WAl_{12} intermetallic phase. When the annealing temperature was raised to 600°C, the microhardness of composites decreased from 176 HV to 141 HV, while their Young's modulus dropped from 110 to 80 GPa. However, they still remained fairly high compared to the corresponding parameters of the initial AMCMs. It has also been noted in [14] that the formation of WAl_{12} may lead to a natural enhancement of microhardness and the Young's modulus (due to compression of Al). A new approach to improving the properties of AMCMs has been demonstrated in [15]. It consists in the introduction of a mixture of carbon nanofibers and SiC NPs into AMCMs. The tensile strength and Vickers hardness of composites were increased by 71 and 88%, respectively; thus, fibers and NPs used together in a single composite were found

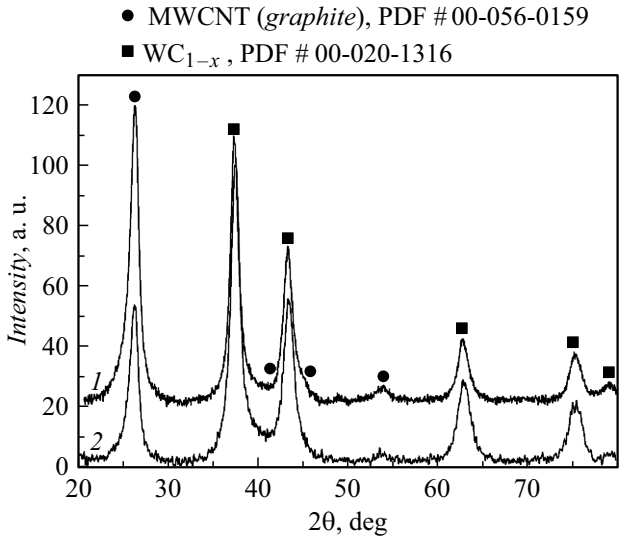

Figure 1. Diffraction patterns of samples Nos. 1 and 2 produced with a MWCNT:THC ratio of 1:7 (*1*) and 1:10 (*2*).

to produce a synergistic strengthening effect. Similar effects were observed when MWCNTs and SiC NPs or MWCNTs and TiC NPs were introduced into AMCM matrices [16]. Since different research groups are currently working on the development of new reinforcing fillers for AMCMs based on MWCNTs and ceramic NPs, we believe that the production of a novel reinforcing filler based on a mixture of WC_{1-x}/MWCNT and WC_{1-x} NPs is a relevant task. Thus, the aim of the present study is to develop a method for single-stage synthesis of a reinforcing filler for AMCMs in the form of a mixture of a WC_{1-x}/MWCNT hybrid nanomaterial and WC_{1-x} NPs and to examine the obtained filler.

MWCNTs were synthesized using the metal organic chemical vapor deposition (MOCVD) technique in accordance with the procedure outlined in [9]. A laboratory setup featuring a tube quartz reactor and a double-stage system of heating furnaces was developed for synthesis of a reinforcing filler for AMCMs in the form of a mixture of a WC_{1-x}/MWCNT hybrid material and WC_{1-x} NPs. A batch of MWCNTs 0.1 g in mass was introduced into a quartz cylinder insert 5 cm in length with a stainless-steel fine mesh at both ends. This insert was positioned at the center of the pyrolysis furnace zone and heated to 300°C. Meanwhile, the temperature in the evaporator furnace was raised to 140°C. A quartz boat containing 0.5–1.0 g of THC was then introduced into the evaporator furnace zone. The reactor ends were sealed tightly with teflon plugs with channels for argon inlet and outlet. An argon flow of 500 cm^3/min was set using an AALBORG GFS17 argon flow adjuster. THC vapor was carried with the flow of argon into the hot zone of the reaction furnace and underwent pyrolysis on the MWCNT surface. Depending on the reaction conditions, a coating or a coating and a powder of tungsten carbide NPs formed as a result. Gaseous pyrolysis products were removed from the reactor via a water seal. The coating deposition time varied from 60 to 90 min depending on the mass of THC in the quartz boat. Following cooling to room temperature, atmospheric air was admitted into the reactor, and the obtained material was retrieved.

X-ray phase analysis was carried out using a Shimadzu XRD-7000 powder diffractometer. Figure 1 presents the diffraction patterns of samples with an initial MWCNT:THC ratio of 1:7 (sample No. 1) and 1:10 (sample No. 2). It was found that the obtained samples contain a carbon nanotube phase and a non-stoichiometric WC_{1-x} tungsten carbide phase. The MWCNT surface coating may be identified as an ultradisperse phase of tungsten carbide WC_{1-x} $Fm3m$ (PDF # 00-020-1316) with lattice constant $a = 4.205$ Å and the hybrid material should be characterized as a material based on MWCNTs with their surface decorated with non-stoichiometric tungsten carbide NPs (WC_{1-x}/MWCNT). According to the Vegard law, the formula of tungsten carbide at this lattice constant is $WC_{0.47}$. The mean size of WC_{1-x} crystallites, which was calculated for peak (311) ($2\theta = 75°$) in the spherical particle approximation in accordance with the Scherrer formula

$$d = \frac{K\lambda}{\beta \cos\theta}, \qquad (1)$$

is ~ 8 nm for sample No. 1 and ~ 6 nm for sample No. 2. Here, d is the mean size of crystallites, K is the Scherrer constant, λ is the wavelength of X-ray radiation, β is the full width at half maximum of a reflection in radians, and θ is the diffraction angle.

The morphology of samples was examined with a Hitachi Regulus SU8100 scanning election microscope (SEM). It was found in the study of sample No. 1 (Fig. 2) that the WC_{1-x} coating on the MWCNT surface has a rough surface of a granular structure with grains 3.5–31 nm in size (Fig. 2, *c*).

Two fundamentally different types of coatings were noted in the investigation of various local regions of samples synthesized at a MWCNT:THC ratio no greater than 1:7. The first type is represented by disconnected drop-shaped WC_{1-x} NPs with their size ranging from 3 to 30 nm (Fig. 2, *b*), and the second type is continuous nanocoatings with a thickness greater than 30 nm (Figs. 2, *a* and *c*). The continuous nanocoating has a polycrystalline structure and consists of segmented grains that are characterized accurately (just as disconnected NPs). Same-type nanocoatings are normally observed within a single MWCNT bundle (the size of bundles may exceed 1 mm) and in adjacent bundles; the coating thickness and the NP size are also highly uniform. All this is indicative of a high homogeneity and uniformity of conditions established in the deposition process, which are preserved within regions that are much greater in volume than typical objects under study. When the MWCNT:THC ratio was raised from 1:7 to 1:10 (sample No. 2), an increase in thickness of the WC_{1-x} nanocoating was accompanied by the growth of WC_{1-x} NPs on the MWCNT surface in the form of separate

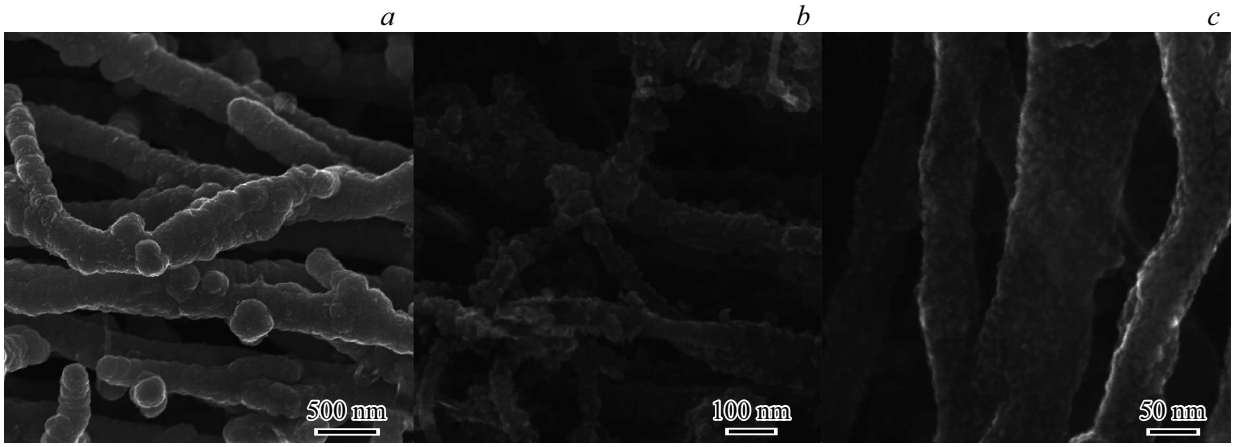

Figure 2. SEM images of the sample of a WC_{1-x}/MWCNT hybrid material (sample No. 1).

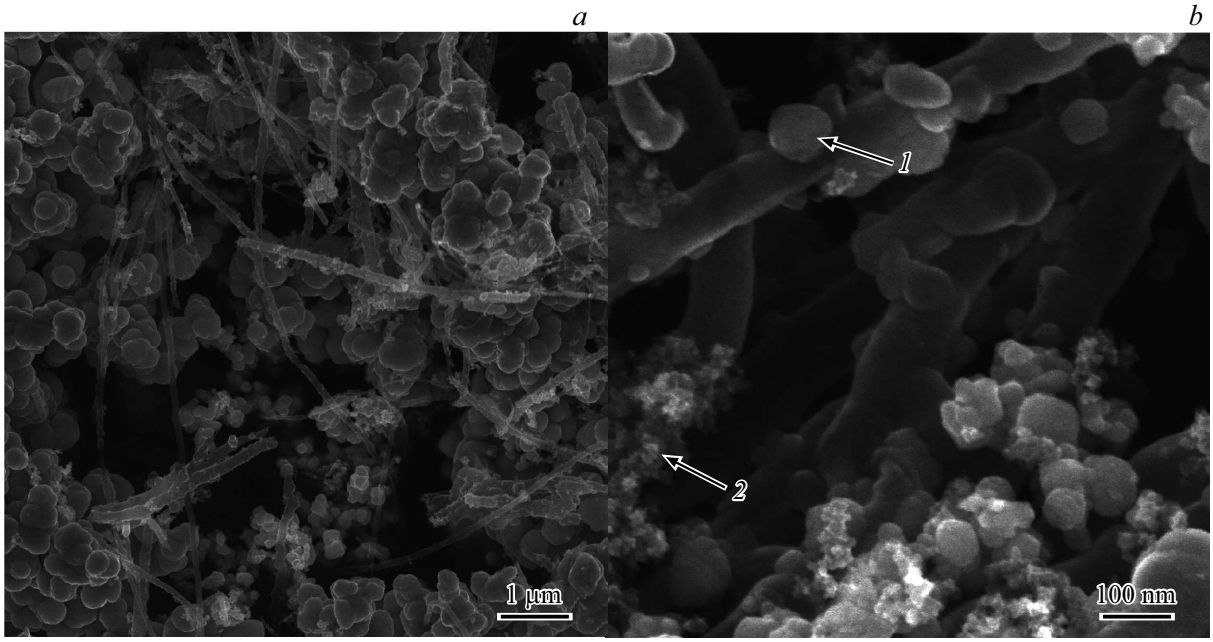

Figure 3. SEM images of samples of a mixture of WC_{1-x}/MWCNT and WC_{1-x} NPs (sample No. 2).

crystallites (numbered *1* in Fig. 3, *b*) and dendrite NP assemblies (numbered *2* in Fig. 3, *b*) and the formation of a powder of WC_{1-x} in the form of spherical grains ranging in size from several tens of nanometers to $0.5\,\mu$m (Fig. 3, *a*).

Thus, it was found that hybrid materials with different morphologies of a tungsten carbide coating, which vary from NPs distributed chaotically over the MWCNT surface and continuous granular WC_{1-x} coatings to a mixture of a WC_{1-x}/MWCNT hybrid material and a WC_{1-x} micropowder, may be produced by adjusting the conditions of synthesis of a WC_{1-x}/MWCNT hybrid nanomaterial under atmospheric pressure in a flow of argon with THC used as a precursor. The obtained mixtures are promising reinforcing fillers for aluminum matrix composite materials.

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Conflict of interest

The authors declare that they have no conflict of interest.

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