The influence of hybrid nanostructures TiC/MWCNT concentration on the properties of bulk composites based on aluminum alloy

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Abstract. In this paper, we present the results of producing bulk composite materials based on aluminum alloy AlMg2, hardened 0.1 -5 wt.% MWCNT and decorated with TiC nanoparticles by powder metallurgy method. Powder and bulk composites were characterized by electron microscopy, X-ray diffraction, kinetic indentation and compression tests. The influence of hybrid nanostructures TiC/MWCNT concentration on the properties of bulk composites was studied.

1. Introduction
Increasing strength of composites based on aluminum and its alloys is possible by improving the interfacial load transfer through the in situ of Al4C3 formation at the matrix-filler interface [1-3]. However, the problem of this approach is associated with the difficulty of degree reaction control of the Al4C3 phase formation, as well as its tendency to hydrolysis [4].

Another way is a MWCNTs pre-processing with formation the ceramic nanoparticles or coatings on the surface [5-7], which can be used as a boundary phases with the developed surface to improve the interaction with the matrix material [8].

Currently, the main methods of hybrid materials synthesis are electrochemical reduction of metal salts using a sol-gel process, metalorganic chemical vapour deposition (MOCVD-method) and physical deposition (electron beam deposition, thermal spraying, etc.). Among these methods, a special place is taken the MOCVD-method, in which metal-containing nanoparticles are deposited on the MWCNT surface at pyrolysis of metalorganic compounds vapors (MOC) as a result of chemical reactions on the MWCNT surface. The advantages of this method over others are that there is a large selection of volatile MOC. This method operates at medium temperatures (400°C – 900°C) and volatile reaction products are removed from the deposition zone of the coating, thus achieving a high deposition rate and regulation of the coating composition. In this regard, this method was used to form metal-containing nanostructured particles and coatings based on titanium carbide on the MWCNT surface.
2. Methods and equipment
The process of synthesis of bulk composites based on aluminum alloy consisted of three stages (figure 1).

In the first stage, by MOCVD processing of initial MWCNTs, the TiC nanoparticles were deposited on their surface. At the second stage, the joint mechanical processing of the initial granules of aluminum alloy and MWCNT-hybrid filler in the planetary mill was carried out. The initial charge was globular granules with a diameter of 1-2 mm made of aluminum alloy AMg2 with the addition of 0.1-5 wt.% of MWCNTs decorated with the nanoparticles of TiC [9]. Mechanical treatment of the initial charge was carried out in the planetary ball mill FRITSCH PULVERISETTE 6 using surfactants (stearic acid 0.8 wt.%). For milling, we used steel balls (8 mm in diameter) at a ratio of the mass of the loaded components to the mass of the milling media 1:15. The processing was carried out at a speed of 600 rpm for 6 hours. Sintering under pressure of the obtained powders was the third stage of synthesis of bulk composites. Sintering under pressure is performed at a temperature of 450°C.

Characterization of structure and properties of powder and consolidated composites was performed by scanning electron microscopy (ZEISS ULTRA PLUS), particle size (MICROSIZER 201) and X-ray phase analysis (BRUKER D8 ADVANCE), hydrostatic weighting, kinematic indentation (CSM INSTRUMENTS MICRO COMBI TESTER) and mechanical compression tests (TIME GROUP WDW-100E).

3. Results and discussion
The study of synthesized composite powders by SEM shows that the powder particles have an irregular shape characteristic of aluminum alloy powders after processing in a planetary mill. At higher magnification on the surface of the powder particles is visible nanoscale geometry, formed as a result of destruction under the influence of milling media (figure 2).

The study of the fractography of the powder particles surface suggests the intercrystalline nature of the destruction characteristic of nanocrystalline materials. In this case, the crystallite size of the powder particles, according to SEM, is about 50-80 nm. SEM of powder mixes with 5 wt.% of the filler allowed to reveal the features of interaction of MWCNT-hybrid structures with matrix material during processing in the planetary mill. In particular, it was found that, in contrast to the initial MWCNTs, for decorated ones with ceramic particles, sticking to the surface of MWCNT-hybrid structures of plastic matrix material is characteristic. That is, already at the stage of mechanical processing, decorating MWCNTs with ceramic particles improves the adhesion interaction of the filler with the matrix material.
Analysis of the particle size distribution of the synthesized powders shows that the average particle size of the forming powders at the increasing of filler concentration from 0.1 to 5 wt.% is decreases from 60 to 45 microns.

X-ray phase analysis of synthesized composite powders (figure 3a) show the absence of new phases formation during machining in the planetary mill. In this case, at the X-ray diagrams of composite powders with a mass fraction of the filler 0.1 and 1 wt.% recorded only X-ray diffraction peaks of the matrix material. On the X-ray diagram of powder with 5 wt.% the presence of low intensity peaks corresponding to TiC was marked. It was also note the broadening of diffraction peaks of the matrix material after processing in the planetary mill, which indicates a decrease in the size of the crystallites in the machining process caused by the intense plastic impact of milling media on the processed material.

According to the Scherrer formula based on the X-ray data the size of crystallites is calculated. The results show that the synthesized composite powders have a nanocrystalline structure. As the filler concentration increases, the average crystallite size decreases from 77 to 70 nm. The crystal lattice deformation increases from 0.299 to 0.324% with the filler fraction.

Kinetic indentation of the synthesized powders particles shows that at the increasing of filler content from 0.1 to 5 wt.% the microhardness is enhanced from 222 to 254 HV. It should be noted that the main contribution to the increase in microhardness is not the filler, but the reduction of the matrix material grain size (Hall-Petch effect).

X-ray diagrams of powder and bulk composites filled with 0.1 and 1 wt.% have qualitatively similar character. It is possible to note a decrease in the half-width of the X-ray diffraction peaks of
bulk composites compared to powder ones. That is, isothermal exposure at 450°C leads to an increase in the size of crystallites, which levels the effect of intense plastic deformation.

At X-ray diagrams of bulk composites with the filler mass fraction 0.1 and 1 wt.% recorded only peaks of X-ray diffraction of the matrix material. While for samples containing 5 wt.% TiC/MWCNT the presence of peaks corresponding to Al₄C₃ was noted.

Measurements of the consolidated samples density using the hydrostatic weighing method showed that consolidated samples have a residual porosity of not more than 3%. During the compression tests, it was found that the obtained bulk samples have a high yield strength (figure 4).

Analysis of the results shows that the increase in filler concentration from 0.1 to 5 wt.% contributes to the growth of the contingent yield point at compression from 600 to 770 MPa. However, the increase in the mass fraction of the filler reduces the plasticity of bulk composites. For example, composite materials with 5 wt.% TiC/MWCNT were brittle destroyed without formation of sites fluidity. Another important point is that the increase of filler proportion from 0.1 to 0.3 wt.% leads to a local reduction of 5% of the nominal yield strength. It should also be noted that the resulting composite materials have a yield strength of ~7.5 times higher than the materials obtained by the consolidation of the initial granules of the matrix alloy.

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