Synthesis and characterization of new hybrid material based on MWCNTs decorated with titanium carbide nanocoatings with different morphology as reinforcing components of alloys

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Abstract. New hybrid nanomaterials based on multi-walled carbon nanotubes (MWCNTs) and nanoscale coatings of titanium carbide were synthesized using the MOCVD method. Titanocene dichloride was used as a precursor. It is established that the deposited coating depends on the initial mass ratio of MWCNTs and titanocene dichloride. Four characteristic morphological types of the obtained TiC/MWCNTs hybrid nanomaterials were found. A high efficacy of using synthesized hybrid materials TiC/MWCNTs as reinforcing fillers in aluminum matrix alloys has been found.

1. Introduction
Synthesis of new hybrid materials based on multiwalled carbon nanotubes (MWCNTs) and nanoscale coatings is a very promising direction of materials research, since such objects can be used as reinforcing fillers in various alloys and composites. The most relevant for such studies are hybrid materials based on MWCNTs and nanoscale coatings of titanium carbide. Such objects, due to the combination of their expected properties, can greatly improve the strength characteristics of various alloys and composites, in particular aluminum-based alloys.

2. Synthesis
To create such hybrid materials, the initial MWCNTs were first synthesized, and then the nanocoating coatings of titanium carbide were deposited on their surface by the MOCVD method. Synthesis of the source MWCNTs was carried out by MOCVD method also and is described in detail in [1]. Ferrocene and toluene were used as precursors. The ferrocene evaporator furnace temperature was 95 °C. The temperature of pyrolysis furnace was 825 °C. Flow rate of argon was 450 cm³/min.
Deposition of titanium carbide coatings was carried out in vacuum glass reactor. The synthesis procedure is similar to that used in [2]. Cp₂TiCl₂ and source MWCNTs were used as precursors and were placed into reactor before synthesis. Then reactor was heated up to 900 °C. Various parameters of synthesis have been used to study the various deposition modes of coatings. Thus, the initial mass ratio of MWCNTs and Cp₂TiCl₂ was 1:2, 1:3, 1:4, 1:5 and 1:6 respectively.
3. Analysis

3.1. XRD
Synthesized hybrid materials were analyzed by various physicochemical methods. With the help of powder x-ray diffractometer Bruker D8 Discover, it is established that the samples contain only two phases – carbon nanotubes and a phase of titanium carbide (Figure 1). Thus it is unequivocally confirmed that the synthesized material is the composite of titanium carbide and MWCNTs without any impurities.

![Figure 1. XRD pattern of synthesized hybrid material based on MWCNTs and nanoscale coatings of titanium carbide.](image)

3.2. Thermogravimetry
The thermogravimetry method on thermoweights Perkin Elmer Pyris 6 TGA helped to obtain the curves of mass loss and mass loss rate during air oxidation of samples of hybrid materials TiC/MWCNTs with different initial ratio of synthesis precursors.

![Figure 2. The curves of mass loss (a) and mass loss rate (b) during air oxidation of samples of hybrid materials TiC/MWCNTs with 1:2 initial ratio of MWCNTs and Cp₂TiCl₂ (green), 1:4 initial ratio of MWCNTs and Cp₂TiCl₂ (blue) and pristine MWCNTs (red).](image)

Using TGA, it was found that the oxidation of new hybrid materials starts at temperatures > 500 °C. The maximum oxidation rate is achieved at higher temperatures than for the pristine MWCNTs, which is due to the diffusion of oxygen to the surface of MWCNTs coated with titanium carbide. The data obtained suggest an increase in the thermo-oxidative stability of the pristine MWCNTs when they are modified with titanium carbide.

3.3. SEM
With the help of a scanning electron microscope Carl Zeiss SUPRA 50 VP, it was found several morphological types of a new hybrid material, depending on the initial ratio of MWCNTs and Cp₂TiCl₂. Thus, the first type is the titanium carbide coating deposited on the MWCNTs surface in the form of thin films. The thickness of continuous coatings is from 10 to 30 nanometers, depending on the features of the structure of the MWCNTs surface (Figure 3, a). Another detected morphological
type is TiC/MWCNTs in the form of columnar structures with an advanced surface of titanium carbide. In length, such structures reach 300 nm at a thickness of about 40 nm (Figure 3, b). The third type of object is the so-called whiskers – a kind of a crystal with a ratio of length to diameter > 100. On average, the cross section of such whiskers is about 300 nm, and the length is of the order of hundreds of microns (Figure 3, c). Finally, the fourth type of discovered objects is the so-called mesocrystals of titanium carbide with classical outer shape. Such crystals are uniformly distributed throughout the sample volume and are rather firmly fixed both on the beams and on single MWCNTs (Figure 3, d).

Figure 3. SEM micrographs of hybrid materials synthesized with different initial precursor ratios.

3.4. HRTEM
The structure of the hybrid material TiC/MWCNTs was studied using high-resolution transmission electron microscope Carl Zeiss LIBRA 200MC. Due to the fact that the titanium carbide coating thickness on the MWCNT surface with an initial ratio of MCNT and titanocene dichloride more than 1:3 does not allow to investigate such hybrids using HRTEM, was carried out an analysis of hybrid materials synthesized with an initial ratio of MWCNTs and titanocene dichloride less than 1:3.

Figure 4. HRTEM micrograph of hybrid material synthesized with an initial ratio of MWCNTs and titanocene dichloride less than 1:3.

In fig. 4 shown an image of a section of the hybrid material TiC/MWCNTs. It is seen that the surface of the MWCNT is fully coated with a layer of titanium carbide. Also in this image it shows the presence of slight thickening of coating. HRTEM studies of samples with other initial mass ratios of
precursors made it possible to establish that with an increase in the mass fraction of titanocene dichloride, such thickenings transform into sprouts, which are shown in Fig. 3 (b).

4. Additives to alloys
As a result of this study different types of new hybrid material TiC/MWCNTs synthesized using the MOCVD method were discovered, which can be tested as fillers in various aluminium matrix composites to improve their strength properties.

The method of mechanical synthesis in a planetary mill [3] obtained composite powders of the system AlMg2 + 0.05 wt.% TiC/MWCNT (initial ratio 1:2). Mechanical treatment of the initial mixture was conducted in a planetary mill Activator-4M using surface-active materials (stearic acid 0.3 wt.%).

Milling was conducted using steel balls 14 mm in diameter at the ratio of mixture components to milling balls 1:5. Mechanical synthesis was conducted at rotation rate 700 rpm during 6 hours. Using hot extrusion at a temperature of 450° C, the obtained composite powder was consolidated. Tests of the obtained bulk composite materials for compression showed an increase in the conditional yield strength, which amounted to 450 MPa. At the same time, as for composite materials obtained under similar conditions and strengthened with 0.05 wt.% of the original MWCNTs, the conventional yield strength was 390 MPa.

Thus, the presented results confirm the efficiency of using hybrid carbon nanostructures (even at low concentrations) as fillers for aluminum-matrix composites.

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