Morphology and phase composition of hybrid powders based on aluminum, synthesized for a gas-dynamic spraying of coatings by milling

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Abstract. Hybrid powders of the AlMg$_2$ + 1 wt % TiC/MWNT + 10–50 wt % Al$_2$O$_3$ system were obtained using the method of mechanical processing in a planetary ball mill. The powders were characterized using the methods of scanning electron microscopy, particle size distribution testing and X-ray analysis. It is shown that an increase in the content of Al$_2$O$_3$ particles from 10 to 50 wt % leads to a decrease in the average particle size of the synthesized powder from 49 to 16 μm, respectively. The proportion of particles smaller than 5 μm, depending on the concentration of Al$_2$O$_3$, varies in the range of 1.2–15.1%. At the same time, the size of the matrix material crystallites decreases from 58 and 52 nm, respectively. The resulting hybrid powder can be used to create functional coatings using cold gas-dynamic spraying.

1. Introduction
At present, both in the Russian Federation and abroad, intensive studies of the structure-phase composition and functional properties of coatings obtained by gas-dynamic spraying are carried out. The diversity of the research and the results obtained can be judged at least by detailed reviews [1–4], most of which is occupied by the development of new powder materials for the synthesis of coatings with an increased complex of properties.

Currently, the possibilities of improving the properties of coatings due to the introduction of ceramic particles are limited or even exhausted. Therefore, it is important to conduct research on the synthesis and study of the properties of hybrid coatings with two or more types of reinforcing additives. In this case, the most promising is the creation of coatings with the nanocrystalline structure of a matrix material that simultaneously contains nano- and micro-sized reinforcing particles.

The creation of hybrid powders is possible through the introduction of reinforcing particles into the matrix material using the method of mechanical synthesis in high-energy ball mills. In [5], a significant increase (more than two times) in the tribological properties of coatings obtained by surfacing babbit powders modified with carbon nanostructures additives was shown.

At the same time, promising carbon nanostructures that can be used as reinforcing nanoparticles should include multiwalled carbon nanotubes (MWCNTs) decorated with TiC coating. Confirmation of the promise of using TiC is the positive experience of creating bulk aluminum matrix composites strengthened with nano- and micro-sized TiC additives, which made it possible to significantly increase tribological properties [6].

However, the gas-dynamic spraying of powders with a particle size of less than 2 μm is difficult due to their inhibition in the compressed layer, which occurs when an ultrasonic gas stream flows onto an
obstacle. In addition, when accelerating particles of a powder in a gas stream, there is a strong variation in velocity for particles of different sizes, while the nanoscale fraction can scatter without falling into the coating. Therefore, the use of polydisperse powder, which is a mechanical mixture of nano- and micro-sized particles, for gas-dynamic spraying seems to be unpromising. For the formation of hybrid coatings containing, in addition to micro-sized nanoscale particles, it is necessary to use powder in the form of a mechanical mixture consisting of agglomerates of complex composition and ceramic particles. Use for gas-dynamic spraying of powders having such a structure, allows to obtain hybrid coatings with a uniform structure and a high level of mechanical properties [7, 8]. Since the presence of nanoscale particles increases the mechanical properties of the matrix material, increasing the strength of fixing in the matrix of micro-sized ceramic particles. At the same time, the plasticity of the particles of the matrix material remains sufficient for the effective formation of a coating with a low porosity [9].

2. Research methods and equipment
Mechanical synthesis of the powder was carried out in two steps. As the matrix material, granules of aluminum alloy AlMg\textsubscript{2} obtained by spraying the melt were used. As reinforcing particles, we use multi-walled carbon nanotubes decorated with TiC particles. The weight fraction of TiC/MWCNT was 1 wt %. The mechanical treatment of the raw materials was carried out in a FRITSCH PULVERISETTE 6 planetary ball mill with the use of surfactants [10]. Next, α-Al\textsubscript{2}O\textsubscript{3} (n = 10, 30, and 50 wt %) with an average particle size of 18 μm was added to the obtained nanocomposite powder and mechanical processing was continued.

The study of the morphology of the composite powder particles was performed using a Quanta 200-3D scanning electron microscope. The granulometric composition of the obtained powders was determined on a Microsizer-201C instrument. Studies of the structural and phase composition were performed using a D8 ADVANCE X-ray diffractometer. The size of the matrix material crystallite was calculated using the Selyakov-Scherrer formula. The volume-averaged crystallite sizes were calculated on the assumption of their spherical shape.

3. Results
Figure 1 shows the SEM images of composite powders based on the AlMg\textsubscript{2} alloy obtained after the first step. From figure 1 it can be seen that the particles of the obtained powders have sizes varying in a wide range of 5–100 μm with an average particle size of d\textsubscript{50} = 53 μm. Particles have an irregular shape with a developed surface.

![Figure 1. SEM images characterizing the morphology of the powder particles.](image)

The study of the surface of the powder particles using a scanning electron microscope shows a small amount of reinforcing particles on their surface. The length of the reinforcing particles visible on the powder surface was ~ 600 nm (see figure 1, indicated by the arrow). A small amount of reinforcing particles on the surface is due to the peculiarities of the formation of powder particles under the conditions of mechanical processing in a ball mill. In the process of mechanical synthesis, a significant part of the reinforcement may not be on the surface, but inside the agglomerates based on the matrix.
material. This can protect them from destruction under high-energy effects of grinding bodies during mechanical processing.

The powder obtained after the second step was a mechanical mixture consisting of agglomerates of complex composition and micro-sized ceramic particles. Agglomerates are particles of a nanocrystalline matrix material containing TiC/MWNTs with micro- and nano-sized Al$_2$O$_3$ particles embedded in them, as well as on the surface. The study of the particle size distribution of mechanically synthesized powders of different composition shows that an increase in the content of ceramic particles from 10 to 50 wt % leads to a decrease in the average particle size of the synthesized powder from 49 to 16 μm, respectively. At the same time, the proportion of particles with a size of less than 5 μm, gas-dynamic spraying of whose is difficult, varies depending on the concentration of Al$_2$O$_3$ in the range of 1.2–15.1%.

The results of X-ray phase analysis of the original matrix material show the presence of only peaks of aluminum. The X-ray diffraction patterns of the reinforcement were recorded with Bragg diffraction peaks corresponding to MWCNT and TiC. According to X-ray diffraction data, the phase composition of the composite powder is similar to the original AlMg$_2$ matrix alloy. Also noted the absence of peaks corresponding to the reinforcement. The broadening of aluminum peaks is associated with a decrease in the size of the structure of the material due to severe plastic deformation of particles when exposed to grinding bodies. The results of the X-ray phase analysis of the powder obtained at the second step are shown in figure 2. Analysis of the data obtained shows that diffraction patterns have a qualitatively similar character. The presence of peaks corresponding to aluminum and Al$_2$O$_3$ is noted. Moreover, the intensity of Al$_2$O$_3$ peaks increases with an increase in its share in the charge. The calculation of the crystallite size, performed for the powders obtained both in the first and second steps using the Selyakov-Scherrer dependence, shows that the nanocrystalline structure corresponds to the matrix material. At the first step, the crystallite size of the AlMg$_2$ + 1 wt % TiC/MWCNT composite powder is 68 nm. The introduction of 10–50 wt % Al$_2$O$_3$ into the powder mixture and the subsequent processing in a planetary mill lead to a decrease in the crystallite size to 58 and 52 nm, respectively.

**Figure 2.** X-ray diffractometry results of mechanically synthesized powders.

Thus, powder mixtures AlMg$_2$ + TiC/MWNT + Al$_2$O$_3$ were synthesized by the method of mechanical processing in a spherical planetary mill. The resulting composite powder will be used to create coatings using cold gas-dynamic spraying.

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