Development of aluminum-based composite with two reinforcing modifiers (TiC/Ni, CNTs/Ni) with improved mechanical properties

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Abstract. The main direction in obtaining metal-matrix composites (MMCs) with a multilevel hierarchical structure is the development of new approaches to the creation of materials with two or more reinforcing modifiers, which makes it possible to improve a whole range of functional properties and, at the same time, reduce the total cost of the material. Carbon nanotubes and carbide particles additives can significantly improve the strength properties of aluminum and its alloys. In this work, the possibility of directed control of the composition, the structure and properties of composites was shown, using the methods of powder metallurgy and surface modification. As a result of the study, aluminum-based MMCs reinforced with carbide nanoparticles and carbon nanotubes (CNTs) with a Ni-plated surface were synthesized. As a result, it was shown that the combined use of two reinforcing phases makes it possible to diminish their negative qualities in the bulk of the metal and obtain a composite material with high strength properties while maintaining plasticity.
Keywords: composite materials, carbon nanotubes, ceramic nanoparticles, aluminum, mechanical properties

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Introduction

The important direction in obtaining new metal matrix composites (MMCs) is the development of approaches to the selection of strengthening additives. This includes identifying relationships between the properties of the resulting material and the composition, concentration and morphology of the introduced additives; creation and search for new available and cheap additives; establishing algorithms for MMC properties modeling. Addition of CNTs and TiC particles can significantly improve the strength properties of metal matrix composites [1–3]. Two trends can be distinguished in modern works on the topic of MMCs:

a) optimization of MMC properties by using nanosized modifiers (less than 100 nm) instead of microsized fillers (that are usually less than 50 μm). It is shown that such a substitution makes it possible to significantly improve the fracture toughness, viscosity of the material, and resistance to abrasive wear without loss of strength [4–6];

b) creation of hybrid composites with two or more reinforcing modifiers, which makes it possible to improve a whole range of properties and at the same time to reduce the total cost of the material [7–10].

An analysis of the conditions for obtaining MMC makes it possible to identify problems that need to be solved to get a material with improved properties:

1) the need to ensure good wettability of the hardening dispersed phase in order to prevent agglomeration of ceramic particles and uneven distribution of particles in the volume of the metal composite. One of the effective methods to solve this problem is the modification of the surface of the dispersed ceramic phase with metal structures [11,12];

2) the need to control the chemical reactions between the components of the composite. Under high pressure and high temperature, a chemical reaction between carbide particles and a metal matrix is possible, which significantly affects the properties of the composite [13]. This leads to embrittlement of the resulting composite and deterioration of the strength properties and ductility of aluminum composites;

3) ensuring uniform distribution of the reinforcing filler [14].

It has been repeatedly noted that the main technological problems in the synthesis of hybrid composite materials containing carbon nanotubes (CNTs) are the distribution of the strengthening phase in the composite bulk, the strength of its adhesion to the matrix, chemical and structural stability of carbon ordered structures within the composite. These problems are solved by the authors in various ways, mainly at the stage of preparing a composite powder [15–20].

To obtain hybrid CNT-containing composites (titanium carbide and carbon nanotubes), we used powder metallurgy methods to create nanocomposites of the system aluminum - carbon and carbide nanostructures; nickelized CNTs; cold pressing and sintering at temperatures below the melting point of aluminium. Hot pressing was not used, since high temperature revokes the advantages achieved at the mixing stage. The formation of aluminum carbide adversely affects the strength of aluminum matrix materials [21]. In our work, to eliminate this problem, we introduced into the aluminum matrix a dispersed phase (CNTs and carbide particles) protected by a metal shell (nickel).

Materials and methods

Ni plating of the dispersed reinforcing phase (DRP) (CNTs and TiC particles) for the introduction into the Al matrix. A portion of catalyzed (i.e. pretreated with $SnCl_2$ and $PdCl_2$ solutions) DRP is added to the $NiCl_2$ solution at 80 °C with constant stirring. To the resulting suspension, $NaH_2PO_2 \cdot H_2O$ was added up to a concentration of 18 g/l in the final solution. After 30 minutes of stirring, the resulting solution was centrifuged, the DRP precipitate is separated, washed with water and centrifuged. The resulting precipitate of Ni-plated DRP is dried in an oven for 1-2 h at 105 °C. Treatment of TiC particles with $SnCl_2$ solution increases the adsorption of Pd^{2+} ions at the next activation step. Ni is reduced by Pd and attached to the original TiC surface, forming a Ni layer [22].

Production of bulk Al matrix composites containing DRP. ASP-50 Al particles were mixed with DRP (CNTs) in the following Al:CNT: 99.9:0.1; 99:1; 97:3; 95:5.

ASP-50 Al particles were mixed with DRP (CNTs and TiC) in the following Al:CNT:carbide ratios: 98.9:0.1:1. The components were mixed on a planetary ball mill PM 100 CM.

DRP was introduced in one stage - the components were weighed and then mixed in one

run with simultaneous introduction. Such a relatively mild mode of DRP introducing into the dispersed Al phase was chosen due to the high plasticity of Al, as well as the in order to avoid mechanical activation of chemical reactions between Al and the DRP material, which was repeatedly described when trying to introduce metallic Ni or its compounds into dispersed Al.

The 3 g sample was placed in a collapsible mold with a diameter of 20 mm, after which compaction was carried out, for which the mold was placed in a MEGA PRS15 press and a load of 12 tons was applied to the plunger. After that, the sample was kept under load for 15 minutes. The compacted billet was placed in a quartz reactor, which was placed in an LF-50/500-1200 tube furnace and sintered at 600 °C for 1 h in H_2 atmosphere. The sintered workpiece was pressed using a SOROKIN 7.75 pneumohydraulic press under a load of 50 tons for 30 minutes. The preform transferred from the mold into a quartz reactor, which was placed in an LF-50/500-1200 tube furnace and sintered at 600 °C for 1 h in H_2 atmosphere.

The samples were studied by electron microscopy, their phase composition and mechanical properties were studied.

Mechanical tests. Taking into account the dimensions of the Al-matrix composites synthesized by the powder metallurgy, a mechanical testing technique was developed, equipment for testing samples was made, and the geometry of flat samples for static and cyclic tests was selected.

The test blades were made on an ARTA 123 PRO electroerosive machine of LLC NPK Delta-Test.

For mechanical testing, we used a flat double-sided blade with a thickness of ≤ 1.8 mm with a width and length of the working part of 2 and 5 mm, respectively. The width of the sample heads is 6 mm, the height of the working part of the head, which provides adhesion to the testing machine clamps, is 2 mm.

Finished blades were transferred to the testing machine AG-50kNXD (Shimadzu). The blades were attached to a specially made fixture for testing small-sized samples, and then they were uniaxially loaded until the complete destruction of the blade of the studied MMC sample.

Results and discussion
Production of a metallic composite with two hardening modifiers. For dispersion-strengthened MMCs, the processes occurring at the boundary between the metal matrix and the dispersed strengthening phase are especially critical. This is because the material combines substances with radically different chemical and physical properties. One of the problems is the strong difference in the thermal expansion coefficients of the metal and DRP. To avoid this problem, we selected a shell for DRP, which would have a CTE average between the CTEs of the matrix and of DRP. Thus, stress unload occurred at the matrix-DRP interface, and the strength characteristics of the material would remain constant over a wider temperature range.

At the stage of preparing DRPs (CNTs and TiC particles), Ni plating was performed before introduction into an aluminum matrix. The microphotographs show the Al powder particles size of 50 μm, the size of TiC particles after Ni plating does not exceed 200 nm, the CNT particles length after Ni plating does not exceed 5 μm (Fig. 1).

Nickel-coated samples of CNTs and titanium carbide particles were analyzed by X-ray phase analysis (Fig. 2). Peaks characteristic of carbon, titanium carbide and nickel were found in the spectra of the samples. The absence of a clear nickel peak in the TiC/Ni samples can be explained by the amorphized state of the Ni shell [23].
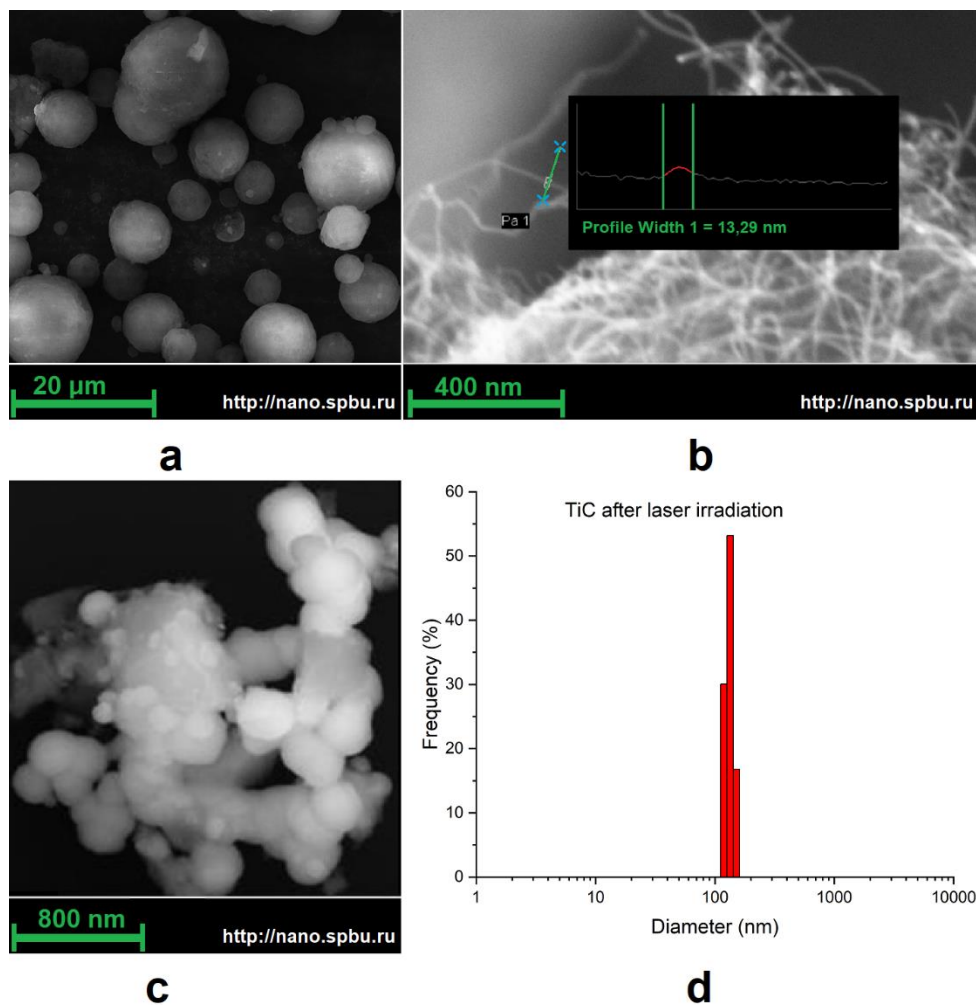
Fig. 1. Micrographs of Al particles and particle size distribution TiC:
(a) ASP-50 aluminum particles after sieving; (b) Taunit CNTs after Ni plating;
(c) TiC particles (80-150 nm) after Ni plating; (d) particle size distribution TiC (PSD)
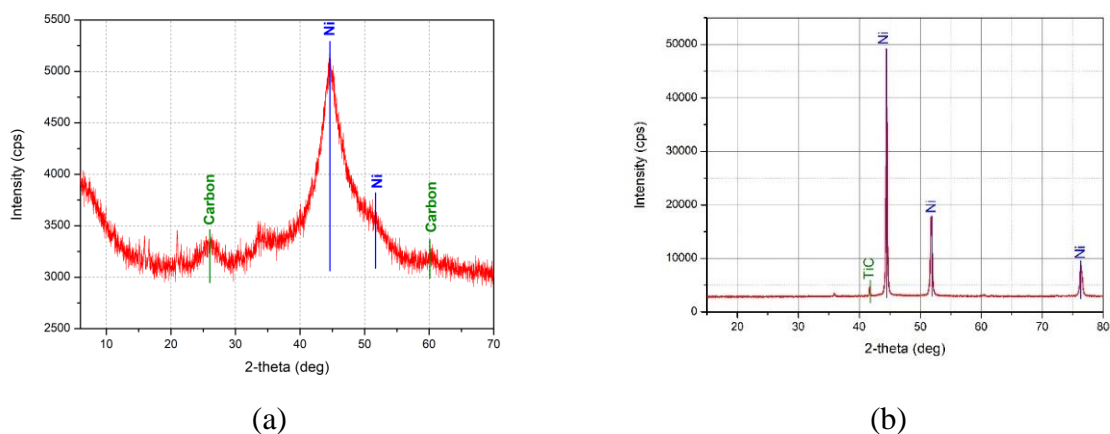

Fig. 2. XRD patterns of DRPs after Ni plating:
(a) CNT; (b) TiC after Ni deposition and Pd activation

To obtain samples with minimal porosity, they were subjected to a multistage pressing–sintering treatment. Hot pressing was not applied because of the undesired aluminum carbide formation and, as a result, a deterioration in mechanical properties. The pressing and sintering modes were optimized. When initially high loads were applied to the sample, skipping compaction led to elastic depressurization, with the formation of cracks and gas pockets.

The modes of pressing and sintering chosen by us, as well as nickel plating of nanotubes and titanium carbide, made it possible to avoid the formation of aluminum carbide at the metal-ceramic interface and, as a result, the deterioration of the mechanical properties of the samples. Similar processes began to occur at temperatures close to the aluminum matrix melting, or above it (700 ºC).

Thus, a pressing and sintering technique was developed to provide a monolithic metal matrix with included DRP. This is confirmed by the microphotographs below. The micrographs (Figs. 3,4) show a sample of a CNTs and TiC containing MMC. No CNTs were found on the sample surface. To detect them in the bulk sample, a cleavage of the sample face was made.

As can be seen from the micrograph, the Al particles are significantly deformed and form a densely compacted material. The material density is sufficient for the Al grain destruction during cleavage. Also on the sample cleavage, CNTs pressed into the matrix are clearly visible. The CNTs are not destroyed, they are located at intervals, one of the CNT ends is immersed in an MMC array. Based on these micrographs, we can state that the CNTs are embedded in an array of Al-matrix material. TiC particles are also visible on the cleavage. The DRP does not form agglomerates but is present as particles uniformly located in the Al matrix bulk. The homogeneity of the particles distribution with different elemental compositions was confirmed by additional studies.
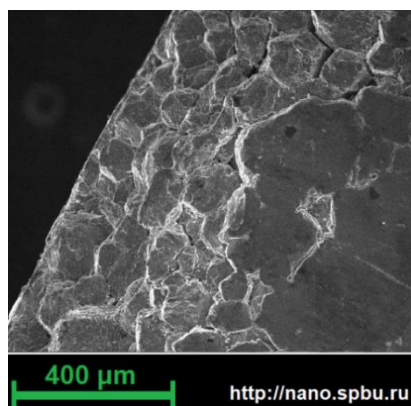

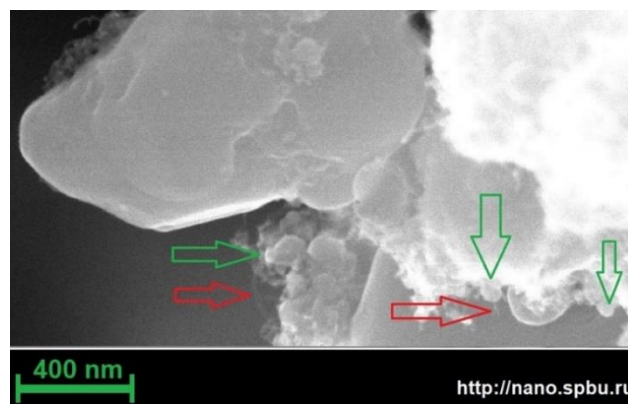**Fig. 3.** Cleavage of a tablet face of a CNTs and TiC containing material

Fig. 4. Cleavage of a tablet face of a sample containing CNTs and TiC. Green arrows indicate TiC, red arrows indicate CNTs

To study the uniformity of CNT and TiC distribution in samples of mixed reinforcement (CNT+TiC) (Fig. 5), the distribution of elements on the sample section was additionally analyzed. Two phases are visually distinguished in the sample (Al phase and DRP). The phase with a lower percentage (DRP) is distributed along the former boundaries of ASP-50 Al particles. The particles themselves are densely compacted and represent a uniform metal matrix without cracks and cavities.

The absence of interfacial boundaries between Al particles and CNTs minimizes internal porosity.
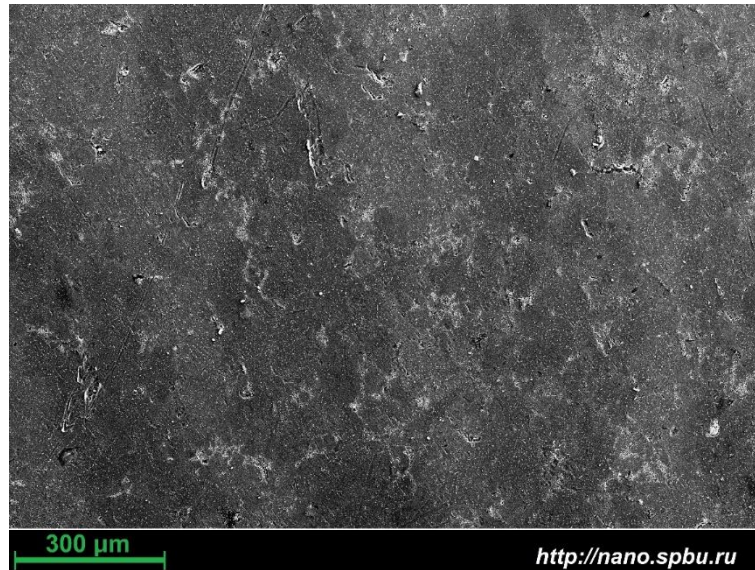
Fig. 5. Micrograph of a polished cut of MMC containing Ni-coated CNTs and TiC

Table 1. Chemical composition of a sample MMC containing Ni-coated CNTs and TiC according to EDS data

Element	[C]	[Ni]	[Ti]	[Al]
Concentration, wt.%	4.76	1.96	2.29	91.09

An additional study of the elements distribution on the sample section was carried out. The EDS data (Table 1) measured in the area of the sample selected in the SEM image confirmed the material composition. In addition to the main element Al, the presence of Ti, C, and Ni is observed.

Mechanical uniaxial stretching tests. The mechanical properties of Al matrix composites were examined by the uniaxial tension method. The reference samples were also made of pure dispersed ASP 50 Al.

As a result, deformation diagrams of the matrix composites were obtained. Characteristics of samples of Al-matrix composites with different CNTs amounts are given in Table 2 and in Fig. 6. The mechanical properties of Al matrix composite samples with different DRP compositions are compared in Table 3 and in Fig. 7.
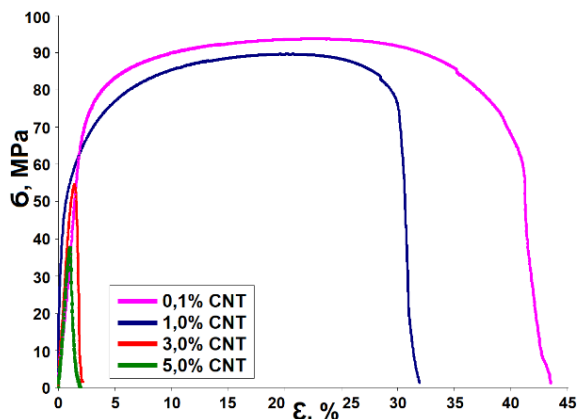

Fig. 6. Destruction curves for samples containing different amounts of CNTs
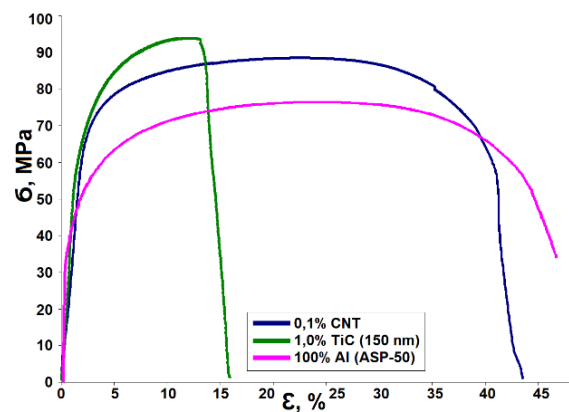

Fig. 7. Destruction curves of a composite with nano-TiC and a composite with CNTs

As can be seen from the data obtained during mechanical tests by the method of uniaxial loading, with an increase in the content of the mass fraction of CNTs in a sample, its strength decreases and material embrittlement occurs (Fig. 6, Table 2). The most promising is the 0.1 % CNT containing sample. The tensile strength of the sample reaches 85 MPa (compare with 74 MPa for pure Al), while maintaining the plasticity characteristic of pure Al.

Table 2. Characteristics of samples of alumina-matrix materials containing different amounts of CNTs

CNT content	σ_V, MPa	ε, %
ASP-50 aluminum	74.0	38.0
ASP-50 aluminum +0.1 % CNT	85.4	43.5
ASP-50 aluminum +1 % CNT	87.6	31.9
ASP-50 aluminum + 3 % CNT	54.6	2.1
ASP-50 aluminum + 5 % CNT	37.5	1.9

The increased mechanical strength for materials containing 0.1 and 1 % CNTs is explained by the redistribution of loads applied to the material along the quasi-one-dimensional defect formed by CNT, which significantly reduces the loads at the shear boundary and redistributes the energy along the defect, contributing to the relaxation of the material in the incipient shear zone, without significant destruction of the existing micrograin structures. For a 0.1 % CNTs containing sample, plasticity is equal to that of pure Al, a tensile strength is slightly increased. At the same time, for 1% CNT sample, a decrease in plasticity is observed, assisted with a slight decrease in the tensile strength (compared to 0.1 % CNT). This indicates the formation of agglomerates by CNTs and numerous intersections in the matrix array, which leads to sample embrittlement due to the fatigue defects along the network of intersecting CNTs, which leads to a decrease in relaxation processes in the matrix material, an increase in stresses in the nanotube intersection zone and matrix destruction in the intersection zone, due to a decrease in the effective cross-section of the metal resisting loads in these zones. This ultimately facilitates sliding of grain boundaries, leads to a decrease of plasticity and tensile strength. A further increase in the CNTs content in the Al matrix only enforces these processes by additional formation and growth of CNT aggregates, and a decrease in the effective cross-sections of the metal matrix in the zones of CNT aggregates [24].

It should be noted, however, that the resulting material was not subjected to alloying, thermal or mechanical hardening by rolling methods. The properties of our material (containing 0.1 and 1 % CNTs) can be significantly improved by mechanical and thermal strengthening. The high ductility of our material guarantees protection against the formation of cracks during mechanical hardening.

The mechanical properties of Al matrix composite samples with different DRP compositions are compared in Table 3 and in Fig. 7.

Table 3. Characteristics of the mechanical properties of Al matrix composites with different DRP

CNT content	σ_V, MPa	ε, %
0.1 % CNT	85.4	43.5
1% TiC (150 nm)	93.8	16.0
ASP-50 aluminum	74	47.2

As can be seen from the curves (Fig. 7), various reinforcing phases have a different effect on the Al matrix composite - CNTs allow maintaining plasticity already at 0.1 %

reinforcement and slightly increase the strength of the composite, at the same time, the TiC phase with a dispersion of 150 nm significantly reduces plasticity and significantly increases the strength of the composite. From our point of view, the combined use of these two reinforcing phases will make it possible to neutralize their drawbacks and to obtain a composite with higher strength characteristics while maintaining the composite plasticity.

As a result of structural and mechanical studies of composites with different DRP, the optimal composition of the sample of the Al matrix composite was revealed. Figure 8 and Table 4 show the mechanical properties of such a composite containing 0.1 % CNT + 1 % TiC (150 nm) as DRP.
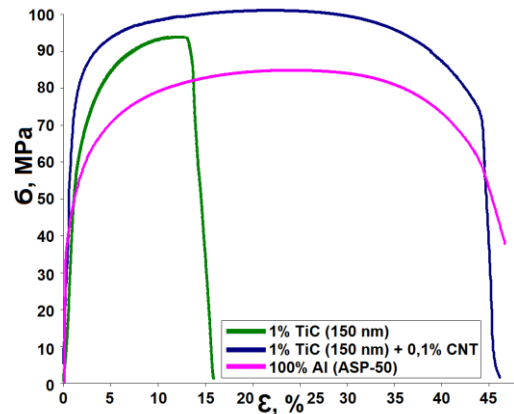

Fig. 8. Destruction curves showing the effect of introducing CNTs on samples containing DRP with a grain size of up to 150 nm

Table 4. Mechanical properties of samples of Al matrix composites with different DRP

CNT content	σ_V, MPa	ε, %
0.1 % CNT + 1 % TiC (150 nm)	103,4	46.1
1 % TiC (150 nm)	93.8	16.0
ASP-50 aluminum	77	47.2

The introduction of 0.1 % CNTs into the MMC sample preserves the material plasticity, and 1 % nanosized TiC makes it possible to increase the tensile strength.

Thus, based on experimental data, we can state that the introduction of 0.1 % Ni-plated CNTs makes it possible to maintain the plasticity of the metal-matrix material at the level of pure Al, due to the CNTs influence on the stress distribution inside the composite matrix. Joint reinforcement of MMC by CNT and TiC is promising for obtaining materials with improved strength properties. Production of such materials and controlling their properties will make it possible to create a whole class of materials for promising applications in science and technology.

Conclusion

As a result of the study, Al-based metal-matrix composite materials reinforced with both ceramic nanoparticles (TiC) and carbon nanotubes (CNTs) were synthesized. The composite formation has been structurally studied.

In this work, we have developed a method for obtaining a monolithic Al matrix composite with zero porosity by the method of repeated cold pressing and sintering at a heat treatment below the melting temperature of the Al matrix. This made it possible to obtain a composite with stable properties without the formation of undesired phase at the metal-ceramic interface in the MMC material, which could lead to material embrittlement and

deterioration of mechanical properties.

A technique has been developed for the uniform introduction of CNTs into the bulk composite using powder metallurgy methods. In our work, to ensure good wettability of the dispersed phase and its uniform distribution in the Al bulk, CNTs and TiC were metallized with a thin layer of metallic Ni.

In the course of the work, 600 °C was selected as the most effective temperature for samples sintering. This sintering temperature made it possible to form an aluminum matrix and bond the matrix to the nickel shell. The modes of pressing and sintering were selected on the basis of experimental studies. On the basis of experimental data, it was shown that Ni-plated CNTs (0.1 %) allow maintaining the plasticity of the Al matrix material. At the same time, the TiC phase with a dispersion of 150 nm significantly reduces plasticity and significantly increases the composite strength.

It was shown that the combined use of two reinforcing phases (CNT and TiC with a dispersion of 150 nm) makes it possible to level their negative qualities and obtain a composite material with higher strength characteristics while maintaining the plasticity of the composite.

As a result of the work, a method was developed for obtaining a composite material with two reinforcing modifiers Al-TiC-CNTs with improved strength and high ductility.

Studies have been carried out comparing the mechanical properties of AD00 grade Al and the resulting aluminum composite with a reinforcing phase of 0.1 % CNT + 1 % TiC (150 nm). The tensile strength of the composite obtained by us is 40 % higher than that of Al grade AD00, plasticity is 69 % higher. Such high values make it possible to create new materials based on this reinforced matrix. In addition, these reinforcing additives can significantly affect the properties of existing Al alloys and Al-based composites.

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