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Creation of a nickel composite using surface structuring of the reinforcing phase with titanium carbide nanostructures to improve strength properties

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Abstract. The development of metal matrix composite (MMC) materials is one of the demanded areas of research in materials science. In line with this trend, there is an increasing interest in nickel-based MMC materials, which have already become classic in science and technology. This is due to the high demand for Ni-based materials with high strength characteristics, high hardness, and increased heat resistance.

In this research, we proposed an approach to obtain a MMC material using the surface structuring process, ALD (Atomic Layer Deposition) and powder metallurgy method. The developed approach provides a composite with TiC nanostructures (1-5 nm) uniformly distributed throughout the Ni matrix. The absence of interphase boundaries between the Ni matrix particles and carbide nanostructures made it possible to minimize the internal porosity of the sample. This is due to the strength of the interphase boundaries between the matrix and the reinforcing phase in the composite and to the solidity of the structure. As a result, the created material effectively resists plastic deformation and stress. This allows not only to enhance the strength properties of the composite, but also to maintain the MMC plasticity, which increases its processing ability.

1. Introduction

In modern mechanical engineering, there is a need to develop new generation structural materials that exceed existing materials in their characteristics.

The development of metal matrix composite (MMC) materials is one of the demanded areas of research in materials science. At the same time, in line with this trend, there is an increasing interest in nickel-based MMCs, which have already become classic in science and technology [1]. This is due to the high demand for Ni-based materials with high strength characteristics and high hardness, with increased heat resistance.

One of the ways to strengthen a metal matrix is its reinforcement, i.e. the introduction of additives with high hardness and strength.

Metal oxides, carbides or nitrides, as well as carbon nanotubes can be used as a reinforcing phase. However, the micron dispersed reinforcing phase induces the material brittleness, which leads to difficulties in its processing and operation of products made from it. Modern technologies for creating MMCs are based on the controlling properties through targeted nanostructuring (reinforcement) of a metal matrix with ceramic nanostructures thus creating dispersion-strengthened materials with improved mechanical characteristics [2–4].

The observed increase in the strength of such composites is directly related to a decrease in the particle size of the reinforcing phase to tens of nanometers. This is due to an increase in the specific area of contact between grains of the reinforcing phase and matrix grains, a decrease in the size of material defects, which are also particles of the reinforcing phase [5, 6]. The processes of materials strengthening in this case are in good agreement with the Hall-Petch, Orowan and Nardan-Prévot mechanisms.

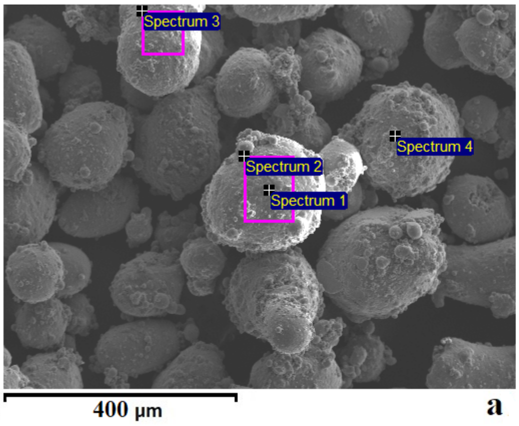
Titanium carbide (TiC) as a reinforcing additive is interesting, that is caused by its properties: high hardness (30 GPa), elastic modulus (440×10^9 N/m^2), significant melting point (3523°C). Moreover, TiC is the only reinforcing additive known and currently used, which, in addition to high mechanical properties, has also a strong modifying effect (due to the similarity of the type and size of the crystal lattice with Ni and Al matrices). This also increases the strength and plastic properties of the resulting composites.

One more important parameter when creating MMC is the amount of reinforcing phase introduced into the matrix. As experiments have shown, if the reinforcement amount increases, the material becomes brittle, which is associated with the formation of local zones with an increased content of the reinforcing phase particles that are not connected with each other or with the matrix grains. Also, even if the reinforcing phase is uniformly distributed throughout the material, the fragility also increases with increasing reinforcement volume. This is also due to insufficient interaction between the matrix grains, when the Orowan strengthening mechanisms stop working due to insufficient volume of matrix material to form loops. This effect cannot be compensated by the processes described by the Hall–Petch law, since the minimum possible grain size in the material has already been reached.

Thus, based on reviewed scientific works, we concluded that to achieve the maximum possible effect of strengthening a metal matrix (including Ni), it is necessary to introduce into the matrix reinforcing particles with the smallest possible size, and also to reach the highest possible uniformity of reinforcement throughout the entire material bulk.

Traditional consolidation methods, such as high-temperature sintering and hot pressing, have significant limitations, e.g. the inability to maintain the original grain size in the matrix due to excessive grain growth at high temperatures [7]. Also, the combination of a matrix and a reinforcing component in one material inevitably encounters interfacial interaction. If adhesion is poor, the strength of the final composite is lost. A number of methods are used to solve this problem, for example, in fiberglass plastics, sizing additives are added to the resins, creating a covalent bond between the glass surface and the polymer matrix. From the adhesion point of view, MMCs compacting is hard. Poor wetting leads to sedimentation and agglomeration of the reinforcing component, which negatively affects the mechanical properties. At the moment, a number of research groups are developing new ways to produce MMCs with improved performance characteristics [8–10].

In our research, an approach was proposed to obtain MMC using the surface structuring process, the ALD method and the powder metallurgy method. It makes possible to obtain a composite material in which TiC nanostructures measuring 1–5 nm are uniformly distributed throughout the Ni matrix. The absence of interphase boundaries between the Ni matrix particles and carbide nanostructures made it possible to minimize the internal porosity of the sample. This allows to most effectively influence not only the mechanical properties of the composite, but also to preserve the material plasticity, which will have a positive effect on performance characteristics and suitability for processing.



Spectrum	In stats.	C	O	Al	Ti
Spectrum 1	Yes		4.20	95.74	0.06
Spectrum 2	Yes	8.09	5.64	85.91	0.36
Spectrum 3	Yes	11.31	5.86	82.54	0.28
Spectrum 4	Yes	10.25	8.00	81.53	0.21
Max.		11.31	8.00	95.74	0.36
Min.		8.09	4.20	81.53	0.06

b

Figure 1. Microphotographs of an Al particle (a) with TiC nanostructures and the elemental composition of the particle surface (b).

2. Synthesis and study of Ni-based composite with reinforcing phase of Al&TiC

2.1. *Synthesis of TiC nanostructures on Al particles (Al&TiC)*

The particles of the Al&TiC type were synthesized by the ALD method in a specially designed device operating as a plug-flow reactor [11].

This device implements a flow-through vacuum circuit. A vacuum was kept in the system using a rotary vane pump, while an inert carrier gas (helium) was continuously supplied to the system. An inert gas is needed to transfer reactants, remove reaction products, and prevent hydrolysis. So, the device implemented the principle of "dynamic vacuum", using which most ALD instruments operate. An important feature of this instrument is the ability to work also with dispersed substrates, not only with massive ones.

The substrate was ASP-50 grade Al powder. This is a spherical powder (figure 1) containing 99.7% Al and no more than 0.3% impurities.

In order to standardize the particle size, ASP-50 Al was pre-screened on a VP-30T vibratory scatterer using sieves with mesh sizes of 50 μm and 80 μm. As reagents we used titanium isopropoxide and propylene glycol. Reagents were supplied to the system using a valve system. First, titanium isopropoxide was introduced to the system for 15 min, followed by purging of the system for 15 min to remove reaction products. Next, propylene glycol was supplied to the system for 15 minutes, then the system was purged for 15 minutes.

As a result, we obtained samples of TiC ranging in size from 1 to 5 nm on the Al particles surface.

2.2. *Method for producing bulk Ni-based composite material with Al&TiC reinforcing phase and varying reinforcement degree*

The first stage leading to Ni-based composite material is the introduction of Al&TiC type particles into the initial Al matrix in a ratio of 1:99, 3:97, and 5:95 wt.%. Two powders (modified Al particles and reinforcing phase) mixed in a planetary ball mill PM 100 SM. To do this, the particles were placed in a steel beaker (125 ml) together with 5 mm steel balls and mixed for 10 minutes at 150 rpm. The material to balls ratio was 1:25.

Then the resulting mixture was pressed. 7.2 g of the mixture was placed in a collapsible mold with a punch size of 20 × 20 mm and pressed using a Sorokin 7.75 pneumohydraulic press. Pressing was carried out at room temperature in 3 stages (with loads of 15 tons, 35 tons, and finally 50 tons, 15 minutes each stage). After each pressing stage, the material was sintered in an inert atmosphere at 600°C for 1 hour. At the final stage after the third sintering, the sample was heated to 900°C and kept at this temperature for 1 h. After heating was completed, the reactor was cooled to 50°C, the supply of inert gas was stopped, and the sintered sample was removed.

The samples of MMC obtained in this way were gray metal plates 20 × 20 × 2 mm with a metallic luster. The material plates were without visible defects, durable, and can be machined.

2.3. Characterization

Morphology and elemental analysis of the composite material and Al&TiC particles was performed using a Zeiss Merlin scanning electron microscope with additional Oxford Instruments INCAx-act X-ray microanalysis attachments and an Oxford Instruments CHANNEL5 electron backscatter diffraction (EBSD) recording system. Elemental analysis of dispersed samples was carried out for dry particles.

To confirm the presence of TiC, we used X-ray photoelectron spectroscopy of a composite. The resulting spectra were recorded for a compacted sample manufactured according to a previously described method. The energies were calibrated using the Au 4f7/2 ground level peak. Also, to clean the surface from hydrocarbon film and traces of sweat, the sample was etched with an ion beam. Peaks at 455 eV (Ti2p) and 282 eV (C1s) correspond to the C-Ti bond [NIST X-ray Photoelectron Spectroscopy Database, NIST Standard Reference Database Number 20, National Institute of Standards and Technology, Gaithersburg MD, 20899 2000]. This reveals the presence of TiC in the synthesized samples. The studies were performed in the Resource Center “Physical methods of the surface studies” using ESCALAB 250 Xi spectrometer.

2.4. Mechanical tests, uniaxial tensile tests

Double-sided blades with a working part size of 6 × 2 mm were produced from composite material blank plates 20 × 20 × 2 mm, obtained by the above-described method, using an ARTA 123 PRO electroerosive machine from NPK Delta-Test LLC.

The ends of the blades were examined using a Mikmed-6 microscope with side illumination to control the integrity of the samples. To check whether the density corresponded to the calculated values and the absence of pores, the samples were examined by hydrostatic weighing on a Shimadzu AUW220 balance using a density determination kit SMK-401.

Uniaxial tension was measured on a Shimadzu AG-50kNX testing machine at room temperature, the strain rate was $510^{-4}\,\mathrm{s}^{-1}$. The deformation of the samples was controlled by a TRViewX 55S video extensometer. Bending tests were carried out in accordance with GOST 14019-80 “Metals and alloys. Methods of testing for bending”.

2.5. Mechanical tests, Vickers tests

To study the material hardness, we chose the Vickers hardness measurement method. A tool with a diamond pyramid with a tip angle of 136° was used as an indenter. The measurements were carried out on a TV-5214-10 Tochline hardness tester at a load of 10 kgf, the holding time was 10 seconds. The samples for measurement were square metal plates with dimensions of 20 × 20 × 2 mm. For each test sample, at least six measurements were carried out in different parts of the sample in order to obtain an average hardness values over the entire sample surface.

A plane-parallel sample plate was placed on the measuring table of a pre-calibrated hardness tester. During the measurement process, a map of the sample was compiled with the obtained hardness data for each point, which made it possible to select points for study without falling into previously studied areas. The obtained values were averaged for each sample.

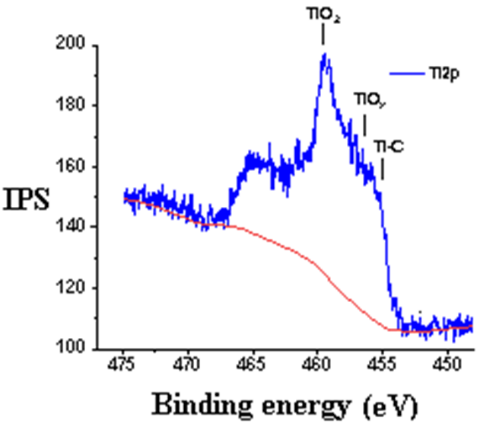


Figure 2. Spectrum of Ti2p sub-level.

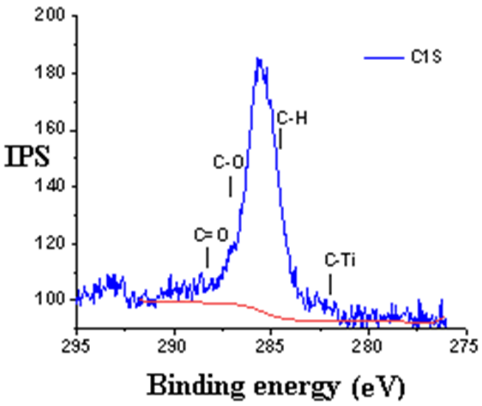


Figure 3. Spectrum of C1s sub-level.

3. Results and discussions

3.1. Composition and structure of a Ni-based composite material with a Al&TiC reinforcing phase

Samples of composite material and Al particles with carbide nanostructures were studied by electron microscopy. The EDX method was used for rapid assessment of the qualitative composition of samples for the presence or absence of Ti and C. Figure 1 shows Al particles with TiC nanostructures.

The micrograph data clearly shows synthesized nanostructures on the Al particles surface, which are structural inhomogeneities uniformly distributed over the surface of the particles. The presence of Ti and C on the Al particles surface in the synthesized samples was confirmed by elemental analysis using an EDS attachment. We can conclude that the synthesized samples contain Al, Ti, C and O atoms. Al corresponds to the dispersed substrate material – ASP-50 Al. The increased C content can be explained by using carbon tape as a substrate for dispersed samples. The presence of a significant amount of oxygen indicates an oxide film on the Al surface. However, the combined presence of C and Ti in the sample still not guarantees the presence of TiC.

To confirm the presence of TiC in the samples, an XPS was recorded (figures 2 and 3). To unambiguously establish the presence of a Ti-C bond, the data from the C1s and Ti2p sublevels were deconvoluted.

The resulting spectra were recorded for the compacted sample. The need to work with a compacted sample is determined by the design of the used equipment and the expected composition of the sample under study. Energy calibration was based on the peak of the main level Au $4f_{7/2}$. Also, to clean the surface from the hydrocarbon film, the sample was etched with an ion beam. Peaks at energies of 455 eV (Ti2p) and 282 eV (C1s) correspond to the C-Ti bond [12], which confirms the presence of TiC in the synthesized samples.

At the next stage of the work, samples of bulk Ni-based composite containing 1%, 3%, and 5% of the reinforcing phase were manufactured and studied.

Figure 4 shows a micrograph of the surface of a composite sample made of PNE-1 nickel with the addition of a reinforcing phase. Studying unpolished sections of samples makes it possible to evaluate not only the presence of micron-sized pores, but also to examine the sample for the presence of nano-sized pores.

The resulting Ni-based MMC samples were a massive material of a given shape with insignificant internal porosity (1%) and zero external porosity. The absence of interphase boundaries between the Ni matrix particles and carbide nanostructures made it possible to minimize the internal porosity (figure 4*a*). It was possible to reach uniform distribution of the

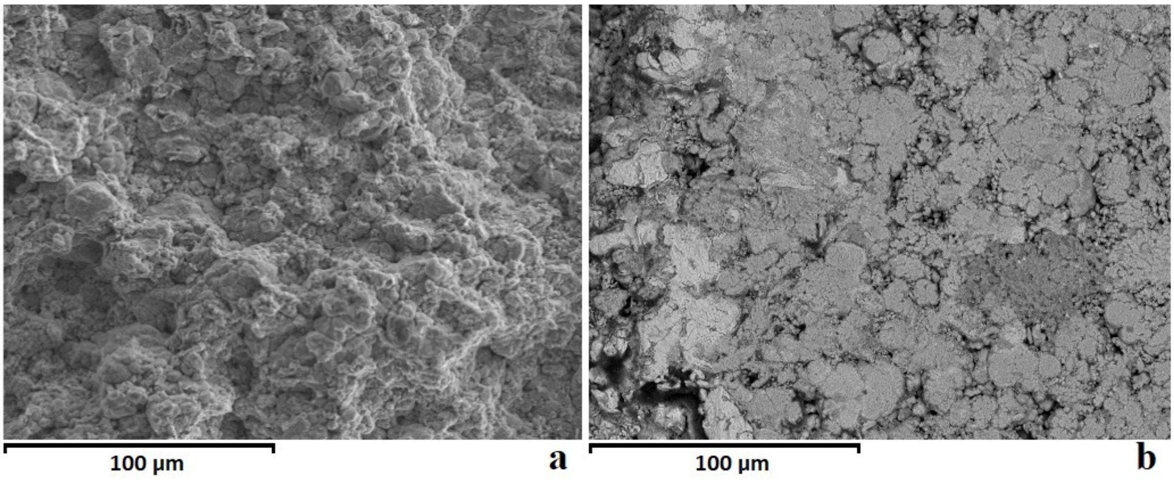


Figure 4. Microphotograph of a cleavage of a Ni-based composite sample: reinforced with Al particles with TiC nanostructures (*a*), reinforced with micron-sized TiC particles (*b*).

Table 1. Composite samples based on a Ni matrix.

Sample No.	Reinforcing phase	Content reinforcing phase, mass. %	Content of TiC, mass. %	Tensile strength σ, MPa at 200°C	ε, %	Plastic limit σ_{02}, MPa, exp	Hardness HV 10/10
1	No	—	—	480	14	80	150
2	Al&TiC	1	0.0004	700	19	103	160
3	Al&TiC	3	0.0012	885	26	122	170
4	Al&TiC	5	0.0028	990	28	130	174

reinforcing phase in the Ni matrix and improve the wettability of the reinforcing phase by the matrix material due to the introduction of TiC nanostructures into the matrix, rather than TiC particles, and to avoid defects and pores between particles in the bulk sample.

For comparison, figure 4*b* shows a micrograph of a Ni-based composite sample reinforced with micron-sized TiC particles ($>$ 1 vol.%). In the microphotograph we see that there is a problem of uniform distribution of micron TiC particles in the matrix and the problem of their aggregation. These aggregates provoke the appearance of internal defects and pores in the Ni matrix (figure 4*b*), which significantly reduces the strength of such composites.

4. Results of mechanical tests of the Ni samples with a reinforcing phase Al&TiC

Further, composites with different ratios of the Ni matrix and the reinforcing phase (Al&TiC) were obtained and their mechanical properties were tested. The characteristics are presented in table 1.

Despite the small volume fraction of TiC in the Ni composite structure, carbide has a significant effect on the strength properties. The samples with a core-shell reinforcing phase (Al&TiC) showed strength characteristics significantly superior to samples with micron-sized reinforcing carbide phases.

By synthesizing TiC nanostructures with a size of up to 5 nm on the surface of Al particles, it was possible to significantly influence the distribution of reinforcing phase particles in the Ni matrix and improve the wettability of reinforcing phase particles by the matrix material. And as a result, we are dealing with a nano-sized fraction of TiC up to 5 nm, evenly crushed and distributed throughout the Ni composite bulk. In this case, the dispersed reinforcing phase has a directed effect on increasing the strength and hardness of the resulting composite.

As can be seen from the values given in the table, for sample 4 with 5% TiC, there is a significant increase in tensile strength and increase in yield strength. This is explained by the influence of the dispersed reinforcing phase – during sintering, particles at the grain boundaries prevent recrystallization of the matrix and contribute to a reduction of the matrix grain size. In addition, TiC nanostructures, interacting with the grain boundaries of the matrix, prevent the movement of these boundaries and the sliding of dislocations. Also, Al&TiC nanostructures form so-called hardening zones around themselves, since they are stress concentrators, thereby preventing the destruction of the composite.

In this case, we observe an increase in mechanical properties according to the Hall-Petch mechanism, which consists of an increase in the yield strength and strength properties with a decrease in the size of the ceramic reinforcing phase, as well as a decrease in the size of defects (micropores, precipitation of secondary phases along grain boundaries). In addition, the material strengthening is clearly related to the influence of the nano-sized reinforcing phase on the grain size and additionally impedes the movement of dislocations at grain boundaries. Moreover, the presence of solid, non-cut particles makes it possible to implement the Orowan mechanism, which consists of the interaction of particles with dislocations. When bending around carbide nanostructures, dislocations form rings (Orowan loops), that strengthen the sliding plane. Orowan strengthening is due to the introduction of nano- and microparticles into the matrix. Due to the obstruction of closely spaced particles to the movement of dislocations, the strength of the material increases. Also, the smaller the size of the reinforcing particles, the smaller the distance between the particles and the stronger the effect of their interaction with the matrix material. Additionally, the material is strengthened when the load is transferred from the soft matrix to the hard and rigid carbide nanostructures under the influence of an external load, which is described by the Nardan and Prevost equation.

Low-temperature plasticity (900°C) of the resulting composites also increases and the tendency to intergranular fracture decreases. This occurs due to the formation of up to 3% intermetallic compound (Ni_3Al) in the Ni matrix. The ductility of the composite increases as a result of a decrease in the activation energy of thermally activated dislocation processes in the sample when reinforced with Al&TiC particles and an increase in the number of active sliding systems.

Thus, the theory is confirmed that the introduction of refractory nanoparticles, including ceramic ones, into composite materials is one of the promising methods of dispersed strengthening of the material. The resulting composites with a nano-sized reinforcing phase of TiC (Al&TiC) from 1 to 5 wt.% in the sample are promising materials for use in mechanical engineering.

Conclusions

As a result of our research, we proposed an approach to obtain a Ni-based metal matrix composite using the process of surface structuring of the reinforcing phase and powder metallurgy. The developed approach made it possible to obtain a composite in which TiC nanostructures 1–5 nm in size are uniformly distributed throughout the metal (nickel) matrix. The absence of interphase boundaries between the Ni matrix particles and carbide nanostructures minimized the internal porosity of the composite, as well as reduced the tendency to intergranular destruction. This allows not only to enhance the mechanical properties of the composite, but also to improve the plasticity of the sample, which has a positive effect on the performance characteristics of the material and its suitability for processing.

Based on the experimental data, we also observe the influence of the dispersed reinforcing phase on the material strengthening. Al particles with TiC nanostructures form so-called hardening zones around themselves, since they are stress concentrators, thereby preventing the destruction of the composite.

The developed approach to Ni-based MMCs provides materials with improved strength properties and preservation of ductility. Hardness tests of a Ni-based composite containing from 1% to 5% dispersed phase (Al–TiC) showed a linear increase in the hardness. This is due to the strength of the interphase boundaries between the matrix and the reinforcing phase in the composite and the solidity of the structure. As a result, a developed material effectively resists plastic deformation and stress.

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