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Nanocomposites of Copper–Titanium–Multiwall Carbon Nanotubes

O. I. Boshko, M. M. Dashevskiy, K. O. Ivanenko, and S. L. Revo

*Taras Shevchenko National University of Kyiv,
Department of Physics,
64/13 Volodymyrska Str.,
01601 Kyiv, Ukraine*

In this work, the effect of process conditions on the structure, microhardness, and tensile strength of copper–titanium–multiwall carbon nanotubes' nanocomposite material (NCM) is studied. The goals of the present study are the obtaining a new copper-based nanocomposite material, analysing the mechanisms of its structure formation and investigating the relationship between its structure and the physical and mechanical properties. The criteria for treatment of NCM precursors, which provide for uniform distribution of its components over a specimen bulk, dispersion of multiwall carbon nanotubes' agglomerates, and optimization of the physical and mechanical properties of the fabricated compositions, are established. Source powders of the materials are mixed in a three-bowl planetary ball mill with acceleration of 50g and pressure on substance particles of about 5 GPa. Such a treatment leads to their mechanical activation and mutual alloying. As shown, after adding both 0.5–1 wt.% of VT 1.0 titanium powder and 0.5–3 vol.% of carbon nanotubes into PMS-1 copper, physical-mechanical properties of NCM specimens fabricated from the component powders after treatment in a planetary-type mill are improved at least twice compared to copper.

В роботі розглянуто вплив умов одержання наноконпозиційного матеріалу (НКМ) мідь–титан–багатостінні вуглецеві нанотрубки (БВНТ) на його структуру, мікротвердість і границю міцності при розтягу. Встановлено критерії оброблення прекурсорів НКМ, які забезпечують рівномірний розподіл його компонентів за об'ємом зразків, диспергування агломератів БВНТ і оптимізацію фізико-механічних характеристик одержаних композицій. Показано, що при додаванні в порошок міді марки ПМС-1 порошок титану марки ВТ 1,0 у кількості 0,5–1 мас.% і вуглецевих нанотрубок у кількості 0,5–3 об.%, фізико-механічні характеристики одержаних після оброблення в планетарному млині порошоків компонентів і виготовлення з них зразків НКМ збільшуються порівняно з міддю не менше ніж у два рази.

В работе рассмотрено влияние условий получения наноконпозиционного материала (НКМ) медь–титан–многостенные углеродные нанотрубки (МУНТ) на его структуру, микротвёрдость и предел прочности при растяжении. Установлены критерии обработки прекурсоров НКМ, которые обеспечивают равномерное распределение его компонентов по объёму образцов, диспергирование агломератов МУНТ и оптимизацию физико-механических характеристик полученных композиций. Показано, что при добавлении в порошок меди марки ПМС-1 порошков титана марки ВТ 1,0 в количестве 0,5–1 масс.% и углеродных нанотрубок в количестве 0,5–3 об.%, физико-механические характеристики полученных после обработки в планетарной мельнице порошков компонентов и изготовления из них образцов НКМ увеличиваются по сравнению с медью не менее чем в два раза.

Key words: microhardness, tensile strength, structure, carbon nanotubes, nanocomposite materials.

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1. INTRODUCTION

The present level of performance characteristics of metallic materials for common use leaves room for their further development. As parameters of the above characteristics are fully dependent on the conditions of their making process as well as on the type and structure of these materials, in this study, we describe such conditions and practically relevant physical-mechanical parameters for copper–titanium–carbon nanotubes nanocompositions.

The known production methods for metallic materials with high-level physical-mechanical properties comprise those, which result in a structure with the grain size h up to a certain critical value. This size is characteristic of all crystals and defines the yield stress of a material (σ_T) by the Hall–Petch equation:

$$\sigma_T = \sigma_T^0 + kh^{-1/2}, \quad (1)$$

where σ_T^0 is the single-crystal yield stress, k is the dimension factor.

In case of high deformation of massive work pieces consisting of two or more components in the form of a package of dissimilar foils, pseudo-alloys or a mixture of metal powders, pressing and subsequent rolling lead to formation of a lamellar nanostructure [1]. In this case, the ultimate stress variation under tension (σ_T) with smaller lamel thickness (h) is also governed by a modified Hall–Petch equation with additional contribution of surface tension force [2]:

$$\sigma_B = \sigma_0 + k_b h^{-1/2} + A_0 \gamma_C / h, \quad (2)$$

where σ_0 is friction stress, k_b is a blocking factor of dislocations by structural barriers, γ_C is coefficient of linear tension on boundaries of adjacent lamels, A_0 is a parameter, which takes into account lamels' orientation about the axis of elongation.

In the case of Fe-Cu-C nanocomposite material produced from the powders, sheets of this material with thickness of 1 mm and with $h = 20$ nm have σ_B value reaching 1960–2060 MPa, which is virtually two times higher than σ_B of the copper-steel pseudo-alloy of the same composition [1].

The goal of the present study is to obtain a new copper-based nanocomposite material, to analyse the mechanisms of its structure formation, and to investigate the relationship between its structure and physical-mechanical properties.

Copper and copper alloys are widely used in the present-day industry. In order to improve their practical application, in this study, we have used pre-treatment of the mixture of powders (to obtain precursors), *i.e.* grinding and activation in a planetary-type ball mill. Effectiveness of mechanical and chemical treatment of powders (grinding and activation) in planetary mills depends on a number of performance characteristics of these mills: power of mill, volume of bowl, diameter and number of grinding balls charged, material of the balls, spinning rates of drum plate and mill bowl; ratio of their rates, *etc.* In the opinion of the authors of Ref. [3], the main parameter, which determines the effectiveness of planetary mills performance, is the absolute rate of production of fines. It is evident that this parameter is directly linked to technical parameters of the mill and especially to acceleration affecting the material in the mill bowl. Therefore, these are the acceleration values affecting the material being treated in the mill bowl that are reasonable and more informative to be discussed for evaluation of effectiveness of planetary mills application for treatment of powders. As a rule, these acceleration values do not exceed 20g in commonly used mills. In our study, the planetary mill used to produce the precursors was capable of acceleration up to 50g. As distinct from the methods known from the literature [4], which provide for a positive mixtures grinding effect over the time of 2.5–5 minutes, in this study, we have experimentally established a longer, up to 180 min, time-period of cyclic treatment optimal for each case. We have also established the influence of the mixture composition, time and treatment modes on the physical-mechanical characteristics of NCM obtained.

2. EXPERIMENTAL PROCEDURE

Specimens of nanocomposite material (NCM) were produced from the following components: PMS1 Cu powder, VT 1.0 Ti powder and multi-

wall carbon nanotubes (MCNT) obtained by the CVD method in a rotating reactor [1, 2]. Al_2O_3 , MoO_3 , Fe_2O_3 oxides were used as catalysts to produce MCNT. Propylene, produced by dehydration of isopropyl alcohol, was used as a source of hydrogen. The mean diameter of carbon nanotubes was 10–20 nm, the specific surface area, which was determined by argon desorption, was 200–400 m^2/g , and their poured bulk density varied from 20 to 40 g/dm^3 . MCNT were added to the Cu-Ti mixture in the amount of 0.5–3 vol.%. To identify what is fundamental in the structure formation and formation of enhanced physicochemical properties of the NCM specimens, the same production method was used to obtain and investigate specimens of copper with nanotubes (Cu-MCNT) and copper with titanium (Cu-Ti).

Source powders of the materials were mixed in proper ratios and treated in cycles (the cycle time was 5 min) in a three-bowl planetary ball mill with acceleration of 50g and pressure on substance particles of approximately 5 GPa. 20 grinding balls made of a hard alloy were used in each bowl. The obtained mixtures were compressed between plane-parallel surfaces at the pressure of 30 GPa at room temperature. Then, the precursor specimens were annealed in argon medium during 30 minutes at 950°C and rolled with 80% reduction at room temperature. Sheets of the produced material were used to make specimens for study.

The tensile strength (σ_B) was calculated on specimens with working area of approximately 20 mm long and 4–5 mm wide at room temperature in the air and at the tensile rate of 5 mm/min. Ten specimens were used to find σ_B .

Microhardness (HV) of the pressed specimens was measured by PMT-3 instrument: the load was 50 g and the load exposure time was 15 seconds.

3. RESULTS AND DISCUSSION

Enhanced characteristics of NCM specimens, obtained by pressing of powder mixtures and then rolling of obtained composite materials, were achieved owing to uniform distribution of its components in the bulk material, dispersion of MCNT agglomerates, and mechanical alloying of copper by titanium in the planetary ball mill. As such, cyclic treatment of the components mixture in the planetary mill provide for a submicrograin structure in the NCM produced, while enhanced physical-mechanical properties of the carbon nanotubes introduced into the composition provide for hardening of the nanocomposite. The hardening occurs due to blocking of dislocations by structural barriers, and owing to a uniform distribution of the components over the material volume, in particular MCNT in pressing and subsequent rolling. Apart from downsizing of Cu and Ti powder particles used in making speci-

mens of compositions, the ball-milling process leads to their mechanical activation and mutual alloying.

The elementary analysis of the specimens produced by pressing of the powders mixture (precursors) was performed on JAMP-9500F Auger microprobe (JEOL, Japan) and established the following composition in atomic percent: Cu—96.8, O—1.6, C—1.3, Ti—0.3. At the same time, the X-ray diffraction analysis results are indicative of presence of cuprum oxide Cu_2O alongside α -phase of Cu with f.c.c. lattice in the precursors. The lattice parameter of Cu in the precursors stays almost the same as the reference value, while treatment in the planetary mill with increased milling time for nanocrystals of Fe with 10 wt.% of Ni leads to an increased b.c.c. lattice parameter [7]. Figure

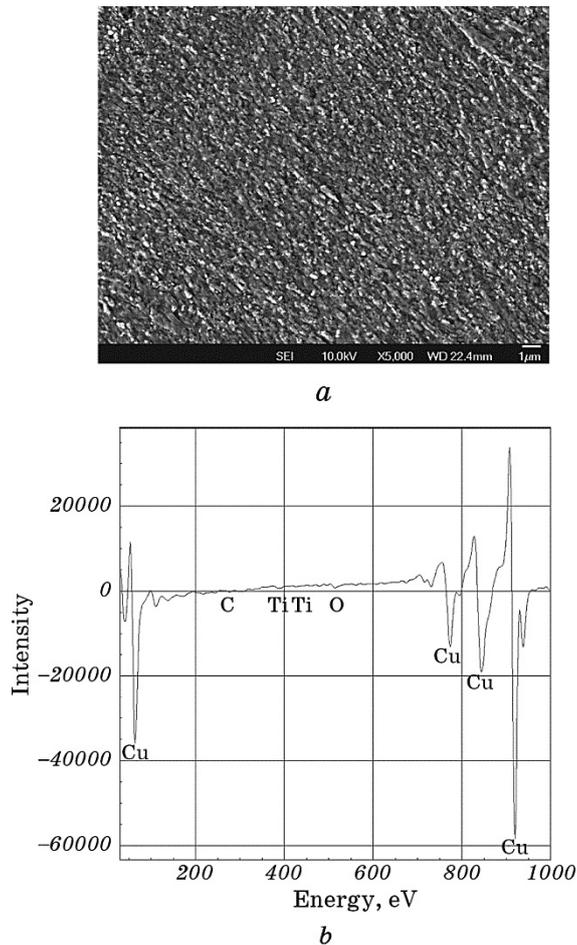


Fig. 1. Microstructure of ion-etched surface of Cu-Ti-MCNT NCM sheet (a) and its composition (b).

1 demonstrates pictures of Cu–Ti–MCNT specimens' ion-etched surface microstructure and a summary of the specimens' composition. It was seen that the structure of sheet surface is fine-grained and the elongated grains are orientated along the direction of rolling.

Analysis of MCNT percentage (CMCNT) on H_V value of the precursors (Fig. 2) allows us to arrive at a conclusion that concentration of nanotubes $CMCNT = 0.5$ vol.% is optimal for both Cu + MCNT specimens (Fig. 2, *a*) and Cu + Ti (1 wt.%) + MCNT specimens. The optimal content of titanium in the powder mixtures is within the range of its

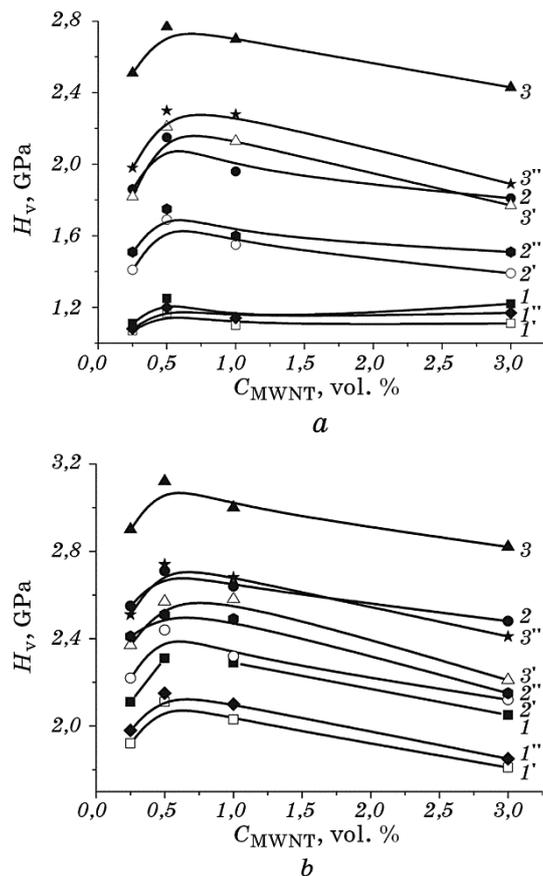


Fig. 2. Dependences of microhardness values of Cu + MCNT (*a*) and Cu + Ti (1 wt.%) + MCNT (*b*) precursors on MCNT content. The precursors were obtained from the respective powders; the total milling time of the powder specimens was 20 minutes (1, 1', 1''), 60 minutes (2, 2', 2''), and 120 minutes (3, 3', 3''). Specimens (1–3) were pressed with 40% reduction (1–3), annealed at 995°C during 30 min (1'–3'), pressed and annealed for the second time in the same conditions (1''–3'').

concentration of 0,5 to 1 wt.%, while the treatment time for the powders in the mill, which allows achieving the highest hardness of the composition specimens, is $\tau \geq 120$ min (Fig. 2, see curves 1, 1', 1"; 2, 2', 2"; 3, 3', 3"). Thus, *HV* value of the precursors is increased with the increase of cyclic pre-treatment time (in this case the time of cycle is 10 min) of powders in the ball mill and reaches its saturation at $\tau > 120$ min (Fig. 2, curve 1). Although authors of Ref. [8] have also reported a huge increase of microhardness of up to 2.6 GPa for precursors result also for mixing copper and aluminium powders (3.5% wt.) during 5–20 hours in a planetary-type mill, formation of aluminium oxide, obtained specimens copper oxide reduction in the argon atmosphere during 1 hour and hot pressing in argon atmosphere, they have not, however, reached the level of microhardness attained in our study.

It needs to be mentioned that in our case such increase in the microhardness is 3–3.5 times greater than in the pressed specimens of pure copper powder mixtures treated by the same method (see curve 2, Fig. 2). It is impossible to roll the obtained precursors because of their brittleness. This, however, becomes possible after vacuum annealing of precursors. Their microhardness in this case drops (Fig. 2, curves 1–3, 1'–3') to the value dependent on the time of pre-treatment of the powders in the ball mill (the greater is the pre-treatment time, the greater is the value of decrease in the microhardness). As was mentioned earlier, annealing was performed at temperatures of at least 950°C. Lower annealing temperatures do not lower microhardness of the precursor specimens, which complies with the results reported by the authors of the study [9]. In this study, high microhardness values of the nanostructural copper ($HV = 1,7$ GPa) went down too, but only after annealing at the temperature $T > 500^\circ\text{C}$ during one hour. It is worth noting that the microhardness of foils remains virtually the same $HV = 2.2\text{--}2.5$ GPa (Fig. 3, curve 5) after rolling of the precursors and is practically independent of the pre-treatment time of the mixtures in the ball mill.

Figure 3 demonstrates relationships of $HV = f(\tau)$ for Cu specimens (Fig. 3, curve 1), Cu + MCNT (Fig. 3, curve 2), Cu + Ti (Fig. 3, curve 3) and Cu + Ti + MCNT (Fig. 3, curve 4). Analysis of these relationships allows us to conclude that microhardness rises after an increase of the pre-treatment time in the ball mill for all precursors studied. The intensity of such increase is greater for Cu and Cu + MCNT than for Cu + Ti and Cu + Ti + MCNT (Fig. 3, curves 1, 2 and 3, 4).

The tensile strength value (σ_B) of the specimens of rolled precursors also depends on the time of pre-treatment of the respective mixtures in the ball mill (Fig. 4). In this case, as opposed to microhardness characteristics (Fig. 3), the optimum pre-treatment time is $\tau \cong 20$ min. The optimum values of *HV* and σ_B are given in the Table below.

The tensile strength of 100 μm thick M1 copper foil (as supplied) is

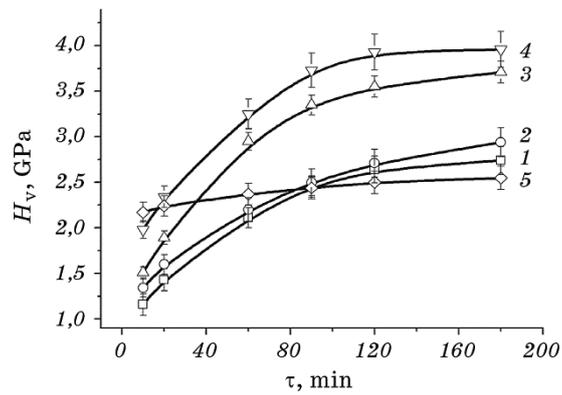


Fig. 3. Dependences of microhardness values of Cu (1), Cu + MCNT (2), Cu + Ti (3), Cu + Ti + MCNT (4) precursor specimens and rolled precursor specimens (5) on the pre-treatment time of the respective powder mixtures in the planetary-type ball mill.

$\sigma_B \cong 314 \pm 22$ MPa and σ_B equals 382 ± 24 MPa for the copper powder rolled in the same way as the precursors, but without pre-treatment in the ball mill, whereas σ_B values reach optimal values given in the Table for the specimens of rolled Cu precursors (Fig. 4, curve 1), Cu + Ti (Fig. 4, curve 2) and Cu + Ti + MWNT (Fig. 4, curve 3) at the pre-treatment time of approximately 20 minutes.

Such behaviour of σ_B can be related to a change of strengthening effect of copper oxides with an increase of the grain structure dispersion of the specimens produced from the mixtures treated for different time periods in the mill. The oxides concentration is insignificant at $\tau \leq 20$ min, so hardness of the precursors is slightly increased, but σ_B

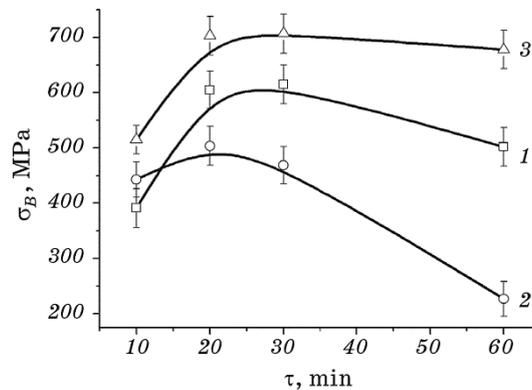


Fig. 4. Effect of the pre-treatment time on σ_B tensile strength of Cu (1), Cu-Ti (2), Cu-Ti-MCNT (3) rolled precursor specimens.

TABLE. Optimal values of microhardness (HV) and tensile strength (σ_B) for the materials studied and their pre-treatment time in the planetary ball mill

No.	Material	Pre-treatment time in the planetary ball mill, min	Microhardness HV , GPa	Tensile strength σ_B , MPa
1	Copper sheet (M1)	–	1.1	314 ± 22
2	Copper sheet made by pressing of PMS1 powder and rolled with 80% total reduction	–	1.11 ± 0.10	382 ± 24
3	Precursor of Cu powder	180	2.74 ± 0.15	–
4	Rolled precursor of Cu powder	20	1.31 ± 0.11	605 ± 31
5	Precursor of Cu + Ti powders	180	3.71 ± 0.12	–
6	Rolled precursor of Cu + Ti powders	20	1.89 ± 0.07	504 ± 35
7	Precursor of Cu + Ti + MCNT powders	180	3.96 ± 0.20	–
8	Rolled precursor of Cu + Ti + MCNT powders	20	2.34 ± 0.12	703 ± 35

value is increased significantly under these conditions. Further increase of the dispersion rate and time of pre-treatment up to 60 min and more and a respective increase of the oxides concentration lead to higher precursors' hardness and a drop of σ_B of the rolled specimens. A decrease of the adhesion strength between the components of the nanocomposite is of note in such conditions.

Some researchers, for example, the authors of Ref. [10], believe that the main contribution into the increase of the specimens' microhardness is made by the change of the alloy grain sizes after treatment of specimens in a high-energy ball mill. We believe that it is necessary that account be taken of the fact that density of dislocations, as was established experimentally, is also increased with the increase of treatment time and reaches its threshold values ($N_D = 10^{12} \text{ cm}^{-2}$) at $\tau > 60$ min. Such an increase of the density of dislocations is caused by introduction of additional grain boundaries with an increase of their dispersion and blocking of dislocations movement by structural barriers. All these factors reduce the plasticity of the composites obtained from the respective precursors. The greatest reduction of density caused by the above factors was observed in Cu + Ti material (Fig. 4,

curve 2), in which the composite was not hardened by MCNT.

Of note is one positive feature of the NCM obtained: the electrical conductivity of the materials studied is almost the same as in pure copper. The drop in conductivity in this case is not greater than 10%.

4. CONCLUSIONS

In this study, we have established topical and novel possibilities of controlling the structure and practically important physical-mechanical properties of nanocomposite materials (NCM) produced from Cu, Ti and multiwall carbon nanotubes.

The novelty of our study is in the fact that the precursors for production of NCM were obtained by pressing the respective mixtures of powders in a planetary-type ball mill with acceleration of up to 50g and pressure on the particles of up to 5 GPa. At that, the concentration, type and treatment modes were optimized and precursor specimens obtained, whose microhardness is three times greater than the microhardness of copper, and plates of nanocomposites were obtained, whose tensile strength σ_B is two times greater than the respective value for copper.

Enhanced NCM characteristics are achieved owing to formation of their microstructure with a uniform distribution of carbon nanotubes over the whole volume of the specimens, dispersion of their agglomerates and copper powder, mechanical activation of NCM components and mutual ligation of copper and titanium, as well as owing to blocking of dislocations by the structural barriers after rolling of the precursors.

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