Metallurgy and Foundry Engineering – Vol. 40, 2014, No. 2, pp. 83–92
http://dx.doi.org/10.7494/mafe.2014.40.2.83

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Studies on obtaining Cu-CNT composites by continuous casting method

Badania nad otrzymywaniem kompozytów Cu-CNT w procesie odlewania ciągłego

Abstract

The progress of civilization force that we look for new materials with higher exploitation properties that can be used in different types of installations and will allow to increase their technological potential. One of the research trends is concentrated on the search of new materials with the above standard electrical conductivity, mechanical and rheological properties, higher thermal resistance and technological properties, all in comparison to pure copper. One of the ideas of such material is composite produced from copper and high quality carbon materials (CNT's or graphene). Regarding to the above, presented paper refers to the research results concentrated on the metallurgical synthesis of Cu-CNT's materials obtained with the use of the continuous casting method. Within this paper research works over the synthesis method and obtained material characterization, for electrical, mechanical and structural properties (for both as cast and after cold drawing tempers) are shown.

Key words: copper, CNT's, composite, metallurgy

Streszczenie

Postęp cywilizacyjny wymusza ciągły rozwój i poszukiwanie nowych materiałów o coraz wyższych własnościach eksploatacyjnych, które zastosowane w różnego typu urządzeniach pozwolą na zwiększenie ich własności użytkowych. Jeden z nurtów koncentruje się na poszukiwaniu materiału, który będzie charakteryzował się większą przewodnością elektryczną, jak również większą wytrzymałością mechaniczną, reologiczną czy odpornością cieplną w stosunku do czystej miedzi, przy zachowaniu wysokich własności technologicznych. Obecny stan wiedzy skłania do wniosku, że będzie to możliwe przez łączenie miedzi z wysokiej jakości materiałami węglowymi w postaci nanorurek czy grafenu. Wobec powyższego niniejsza praca koncentruje się na badaniach nad

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możliwością wytwarzania kompozytów Cu-CNT's metodą metalurgicznej syntezy miedzi i nanorurek w procesie odlewania ciągłego. W artykule przedstawione zostaną badania nad procesem uzyskiwania kompozytów Cu-CNT's oraz ich charakterystyka ze względu na własności elektryczne, mechaniczne i strukturalne. Badania prowadzono na odlewach oraz drutach uzyskanych w procesie ciągnienia.

Słowa kluczowe: miedź, nanorurki, kompozyty, metalurgia

1. Introduction

The world's development in the field of electronics and energy makes that we look for newer and newer materials that would allow an increase of functional properties of devices in which they are used. In particular, we are looking for materials with improved electrical conductivity in comparison to the pure copper. As the literature analysis shows, this is possible in the case of combining modern carbon materials in the form of nanotubes or graphene with copper [1–4]. In [5] the authors achieved a material with 10% increased electrical conductivity in comparison to the pure copper. Similar observations were reported in studies of copper-graphene composite obtained in [6] through electrochemical method. In [3], the authors postulate that on the basis of the analysis of the physicochemical properties of copper, nanotubes or graphene, in the future it will be possible to obtain new composites with the electrical conductivity of up to twice higher compared to pure copper. The results of the own researches of the University of Science and Technology AGH team [7] confirms that it is be possible to obtain a new material with properties exceeding pure copper properties using carbon materials with high electrical properties. It will be possible while guaranteeing an appropriate method of synthesis with stirring the 'metal-carbon material' mixture and ultrafast crystallization. Such conditions can be achieved in the continuous casting process, where there is an immediate cooling of molten metal in the crystallization system of casting stand. As part of the article, the results of research over the possibility of obtaining Cu-CNT's composites in the process of continuous casting were presented.

2. Material for the study and research stations

The base material for the study was the pure copper of CuOFE grade. In the Table 1 chemical composition of the base material was shown. For the synthesis of Cu-CNT composite, Multiwall Carbon Nano Tubes (IGMWNT) were used. In the Table 2 properties of CNT's used to synthesis of composite were shown.

Table 1. Chemical composition of copper used for the synthesis of Cu-CNT

Material	Ag	As	Bi	Pb	Se	Sb	Te	Sn	Zn	Fe	Ni	S	O_2	Cu
	[ppm]													[%]
Base material (CuOFE)	8	<0.3	<0.3	<0.8	<0.3	<1	<0.4	<0.5	1.2	1.8	1.6	1.1	2.5	rem

Table 2. Properties of CNT's used for the synthesis of Cu-CNT composite

Carbon material	Length/ Grain [mm]	Specific surface area [m²/g]	Bulk density [g/dm³]	Carbon content [wt. %]	Other data
Multiwall Carbon Nano Tubes (IGMWNT)	0.01–0.02	60	280	90	Outer diameter: 30–50 nm Inner diameter: 5–10 nm

The synthesis was carried out on a specialized research stand for continuous casting, shown in Figure 1. This device consists of an induction melting furnace with a graphite crucible, mixing system, primary cooling system (crystallizer, cooling unit) and the secondary cooling system. Furthermore, research stand consist of efficient argon protective atmosphere system. The study of the composite synthesis was carried out with the use of the continuous casting method of the rod with the diameter of 8 mm. The stand is designed so that the mixing device allow for intense mixing together of liquid copper and carbon materials and direct injection of Cu-CNT's mixture into the crystallization zone. Upon the inflow of the Cu-CNT mixture into the crystallization zone, it should be followed by its rapid-cooling and fast crystallization. Figures 2 and 3 show details of designed continuous casting device. Tests of casting were performed using crystallizers and crucibles made of graphite in the grade of R4550 and under protective atmosphere (argon gas). The use of a special design of crystallizers with variable cross-section and an efficient cooling system with the appropriate parameters of the casting speed ensures the proper crystallization of the molten metal just after the inflow of Cu-CNT liquid mixture to the crystallizer. This idea must be met because of the large variation in the densities of the materials used for the synthesis (Cu and CNT's) – migration of lighter particles of carbon in copper to the upper areas of the cast. Regarding to above crystallization of the liquid Cu-CNT's composite must be followed immediately after its injection through the mixing system to the crystallizer.

Fig. 1. Research stand for the study of metallurgical Cu-CNT composite synthesis

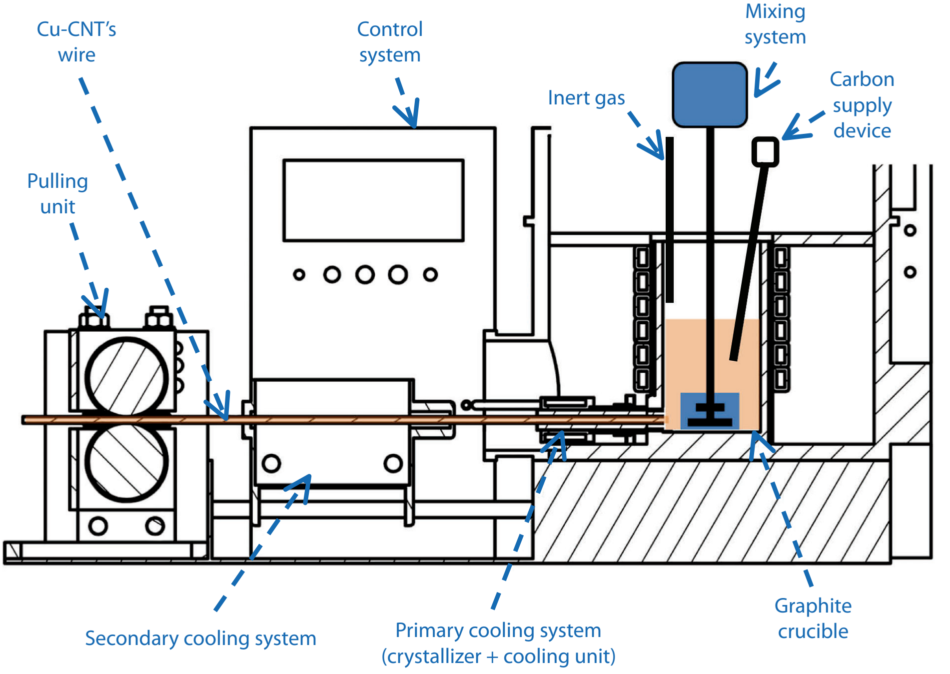

Fig. 2. Continuous casting device of Cu-CNT's composites – idea scheme

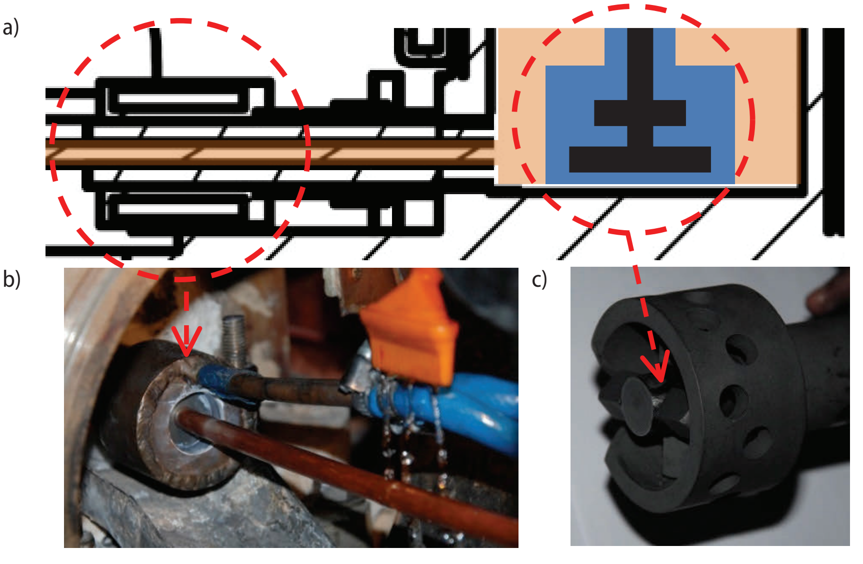

Fig. 3. Device for continuous casting of Cu-C composite materials: a) view of the primary cooling system and the mixing system, b) cooling system with visible Cu-CNT's cast, c) rotor with blades – mixing system

3. Parameters of the Cu-CNT composite synthesis process

In the graphite crucible the pure copper was put in the form of 20 mm cut sections of 8 mm wire rod in an amount of about 5 kg. Then, the entirety was tightly covered with a special lid and the protective gas flow (argon) was turned on in an amount of 5 l/min. The furnace was turned on and after copper melting, Multiwall Carbon Nano Tubes (IGMWNT) were added in an amount of 10 g and then mixing was switched on (rotor speed: 40 RPS) and the process of casting was started. Trials allowed to obtain 2 m (length) rods with designations of Cu-CNT's (1), Cu-CNT's (2) and Cu-CNT's (3). Casted composite rods differed each other mainly by the pulling unit step during the casting process accordingly for subsequent casts by 1 mm, 5 mm, 10 mm. This parameter directly affects the speed of the casting. Other casting process parameters were similar. The increase of the casting speed was the reason of the cast temperature growth at the outlet from the crystallizer. For the comparative studies, the base material of CuOFE was casted with similar technological parameters and with intermediate casting speed (pulling step: 3 mm) but without the mixing of the liquid metal. All wires were cast on a single crystallizer and their final diameter was 8 mm. Casting process parameters are shown in Table 3. Obtained materials were next drawn with the total elongation factor equal to 16. Such obtained materials (castings and wires) were subsequently subjected to tests. The paper presents comparative studies of Cu-CNT's rods with a CuOFE grade casted rod.

Table 3. Parameters of the Cu-CNT and CuOFE casting process

Cast id	Pulling step [mm]	Pulling stop time [s]	Pulling speed [mm/s]	Liquid metal temperature [°C]	Cast temperature [°C]	Rotor speed [RPS]	Water flow in first cooling system [l/min]	Water flow in secondary cooling system [l/min]
CuOFE	3	1	10	1310	310	–	1.2	0.8
Cu-CNT's (1)	1	1	10	1285	230	40	1.1	0.8
Cu-CNT's (2)	5	1	10	1292	300	40	1.1	0.8
Cu-CNT's (3)	10	1	10	1290	360	40	1.9	0.8

4. Study results

Within the frames of studies, the following studies were conducted: chemical composition, density, mechanical and electrical properties, structural studies of casts and mechanical and electrical property testing of wires obtained from casts deformed by wire drawing elongation ratio equal to 16. In the Figure 4 there are rods casted from CuOFE and CuCNT's (1), (2) and (3). Their outer surface has a characteristic shape, typical for continuous casting process resulting directly from parameters of the casting process, *i.e*. length of the pulling step in the crystallizer. The colour of the outer surface of casts is strictly correlated to the temperature of the casts after exiting the crystallizer (the higher temperature of the cast – the faster process of surface oxidation).

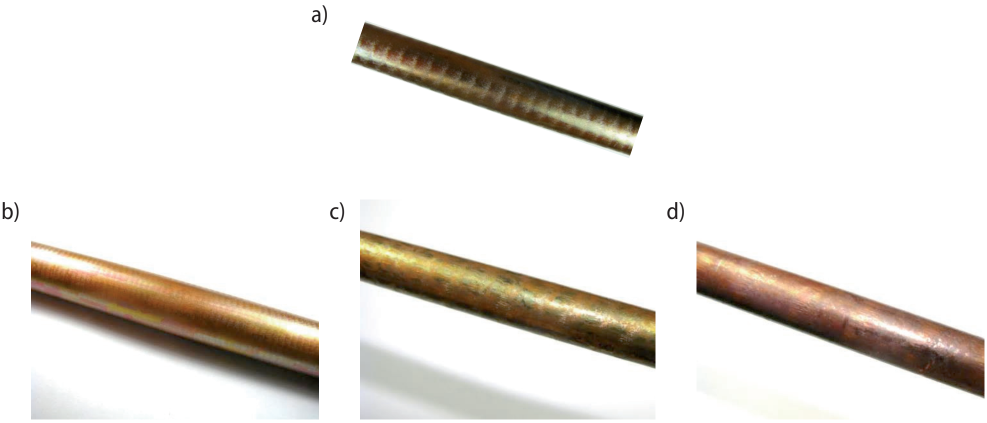

Fig. 4. Surface of casts: a) CuOFE, b) Cu-CNT's (1), c) Cu-CNT's (2), d) Cu-CNT's (3)

Table 4 shows the chemical composition of the obtained materials of CuOFE and Cu-CNT's. From their analysis it results that obtained materials generally have high chemical purity. They have slightly increased Fe content by about 2 ppm, S by about 12 ppm in relation to the CuOFE cast. Moreover, the chemical composition of casts: CuCNT's (1), CuCNT's (2), CuCNT's (3) shows impurities of Ni in an amount of 13, 15.7 and 22 ppm. These impurities originate from the carbon materials. All of the obtained materials have a low oxygen content at the level of max. 2.7 ppm.

Table 4. Chemical composition of casts CuOFE and Cu-CNT's (1), (2) and (3)

Cast id	**Ag**	**As**	**Bi**	**Pb**	**Se**	**Sb**	**Te**	**Sn**	**Zn**	**Fe**	**Ni**	**S**	**O_2**	**Cu**
	[ppm]													**[%]**
CuOFE	9	<0.3	<0.3	<0.8	<0.3	<1	<0.4	<0.5	1.3	1.9	1.3	1.2	1.8	rem
Cu-CNT's (1)	8	0.3	<0.3	<0.8	<0.3	<1	<0.4	<0.5	1.0	3.4	13.0	13.0	2.7	rem
Cu-CNT's (2)	8	<0.3	<0.3	<0.8	<0.3	<1	<0.4	<0.5	1.1	2.8	15.7	13.0	1.8	rem
Cu-CNT's (3)	8	0.5	<0.3	<0.8	<0.3	<1	<0.4	<0.5	1.0	3.4	22.0	14.0	1.8	rem

Table 5 shows the properties of the casts with a diameter of 8 mm. Density tests were carried out using the Archimedes method. The study shows that all composites of CuCNT's have an average density of 8.93 g/cm^3, which is also the density for the used CuOFE base material. The performed studies of mechanical properties have shown that CuCNT (2) and CuCNT's (3) casts have about 13 and 17% higher ultimate tensile strength in comparison to the reference cast of CuOFE. At the same time, CuCNT's (2) and CuCNT's (3) yield strength is 62–67% lower for CuCNT's in relation to the CuOFE cast. The performed studies of mechanical properties on the wires with a diameter of 1.99 mm obtained from the casts show that the increase in yield strength of composite wires is much more intense (YS-CuCNT's (1) from 23 to 400 MPa, YS-CuCNT's (2) from 24 to 430 MPa,YS-CuCNT's (3) from 26 to 431 MPa) than for YS-CuOFE of 70 to 410 MPa. Tensile strength of CuCNT's (2) and CuCNT's (3) is greater by more than 15 MPa as compared to CuOFE. Elongation of composite casts and wires are comparable for the individual condition of the CuOFE material. The analysis of conductivity results of CuCNT's (1), CuCNT's (2) and CuCNT's (3) and CuOFE casts show that all casts have electrical conductivity higher than 58.4 MS/s. The CuCNT's (2) casted rod obtained even the value of 59.2 MS/m. By comparing the results of electrical conductivity of composites with their chemical composition begs the observation of high electrical conductivity even above the conductivity of pure copper (reference casting of CuOFE) taking into account that Fe, Ni, S impurities were reported.

Table 5. Properties of casts: CuOFE and Cu-CNT's (1), (2) and (3)

Cast id	**Density** [g/cm^3]	**Electrical conductivity** [MS/m]	**Hardness HV5**	**Tensile strength** [MPa]	**Yield strength** [MPa]	**Elongation A100** [%]
CuOFE	8.931	58.80	61.6	150	70	39
Cu-CNT's (1)	8.927	59.12	62.9	151	23	35
Cu-CNT's (2)	8.933	58.67	56.2	170	24	–
Cu-CNT's (3)	8.934	58.43	59.9	177	26	37

Table 6 shows the properties of the wires with a diameter of 1.99 mm Cu-CuOFE and CNT's (1), (2) and (3) as well as percentage decrease in the wires electrical conductivity in relation to the casting made of CuOFE and Cu-CNT's (1), (2) and (3) as a result of strain hardening. The studies of conductivity of wires with a diameter of 1.99 mm made from casts shown, that all of the composites achieved the conductivity higher than in case of wires made from CuOFE. Comparing the casts conductivity value with the value of the wires electrical conductivity it is possible to notice a lowering tendency of percentage decrease in the wires electrical conductivity of the wires (CuOFE, CuCNT's (1), CuCNT's (2) and CuCNT's (3)) in relation to casts, *i.e.*: 2.5% of decrease for CuOFE, 2.2% of decrease for CuCNT's (1), 2.1% decrease for CuCNT's (2) and 1.9% of decrease for CuCNT's (3). Mechanical properties analysis were performed on the Zwick Z020 mechanical properties testing machine and Tukon 2500 Hardness tester. Density measurements were performed on Mettler Toledo AB104-s device. The studies of the electrical properties were performed using 4-wire Kelvin Thomson method on the device of High-Precision Automatic Inspection and Test Unit for Electrical Resistance Testing RESISTOMAT Model 2304-Buster.

Table 6. Properties of wires with the diameter of 1.99 mm (λ = 16) and the degree of decrease in the wires electrical conductivity in comparison to the cast made of CuOFE and Cu-CNT's (1), (2) and (3)

Wire id	Electrical conductivity	Tensile strength	Yield strength	Elongation A100	Percentage decrease in the wires electrical conductivity
	[MS/m]	[MPa]		[%]	
CuOFE	57.30	422	410	2.3	2.5
Cu-CNT's (1)	57.82	414	400	2.2	2.2
Cu-CNT's (2)	57.40	440	430	1.8	2.1
Cu-CNT's (3)	57.32	438	431	–	1.9

Within the frames of the studies, also the micro-structure analysis were conducted. Figure 5 shows some photos of the longitudinal cross-section of the casted rods of CuOFE, CuCNT's (1), CuCNT's (2) and CuCNT's (3). These structures are typical for copper cast obtained with the continuous casting method. The arrangement of grains depends on the parameters of the casting process, *i.e.* mainly on the casting speed and cooling conditions. The higher casting speed, the bigger angle of the columnar crystals inclination with respect to the axis. For small casting speed, it is possible to obtain a cast with the columnar crystals, formed along the axis of the cast. In the cross section of the CuCNT's (2) cast (Fig. 6), it is possible to observe the structural diversity within the edge of the cast that may reflect the disorder of grains forming process during the crystallization, resulting from the impact of the carbon material.

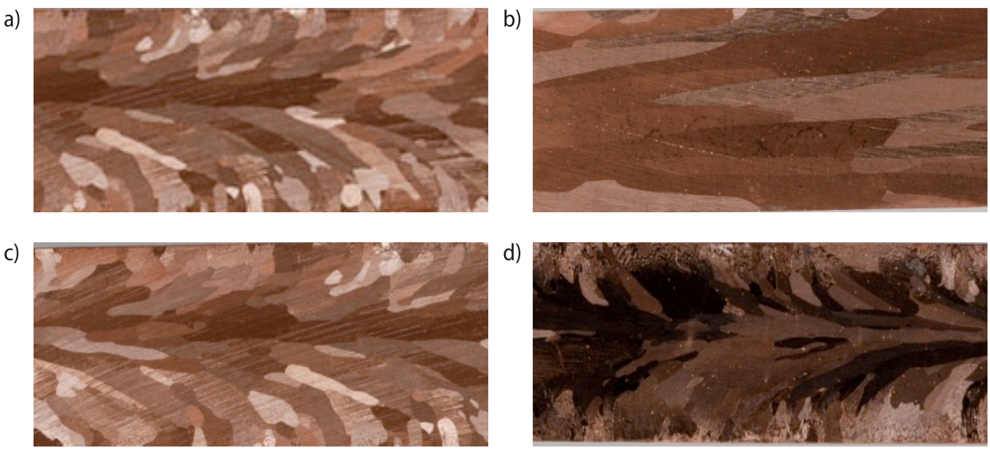

Fig. 5. Macrostructure of casts: a) CuOFE, b) Cu-CNT's (1), c) Cu-CNT's (2), d) Cu-CNT's (3)

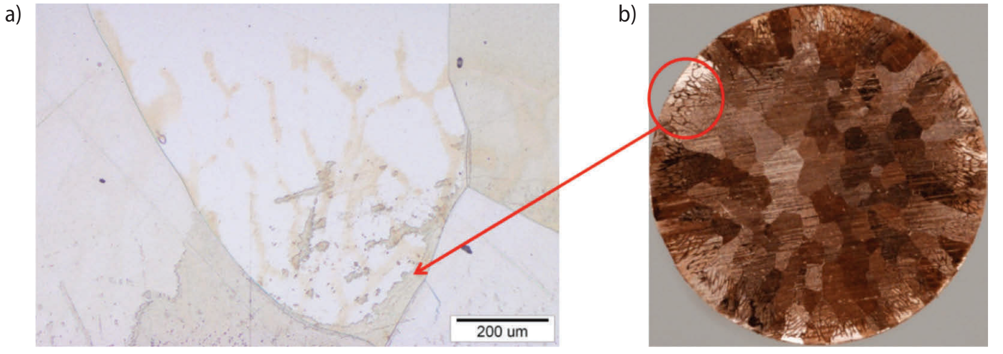

Fig. 6. Microstructure (a) and macrostructure (b) of Cu-CNT's (2) at cross section

5. Conclusions

On the basis of the performed research, the following conclusions were formulated.

1) As part of the metallurgical synthesis of oxygen-free copper of CuOFE grade with Multiwall Carbon nanotubes Nano Tubes (IGMWNT), it was possible to obtain casts with three casting speeds dependant on used pulling step (1, 5 and 10 mm).
2) The obtained composite materials have a density reaching a level of 8.93 g/cm^3 which is the typical value for the density of used base material (CuOFE copper).
3) Cu casts with the additive of CNT's have Fe impurities in the amount of up to 3 ppm, Ni impurities in the amount of up to 22 ppm, and S impurities in the amount of 14 ppm.
4) Tensile strength of composite casts is at the lowest level relative to the reference casting of CuOFE copper, while the yield strength of the casts made from CuOFE is almost two times higher than in case of CNT's casts.
5) The drawing process of casts into wires with the diameter of 1.99 mm results in higher level of mechanical properties for CuCNT's (2) and CuCNT's (3) wires in relation to the CuOFE wires obtained under identical strain conditions.
6) Electrical properties of composite casts are at a very high level above the electrical conductivity of 58.4 MS/m (for CuCNT's (1) casting, even 59.12 MS/m). It is surprising the such a high conductivity when impurities like Fe, Ni and S of such weight amount were reported.
7) After the drawing process, all the CNT's wires obtained the electrical conductivity which is higher than in the case of pure copper.
8) Performed structural studies have shown structural diversity on the cross section of CuCNT's (2) cast within the edges of the cast. This diversity may be the cause of disorder in the process of grains formed during the crystallization, resulting from the impact of the carbon material.

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