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Novel Ti_2CuC_x and $Ti_3Cu_2C_x$ Carbides Obtained by Sintering of Products of Mechanochemical Synthesis of Ti, Cu and Carbon Nanotubes

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Mechanical alloying of the elemental powder mixture of titanium and copper (particle size of both powders is about 40 µm, purity is not less than 99.6% wt. %) was performed in a high energy planetary ball mill to obtain Ti:Cu (2:1 and 3:1) compositions. An addition of 1 vol. % of multiwalled carbon nanotubes (MWCNT, average diameter 10-20 nm) into Ti-Cu charge results in a formation of nanoscaled Ti_2CuC_x and $Ti_3Cu_2C_x$ carbides (containing 0.5 and 4.2 at.% of carbon and 30.8 and 37.5 at.% of copper, respectively). These carbides have synthesized for the first time. Nature of interaction of the charge components at processing in a ball mill has studied on test samples using a complex of X-ray techniques. These techniques include a full-profile analysis for the primary processing of diffractograms obtained with DRON-3M apparatus; qualitative and quantitative phase analysis for determining the phase composition of the products of synthesis; X-ray structural analysis to verify and refine the structural models; Williamson-Hall method for determining the grain sizes. The Vickers hardness of compacted (by sintering) samples with 20.1 and 27.3 at. % Cu varies substantially within (6.9-7.1) GPa. Thus, the average microhardness of synthesized materials is 7 times higher than that of pure titanium microhardness.

Key words: Multiwalled carbon nanotube, Nanocomposite material, X-ray diffraction, Hardness.

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Introduction

Due to its unique mechanical features, the Ti-Cu system, along with Ti-Au and Ti-Ag alloys, have found their application as dental materials. For example, argon arc titanium alloys containing up to 20 wt. % of copper had a high density, as well as plasticity and durability much higher than that of commercially cast pure titanium (CP Ti) [1-3]. Moreover, the addition of copper to titanium improves the grindability of the material manufactured [4] and provides its stable antibacterial properties [5]. The authors of Ref. [3] also indicate that the elasticity of Ti-Cu alloys ensures that they contain impurities of titanium-rich intermetallics (Ti_3Cu, Ti_2Cu, etc.), that is, the scientific interest is also represented by alloys with the copper content of more than 20 wt. %.

It is known that in addition to standard methods (such as arc or induction melting) that are used in the production of compact materials at high temperatures, such an effective powder metallurgy method as a synthesis in a high-energy ball mill was implemented to obtain titanium-copper powders. Thus, a number of $Ti_{1-x}Cu_x$ $(0,10 < x \leq 0,87)$ intermetallic has been synthesized by mechanical alloying of titanium and copper powders [6], resulting in a formation in a wide content range of amorphous powders with similar characteristics to those of rapidly quenched amorphous alloys of the same composition. That is why we selected this efficient and low energy-consuming powder metallurgy method [7] for the synthesis of a series of the Ti-Cu powder materials of 20-30 at. % Cu. At the same time, in order to prevent the amorphization of the powders while processing about 1 vol. % of the multilayer carbon nanotubes (MWCNT) was added to charge. Previously, we have shown the positive effect of MWCNT on the characteristics of metallic materials [8-11].

I. Experimental procedure

The raw materials for the Ti-Cu based nanocomposites synthesis were the powders of PTEM-1 titanium, PM-1 copper (99.5 wt. % Cu), and multiwalled carbon nanotubes (TU U 24.1-03291669-009: 2009 number 02568182/095617 dated 01.09.2009.). Ti:Cu charge of two compositions 2:1 and 3:1 (wt. %)

Table 1

Phase composition of the products obtained by mechanical alloying (MA) of Ti-Cu and Ti-Cu-MWCNT mixtures in a planetary ball mill with further sintering

Charge, at.%			Type of processing	Phase composition	Lattice constants, nm		
					Ti		Cu
Ti	Cu	MWCNT[1)]			*a*	*c*	*a*
Ti:Cu 3:1 (wt. %)							
79,9	20,1	-	60-min milled powder mixture	α-Ti (68)[2)] + Cu (11)+Ti_3Cu (21)	0.2963(3)	0.4685(4)	0.3623(3)
79,9	20,1	+	60-min milled powder mixture	α-Ti (46) + Cu (19)+Ti_3Cu (35)	0.2950(4)	0.4686(4)	0.3630(4)
79,9	20,1	+	Cold pressing and sintering at 980 °C	Ti_2CuC_x (78) + α-Ti (22)	0.2973(1)	0.4768(6)	-
Ti:Cu 2:1 (wt. %)							
72,7	27,3	-	60-min milled powder mixture	α-Ti (66) + Cu (19) + Ti_3Cu (15)	0.2944(9)	0.4708(7)	0.3623(9)
72,7	27,3	+	60-min milled powder mixture	Ti_3Cu (100)	-	-	-
72,7	27,3	+	Sintering at 980 °C	Ti_2CuC_x (53) + $Ti_3Cu_2C_x$ (40) + Ti_3Cu (7)	-	-	-
72,7	27,3	+	Cold pressing and sintering at 980 °C	Ti_2CuC_x (58) + $Ti_3Cu_2C_x$ (42)	-	-	-

1)Charge with 1 vol. % MWCNT; marked as “+”.

2)Phase content (wt.%) according to phase analysis.

corresponding to 25 wt. % (20.1 at. %) of Cu and 33.3 wt. % (27.3 at. %) of Cu has prepared. Multiwalled carbon nanotubes used in this study were synthesized by the catalytic chemical vapor deposition method (CVD) at TM Spetzmash Ltd (Kyiv, Ukraine). The physical properties of the CNTs are as follows: the average diameter is (10 - 20) nm, the specific surface area (determined by argon desorption method) is (200 - 400) m^2/g and their bulk density varies from 20 to 40 g/dm^3 [12].

Elemental powders were mixed to give the desired average composition and sealed in a vial under an argon atmosphere. Hardened zirconia balls (15 units of 15 mm diameter) and a vial (70 mm height, 50 mm diameter) with a ball-to-powder weight ratio of 20:l were used. The vial temperature was held at below 375 K during the experiments by air cooling. The milling process was cyclic with 5 min of treatment and 25 min of cooling time. The rotation speed was equal to 1480 rpm; the acceleration was equal to 50 *g*, the pressure for a substance particle was about 5 GPa).

X-ray powder diffraction data were collected with DRON-4 automatic diffractometer (CoK_α radiation). The diffraction patterns were obtained in a discrete mode under the following scanning parameters: observation range $2\theta = (20 - 100)$ °, step scan of 0.05 °, counting time per step at 3 s. The peak positions and integral intensities of the observed reflections were determined using full profile analysis.

The original software package developed for the automated DRON equipment has been used for analysis and interpretation of the X-ray diffraction (XRD) data obtained. This software package includes full complex of standard Rietveld refinement procedure, namely, determination of both peak positions and integral intensities of the Bragg reflections by means of full profile analysis; carrying out qualitative and quantitative phase analysis using PDF data for phase identification and least square method for lattice constants refinement; testing of the structure models and refining the crystal structure parameters (including coordinates, degree of atomic position filling, texture, etc.).

The Vickers microhardness tests were performed with PMT-3 apparatus at room temperature. The surface of the samples was mechanically polished with diamond paste.

II. Results and discussion

To clarify the data on the nature of the titanium and copper atoms interaction in a ball mill [6], two mixtures for Ti-Cu composition (without MWCNT) containing of 25 wt% (20.1 at. %) and 33.3 wt. % (27.3 at.%) of copper have processes at the first stage of this research. According to the results of the X-ray phase analysis, the samples of these compositions contain mainly primary metals (titanium and copper) with a small admixture of intermetallic Ti_3Cu (Table 1) after 60 min of processing in the mill. The lattice periods of these phases are close to those of the initial metals, namely, $a = 0.4156$ nm and $c = 0.3594$ nm for Ti_3Cu, and $a = 0.2950$ nm and $c = 0.4686$ nm for titanium atoms and $a = 0.3620$ nm for copper atoms. At the same time, all reflections on the diffraction patterns are broadened, which indicates the fine crystallinity of the obtained synthesis products.

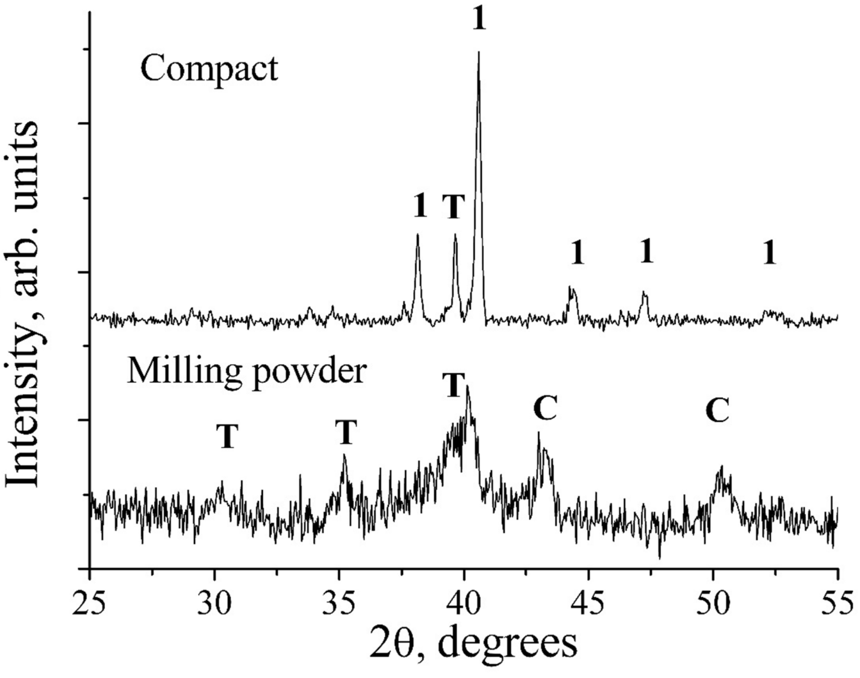

Fig. 1. Diffrcation patterns of mechanically alloyed powder system of Ti:Cu (3:1) with 1 vol. % of MWCNT with further sintering at 980 °C of this charge (compacted sample): T - Ti, C - Cu, 1 - Ti_2CuC_x.

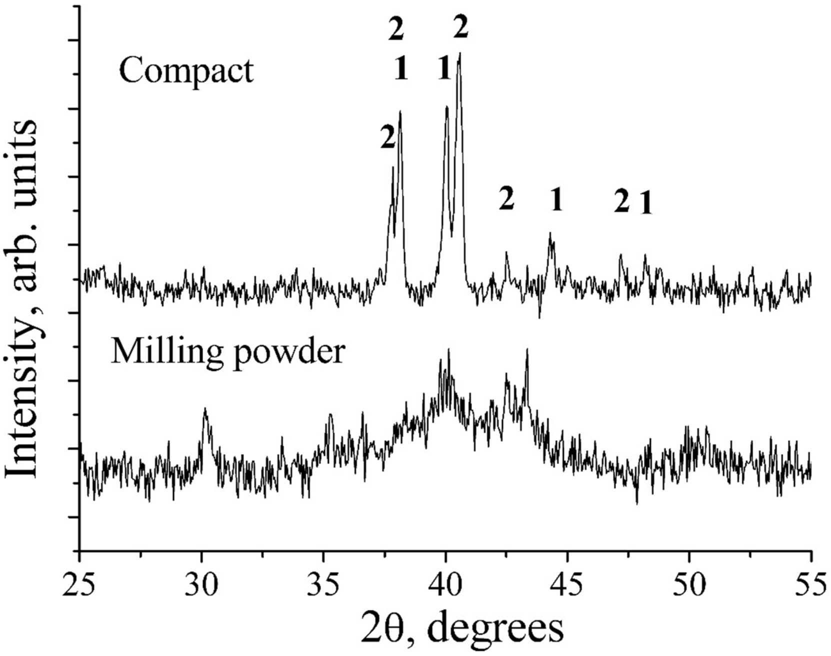

Fig. 2. Diffrcation patterns of mechanically alloyed powder system of Ti:Cu (3:1) with 1 vol. % of MWCNT with further sintering at 980 °C of this charge (compacted sample): 1-Ti_2CuC_x, 2-$Ti_3Cu_2C_x$.

Moreover, the subsequent processing of these powders (over 60 minutes) resulted in sticking the synthesized material to the working surfaces of a vial and milling balls, and the material itself turned out to be X-ray-amorphous, as the authors of Ref. [6] have revealed a tendency to amorphization of the titanium-copper alloys.

Further XRD study of the products of mechanochemical interaction of the two mentioned Ti-Cu compositions was performed for a charge containing 1 vol. % of MWCNT. According to the phase analysis (Table 1), 60 min milled charge with 20.1 at.% Cu contains a significant amount of raw metals along with Ti_3Cu (Fig. 1), while the processed charge with 27.3 at. % Cu is a single-phase product (Fig. 2,). In addition, the comparison of XRD results for charges without and with MWCNT (Table 1) indicates that carbon nanotubes contribute to the interaction of titanium and copper atoms, which leads to the formation of Ti_3Cu intermetallic. Since X-ray reflections of this compound have been significantly broadened (Fig. 1, 2), the average size of its grains was estimated using the Williamson-Hall plot. As a result, it was found that the Ti_3Cu intermetallic formed in the final products of the mechanochemical synthesis is a nanoscaled phase with a grain size of about 7 nm.

The powders synthesized were compacted in two ways, namely, by sintering at 980 °C with or without previous cold pressing at room temperature. As a result of the X-ray study, it was found that the phase composition of the samples compacted is absolutly different from that of the milled powders.

Thus, the heat treatment of a 60 min milled charge of 25 wt. % (20.1 at.%) of Cu (the compact sintered at 980 °C, Table 1) results in a formation of a new phase that is indexed well in *fcc* lattice with *a* = 1.1514 (3) nm (marked as Ti_2CuCx carbide) along with a raw titanium reflections. The lattice period meaning and typical displacement of the diffraction peaks on a diffractogram of this sample (Fig. 1) lets us to suggest that this phase crystallizes in the Ti_2Ni structural type with interstitial carbon atoms. This assumption is entirely natural, since it is in this structural type the well-known Ti_2Cu intermetallic crystallizes. That is why the refinement of the crystalline structure of the mentioned Ti_2CuC_x carbide was carried out in a model of known Ti_2Ni type with a calculation of several variants of the location of interstitial carbon atoms. One of the proposed variants, which provides the best correspondence between experimental and calculated values of the intensity of the reflections, is presented in Table 2. This variant of the placement of atoms in the crystalline structure of the Ti_2CuC_x carbide indicates that the structure is somewhat defective in Cu (calculated composition corresponds to 30.8 at.% Cu, not 33.3 at.%) and contains a small amount of carbon atoms that are immersed in it (only 0.5 at.%). So, the crystalline structure of this carbide is slightly different from the generative Ti_2Cu intermetallic structure.

In the meantime, the nanoscaled Ti_3Cu intermetallic (powder with 27.3 at.% Cu) under high temperature is transformed into a mixture of the described Ti_2CuC_x cubic carbide and $Ti_3Cu_2C_x$ phase whose diffraction spectrum is indexed well in the tetragonal lattice with *a* = 1.1985(2) nm, *c* = 0.3044(1) nm (Fig. 2). Unfortunately, only the Ti_3CuN nitride with an unknown crystalline structure, but close to the values of the tetragonal crystalline lattice, was detected as suitable for identification. The calculation of several variants of the

Table 2

Crystallographic data of triple carbides formed by sintering of products of mechanochemical synthesis of Ti-Cu-MWCNT charge

Ti_2CuC_x					
Atom	Site	Site occ.	*X*	*Y*	*Z*
Ti(1)	*48f*	1,00(1)	0,449(1)	0,125	0,125
Ti(2)	*16c*	1,00(1)	0	0	0
Cu(1)	*32d*	0,82(1)	0,209(1)	0,209(1)	0,209(1)
Cu(2)	*16e*	0,16(1)	0,5	0,5	0,5
C(1)	*8a*	0,06(1)	0,125	0,125	0,125
Space group			*Fd3m, N 227*		
Lattice constant, *a*, nm			1,1516(3)		
Independent reflections			34		
Temperature correction, nm^2			$B = 2{,}89(1)\cdot 10^{-2}$		
Calculated phase content, at. %			68,6 Ti; 30,8 Cu; 0,6 C		
Reliability factor			$R_W = 0{,}078$		
$Ti_3Cu_2C_x$,					
Atom	Site	Site occ.	*X*	*Y*	*Z*
Ti(1)	*2a*	1,00(1)	0	0	0
Ti(2)	*8j*	0,64(2)	0,128(1)	0,182(1)	0,5
Ti(3)	*8j*	0,76(2)	0,423(1)	0,228(1)	0
Ti(4)	*4g*	1,00(1)	0,301(2)	0,199(2)	0
Ti(5)	*4h*	0,24(1)	0,250(1)	0,250(2)	0,5
Cu(1)	*4h*	1,00(1)	0,401(1)	0,099(1)	0,5
Cu(2)	*4g*	0,64(1)	0,099(1)	0,401(1)	0
Cu(3)	*8j*	0,64(1)	0,995(1)	0,206(1)	0,5
C(1)	*4i*	0,33(1)	0	0,5	0,25
Space group			*P4/mbm, N 127*		
Lattice constants, *a*, *c*, nm			1,1986(7); 0,3042(2)		
Independent reflections			80		
Temperature correction, nm^2			$B = 3{,}89(1)\cdot 10^{-2}$		
Calculated phase content, at. %			58,3 Ti; 37,5 Cu; 4,2 C		
Reliability factor			$R_W = 0{,}076$		

arrangement of atoms by regular systems of points of the *P4/mbm* spatial group (this spatial group was identified for Ti3CuN nitride) led to a completely correct model of $Ti_3Cu_2C_x$ carbide structure (Table 2, Fig. 3). This phase can be considered as a new structural type of inorganic compounds. According to the calculated composition of the compound, it is defective in both titanium and copper atoms, and also contains a certain amount of carbon atoms (4.2 at.%) embedded in the tetrahedral voids of the metal lattice (Fig. 3).

Thus, triple carbides Ti_2CuC_x and $Ti_3Cu_2C_x$ are formed as a result of heat treatment (980 °C) of products of the mechanochemical synthesis of the charge with 20 - 27 at. % of Cu. The crystalline structure of one of which is determined for the first time and attributed to a new, previously unknown structural type (Table 2, Fig. 3).

Microhardness (Vickers) of compacted samples varies substantially within (6.9-7.1) GPa. That is, the average microhardness of the synthesized materials is significantly higher than the average pure titanium microhardness (0.97 GPa [13]) and more particularly copper (0.37 GPa [13]), regardless of phase composition (content of Ti_2CuC_x and $Ti_3Cu_2C_x$ carbides, and also related phases). So, the addition of insignificant amount of MWCNT to alloys containing 20 - 27 at. % Cu have a significant effect on the phase composition of both the products of the mechanochemical synthesis of Ti-Cu-MWCNT compositions and on the phase composition of the sintered samples. This, in turn, leads to a fact that the microhardness of these samples substantially exceeds the values inherent to the compact Ti-Cu alloys and the CP titanium (1.4 - 2.7 GPa) [2].

Thus, using the method of mechanochemical synthesis of mixtures of Ti-Cu-MWCNT at the first technological stage, the new triple Ti_2CuC_x and $Ti_3Cu_2C_x$ carbides (containing 0.5 and 4.2 at.% of carbon atoms, respectively) were synthesized for the first time. Their crystal structure has determined by XRD phase analysis. As the content of the mixed compositions (20.1 and 20.7 at.% Cu) turned out to be different from that inherent to indicated carbides (30.8 and 37.5 at.% Cu for Ti_2CuC_x and $Ti_3Cu_2C_x$, respectively), further work is planned to be carried out on stoichiometric mixtures for these compounds. Then, in the case of the synthesis of single-phase carbide compounds Ti_2CuC_x and $Ti_3Cu_2C_x$, it would be reasonable to study microhardness and other mechanical features (such as plasticity, durability, elasticity) to determine the areas of application of these materials.

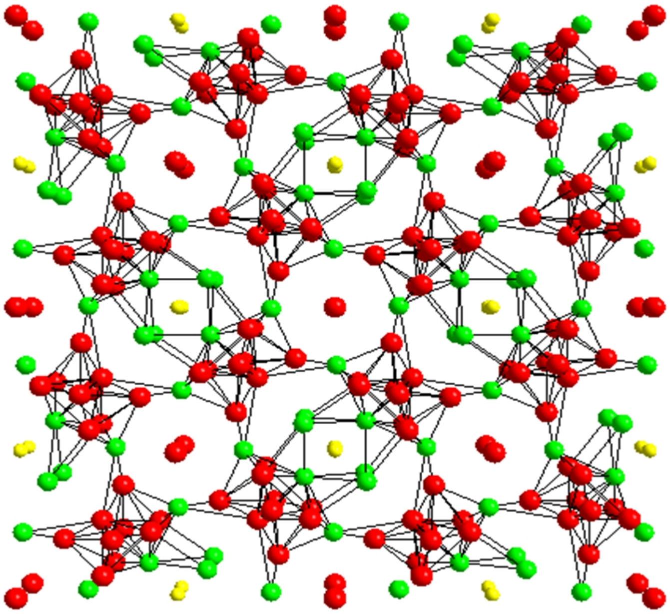

Fig. 3. Structure projection of $Ti_3Cu_2C_x$ carbide on XY plane: black circles are titanium atoms; grey circles are copper atoms; light circles are carbon atoms.

Conclusions

In this work, new triple carbides Ti_2CuC_x and $Ti_3Cu_2C_x$ (containing 0.5 and 4.2 at.% of MWCNT and 30.8 and 37.5 at.% of Cu, respectively) were synthesized for the first time during sintering of products of mechanochemical synthesis of Ti and Cu powders with multiwalled carbon nanotubes. Their crystal structures have defined and described.

Microhardness (Vickers) of the compacted samples was found to be 7 times higher than the microhardness of pure titanium.

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Нові карбіди Ti_2CuC_x та $Ti_3Cu_2C_x$, отримані спіканням продуктів механохімічного синтезу шихти Ti-Cu з добавками вуглецевих нанотрубок

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Механохімічною активацією у високоенергетичному планетарному кульовому млині з порошків титану та міді (розмір частинок ~ 90 μм, чистота не нижче 99,6 мас.%) синтезовано системи Ti:Cu із співвідношенням компонент 2:1 та 3:1. Результатом додавання до шихти 1 об. % багатошарових вуглецевих нанотрубок (БВНТ, середній діаметр 10 – 20 нм) є вперше синтезовані нанорозмірні карбіди Ti_2CuC_x та $Ti_3Cu_2C_x$ (із вмістом 0,5 та 4,2 ат. % вуглецю та 30,8 та 37,5 ат. % міді, відповідно). Дослідження характеру взаємодії після обробки компонентів шихти в млині проведено з використанням комплексу рентгенівських методик, а саме, повнопрофільного аналізу первинної обробки дифрактограм, отриманих на апараті ДРОН-3М; якісного і кількісного фазового аналізів для визначення фазового складу продуктів синтезу; рентгеноструктурного аналізу для перевірки і уточнення структурних моделей; методики Вільямсона-Холла для визначення розмірів зерен синтезованих карбідів. Показано, що модель структури карбіду $Ti_3Cu_2C_x$ можна розглядати як новий, описаний вперше структурний тип, вона є дефектною як по титану так і по міді, і містить певну кількість вуглецю (4,2 ат. %), який занурюється в тетраедричні пори металічної гратки. Визначено, що мікротвердість компактованих зразків із 20,1 та 27,3 ат.% Cu є неоднорідною за значеннями величини, які змінюються в основному в межах (6,9 - 7,1) ГПа, тобто, середня величина мікротвердості синтезованих матеріалів у 7 разів перевищує величину мікротвердості чистого титану.

Ключові слова: багатошарова вуглецева нанотрубка, нанокомпозиційний матеріал, рентгенівська дифракція, мікротвердість.