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STRUCTURE AND PROPERTIES OF NANOSCALE AND MESOSCOPIC MATERIALS

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Effect of the Carbon Nanotubes on Oxidation Behaviour of Mechanically Alloyed Y–Cu Powders

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A set of experiments on mechanical alloying of Cu and Y powders of two compositions is performed in a high-energy planetary mill in air. The first composition consists of equiatomic Y–Cu mixture, while the second composition contains an admixture of 1% vol. of multiwalled carbon nanotubes (CNTs). The synthesis products of Y–Cu and Y–Cu–CNT mixtures, selected after each 10 min of processing, are studied by a combination of X-ray diffraction methods (qualitative and quantitative phase analysis, refinement of the crystal structure of individual phases). Based on the data obtained, the effect of atmospheric oxygen and carbon dopants (CNTs) on the phase composition and the crystalline structure of reaction products are analyzed. As shown, the oxidation of reaction products is accompanied by the formation of a mixture of oxygen-containing phases, namely, $Y_2O_3/Y_{1-x}Cu_xO$ for the Y–Cu composition and $Y_2O_3/Y_{1-x}Cu_xO_{0.5}C_{0.5}$ for the Y–Cu–CNT composition. Moreover, it is established that $Y_{1-x}Cu_xO$ oxide and $Y_{1-x}Cu_xO_{0.5}C_{0.5}$ carboxide (both crystallized in a NaCl type structure) are the substitutional solid solutions, the copper content of which increases to 25 at.%. As shown, the phase transformations during Y–Cu mixture processing occur 10 min earlier than similar transformations during Y–Cu–CNT mixture processing, which means that the carbon dopants (in form of CNTs) could be an oxidation inhibitor at mechanochemical synthesis.

Key words: composite material, carbon nanotubes, nanocrystalline material,

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powder metallurgy, crystal structure, X-ray diffraction.

У високоенергетичному планетарному млині на повітрі проведено механічне легування двох еквіатомних сумішей порошків міді та ітрію, одна з яких додатково містила 1% об. багатошарових вуглецевих нанотрубок (ВНТ). Продукти синтезу Y–Cu і Y–Cu–ВНТ сумішей, відібрані через кожні 10 хв витримки, було досліджено сукупністю методів рентґенівської дифракції (якісний і кількісний фазовий аналіз, уточнення кристалічної структури окремих фаз). На підставі отриманих даних проаналізовано вплив Кисню повітря і Вуглецю (ВНТ) шихти на фазовий склад продуктів розмелювання та кристалічну структуру оксидів. Показано, що в процесі механічного леґування окиснення продуктів синтезу супроводжується утворенням сумішей кисневмісних фаз, а саме, $Y_2O_3/Y_{1-x}Cu_xO$ для шихти Y–Cu і $Y_2O_3/Y_{1-x}Cu_xO_{0,5}C_{0,5}$ для шихти Y–Cu–ВНТ. Більше того, встановлено, що оксид $Y_{1-x}Cu_xO$ і карбооксид $Y_{1-x}Cu_xO_{0,5}C_{0,5}$ (обидва кристалізуються в структурі типу NaCl) є твердими розчинами заміщення, вміст Міді в яких зі збільшенням часу розмелювання збільшується до ≅25 ат.%. Показано, що фазові перетворення при обробці шихти YCu відбуваються на 10 хв раніше, ніж аналогічні їм перетворення при обробці шихти Y–Cu–ВНТ, а відтак, добавка вуглецю у вигляді ВНТ може бути інгібітором окиснення продуктів механохімічного синтезу.

Ключові слова: композиційний матеріал, вуглецеві нанотрубки, нанокристалічний матеріал, порошкова металургія, кристалічна структура, рентґенівська дифракція.

В высокоэнергетической планетарной мельнице на воздухе проведено механическое легирование двух эквиатомных смесей порошков меди и иттрия, одна из которых дополнительно содержала 1% об. многослойных углеродных нанотрубок (УНТ). Продукты синтеза Y–Cu и Y–Cu–УНТ смесей, отобранные через каждые 10 мин выдержки, были исследованы совокупностью методов рентгеновской дифракции (качественный и количественный фазовый анализ, уточнение кристаллической структуры отдельных фаз). На основании полученных данных проанализировано влияние кислорода воздуха и углерода (УНТ) шихты на фазовый состав продуктов размола и кристаллическую структуру оксидных фаз. Показано, что в процессе механического легирования окисление продуктов синтеза сопровождается образованием смесей кислородосодержащих фаз, а именно, $Y_2O_3/Y_{1-x}Cu_xO$ для шихты Y–Cu и $Y_2O_3/Y_{1-x}Cu_xO_{0,5}C_{0,5}$ для шихты Y–Cu–УНТ. Более того, установлено, что оксид $Y_{1-x}Cu_xO$ и карбооксид $Y_{1-x}Cu_xO_{0,5}C_{0,5}$ (оба кристаллизуются в структуре типа NaCl) являются твёрдыми растворами замещения, содержание меди в которых с увеличением времени размола увеличивается до ≅25 ат.%. Показано, что фазовые превращения при обработке шихты Y–Cu происходят на 10 мин раньше, чем аналогичные им превращения при обработке шихты Y–Cu–УНТ, а значит, легирующая добавка углерода в виде УНТ может являться ингибитором окисления продуктов механохимического синтеза.

Ключевые слова: композиционный материал, углеродные нанотрубки, нанокристаллический материал, порошковая металлургия, кристалличе-

ская структура, рентгеновская дифракция.

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1. INTRODUCTION

The powder materials containing mainly equiatomic YCu compound with full ordered CsCl-type structure have been successfully synthesized by mechanical alloying either in air [1] or in argon atmosphere [2]. It was shown that the materials, compacted from the preparing in such way powders, exhibit a nanoscale microstructure and are characterized by an increased microhardness value (almost twice as high as that of bulk YCu obtained by arc melting) and relatively low value of the Young's modulus. More specifically, for these materials, an average value of the Vickers hardness H_V is equal to 5.0 GPa and the Young's modulus E is equal to 120 GPa [2, 3].

However, it should be noted that the Y_2O_3 oxide was present even if the experiment was carried out in a protective argon atmosphere [2]. The powders obtained already contain two impurity oxide phases, namely Y_2O_3 and YCuO [1] at synthesis in air. Therefore, these results clearly demonstrate that the presence of atmospheric oxygen atoms in the reaction zone significantly affects the phase composition of the synthesis products. Moreover, similar bulk products obtained by arc melting with commercial yttrium metal have revealed the existence of Y_2O_3 oxide, too [4].

The oxidation of the initial yttrium powder results in a shift of the composition of equiatomic YCu synthesis products towards the formation of the intermetallic phases with higher Cu component. So, the impurity YCu_2 phase is formed at mechanical alloying under argon atmosphere [2] or both YCu_2 and YCu_5 phases are formed successively at mechanical alloying in air [1]. Considering this, it is important to choose the dopant being an oxidation inhibitor at the synthesis of YCu compound by mechanical alloying method. Moreover, it is the carbon dopant, which could be tested as the effective corrosion inhibitor for the YCu synthesis.

Here we present the results of study of the phase transformations occurred at the milling in air of the equiatomic Y–Cu powder mixture and Y–Cu–CNT blend in a high energy planetary ball mill.

2. EXPERIMENTAL DETAILS

The crushed particles of yttrium (99.8% wt. purity, particle sizes of ≅150 μm) and copper powder (99.5% wt., ≅150 μm) were used to prepare a charge of equiatomic YCu composition. Another charge contains 1% vol. of multiwalled carbon nanotubes (CNT) in addition to Y–Cu

equiatomic powder mixture. Multiwalled CNTs used in this experiment were synthesized by the catalytic chemical vapour deposition method (CVD) at TM Spetsmash Ltd. (Kyiv, Ukraine) [5]. Parameters of 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 poured bulk density varies from 20 to 40 g/dm^3. Both charges were thoroughly mixed and placed into two stainless vials. Mechanical alloying of the charges has been performed in a high energy planetary ball mill. The hardened stainless balls were used to carry out the experiments. The rotation speed was equal to 1480 rpm; the acceleration was about 50 *g;* the pressure for a substance particle reached 5 GPa. The cycled milling process (10 min of treatment and 25 min of cooling time) was carried out in the air. Vial temperature was held at below 375 K during the experiments.

Phase transformations have been studied by X-ray diffraction methods on test samples selected after each 10 min of milling. XRD data was collected with DRON-3M automatic diffractometer (CuK_α radiation) in a discrete mode under the following scanning parameters: observation range $2\theta = (20–100)°$, step scan of 0.05° and counting time per step at 3 s. The original software package, including full complex of standard Rietveld procedures, has been used for analysis and interpretation of the X-ray diffraction patterns obtained, 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 the least square method for lattice parameters refinement; testing of the structure models and refining crystal structure parameters (including coordinates of atoms, atomic position filling, texture, *etc.*) [1]. More details are presented at www.x-ray.univ.kiev.ua.

3. RESULTS AND DISCUSSION

According to results of the XRD phase analysis a small amount of YCu phase has already been detected in the Y–Cu sample processed for 20 min in a ball mill, while in Y–Cu–CNT samples the YCu phase was appeared only after 30 min of processing. Further treatment of both mixtures in a ball mill leads first to the appearance of oxides, amount of which gradually increases, and second to appearance of intermetallic $YCu \rightarrow YCu_2 \rightarrow YCu_5$ phases [1]. Moreover, according to XRD results similar phase transformations occur at processing of the Y–Cu–CNT charge with a delay by 10 min. Therefore, after 40 min of processing the test sample of Y–Cu–CNT charge contains YCu and YCu_2 intermetallics only while the test sample of Y–Cu charge contains some amount of the oxide phase already (Fig. 1).

Since the phase transformations of intermetallic phases at mechani-

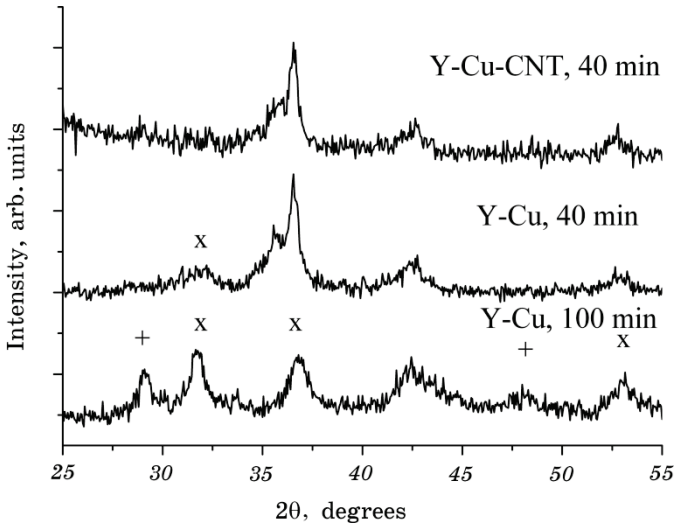

Fig. 1. Fragments of diffraction patterns of the test samples processed in a ball mill. Reflections of Y_2O_3 are marked as '+', of $Y_{1-x}Cu_xO$ are marked as 'x', other reflections belong to the intermetallics.

cal alloying of Y–Cu and Y–Cu–CNT charges are quite similar and described in Ref. [1], here the main attention will be directed to the phase transformations of oxides. So, it was shown that the reflections on diffraction pattern belonging to the first oxide phase (being named preliminary as 'YO'), which appears at mechanical alloying of both charges, are indexing well in a cubic lattice with the NaCl-type crystal structure. The Y_2O_3 oxide is formed in samples with further processing. According to the results of quantitative phase analysis the total content of the coexisting 'YO' and Y_2O_3 oxides (Fig. 1) gradually increases with milling time increasing (Fig. 2).

The lattice parameters of the 'YO' oxides depend on the milling time for both charges (Fig. 3, *a*). So, in order to identify the features of crystal structure of these oxides, the calculations required have been made in a framework of the NaCl-type structure (*Fm3m* space group). In this model both Y and Cu atoms are placed in 4(*a*) (0, 0, 0) position, while O and C (for CNT containing samples) atoms are placed in 4(*b*) (0.5, 0.5, 0.5) position. As a result of crystal structure refinement performed for oxides existing in each test sample studied the following features were found:

1. Oxides forming at processing of the Y–Cu charge in a ball mill contain ≅50 at.% of oxygen atoms, and they are characterized by gradual substitution of yttrium atoms with the copper atoms with milling time increasing. So, the general formula of these oxides could be written as $Y_{1-x}Cu_xO$.

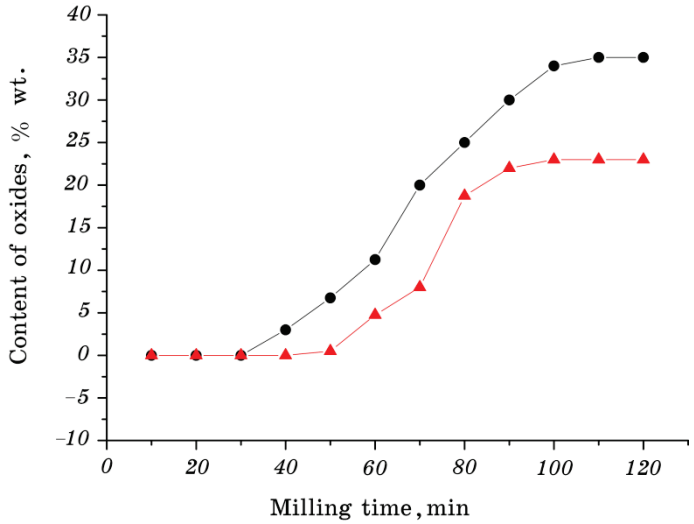

Fig. 2. Fraction of the oxide phases in the synthesis products of Y–Cu (circles) and Y–Cu–CNT (triangles) charges.

2. Oxides forming at processing of the Y–Cu–CNT charge in a ball mill contain approximately equal amount of oxygen and carbon atoms (each of ≅25 at.%) and these oxides are characterized by gradual substitution of yttrium atoms with the copper atoms, too. Therefore, the general formula of these oxides could be written as $Y_{1-x}Cu_xO_{0.5}C_{0.5}$.

Thus, the formation of $Y_{1-x}Cu_xO$ and $Y_{1-x}Cu_xO_{0.5}C_{0.5}$ substitution solid solutions is exactly the reason, which leads to a significant decrease of their lattice parameters (Fig. 3). As far as we know, the cubic 'YO' binary oxide does not exist, but the lattice parameters (Fig. 3) for cubic $Y_{1-x}Cu_xO$ oxide studied are similar to those of rhombohedrally distorted 2*R*- or 3*R*-$YCuO_{2+\delta}$ oxides with $a_H = 0.352$ nm [6]. On the other hand, lattice parameter of the known $YC_{0.33}$ carbide with NaCl-type structure is somewhat higher (0.5102 nm [7]) than that of starting value of lattice parameter for $Y_{1-x}Cu_xO_{0.5}C_{0.5}$ ($x = 0.1$), while this starting value is similar to that for Y_2OC oxycarbide (0.4948 nm [8]). Previously $YC_{0.44}$ binary carbide with $a = 0.5015$ nm was successfully synthesized by us after 60 min of milling the Y–CNT charge [9]. It was found that the lattice parameter of the Y_2O_3 oxide formed at processing of the both charges in a ball mill dose not change ($a = 1.060(1)$ nm).

Therefore, the results obtained have revealed that the phase transformations at milling in the air of the equiatomic Y–Cu and Y–Cu–CNT charges follow the schemes:

$$Y + Cu \rightarrow Y + YCu + YCu_2 \xrightarrow{O_2} Y_{1-x}Cu_xO + Y_2O_3 + YCu_5$$

and

$$Y + Cu \rightarrow Y + YCu + YCu_2 \xrightarrow{O_2} Y_{1-x}Cu_xO_{0.5}C_{0.5} + Y_2O_3 + YCu_5,$$

respectively.

Moreover, the formation of similar intermetallic compounds or oxides at processing of the Y–Cu charge occurs faster than at processing of the Y–Cu–CNT charge. Thus, the carbon (in a form of CNT) dopants (1% vol.) are the oxidation inhibitors for the synthesis of intermetallics by mechanical alloying method.

Note that in order to suppress the oxidation of YCu material synthesized, it seems reasonable to add no more than 1% vol. CNT to the initial Y–Cu charge, since the addition of higher number of nanotubes could lead to a change in the phase composition of the synthesis product due to the formation of carbide phases. However, in our previous study [8] has revealed that test samples selected after 120 minutes of processing the charge in a high-energy ball mill already contain two

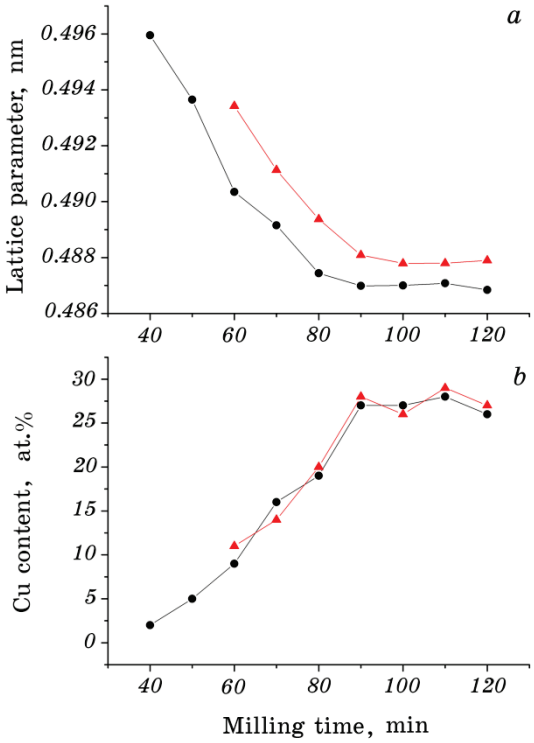

Fig. 3. Dependences of the lattice parameters (*a*) and Cu content (*b*) in the oxides with NaCl-type structure formed in the Y–Cu (circles) and the Y–Cu–CNT (triangles) charges on a milling time.

yttrium carbides in a case of mechanical alloying of Y–CNT charge with a 2–4% vol. CNT. These carbides are the known $YC_{0.44}$ carbide with lattice parameter $a = 0.5015$ nm and new YC_x carbide, the diffraction spectrum of which was indexed in a hexagonal lattice with periods $a = 0.9041$ nm, $c = 0.6296$ nm. Therefore, in the framework of this work, to prevent the possible formation of yttrium carbides, CNT content in a charge does not exceed 1% vol., since this quantity of nanotubes was intended to suppress the oxidation of YCu material studied, and would not initiate the formation of undesirable carbide phases.

Previously it has been shown that gallium dopants increase the oxidation resistance of some dental titanium alloys [10]. Therefore, it would be interesting to test CNT together with gallium dopant as a corrosion inhibitor for the Y and Cu powders at processing in a ball mill, since the gallium additives form an extended solid solution not only with copper and yttrium metals but also with the most compounds of the Y–Cu system [11].

4. CONCLUSION

Phase transformations at simultaneous mechanical alloying in air of equiatomic Y–Cu mixture and Y–Cu–CNT blend (1% vol. of CNT) have been studied by XRD methods, including qualitative and quantitative phase analysis as well as refinement of the crystal structures of the phases formed at processing in a ball mill.

The effect of atmospheric oxygen and CNT on the phase composition of the milling products obtained has revealed. The oxidation of the synthesis products is accompanied by the formation of a number of oxygen-containing phases, namely, Y_9O_8 and $Y_{1-x}Cu_xO$ for the Y–Cu charge and Y_2O_3 along with $Y_{1-x}Cu_xO_{0.5}C_{0.5}$ for the Y–Cu–CNT charge. Moreover, it was established that $Y_{1-x}Cu_xO$ oxide and $Y_{1-x}Cu_xO_{0.5}C_{0.5}$ carboxide (both crystallized in a NaCl-type structure) are substitution solid solutions, the copper content of which increases up to ≅25 at.%. In whole, carbon dopants (1% vol.) in a form of CNT act as oxidation inhibitors for the synthesis of Y–Cu intermetallics at mechanical alloying.

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