ФАЗОВЫЕ ПРЕВРАЩЕНИЯ

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Phase Transformations in Equiatomic Y−Cu Powder Mixture at Mechanical Milling

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Mechanical alloying of the elemental powder mixture of copper and yttrium is performed in a high-energy planetary ball mill. The equiatomic YCu compound with full ordered CsCl-type structure is synthesized by use of powder-metallurgy methods for the first time. Phase transformations taking place at Y−Cu mixture milling are studied by x-ray diffraction methods. An expanded description of original software package for the automated DRON apparatus is presented. This software is used for analysis and interpretation of the obtained x-ray diffraction data. This package is intended for solving different tasks, namely: determination of both peak positions and integral intensities of the Bragg reflections by means of full profile analysis; carrying out the qualitative and quantitative phase analyses using PDF (Powder Diffraction File) data for phase identification and the least square method for lattice-constants' refinement; testing the structure models and refining crystal-structure parameters (including coordinates, atomic position filling, texture, *etc.*). The effect of oxygen on the phase composition of milling products is analysed. As revealed, the mixture of two oxides (Y_2O_3 and $YCuO$) is forming at the last stage of the milling in the air. So, the phase transformation during milling of the equiatomic Y−Cu charge in the air follows the reaction $Y + Cu \rightarrow YCu + YCu_2 \rightarrow YCu_2 + O_2 \rightarrow Y_2O_3 + YCuO + YCu_5$. Only the first stage of this transformation is realized in the case of synthesis under

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argon atmosphere.

Key words: composite material, powder metallurgy, crystal structure, X-ray diffraction.

У високоенергетичному планетарному млині проведено механічне леґування еквіатомової суміші порошків міді й ітрію. Вперше еквіатомову сполуку YCu з повністю упорядкованою структурою типу CsCl одержано методами порошкової металурґії. Фазові перетворення, що мають місце при розмелюванні суміші Y−Cu, досліджено методами рентґенівської дифракції. Представлено розширений опис комплексу програм, розробленого авторами для автоматичного рентґенівського апарата типу ДРОН. Це програмне забезпечення призначено для вирішення різноманітних завдань, зокрема, визначення як позиції піків, так і інтеґральної інтенсивности Бреґґових відбиттів методою повнопрофільної аналізи, проведення кількісної та якісної фазових аналіз із використанням банку даних для ідентифікації фази та методи найменших квадратів для уточнення параметрів ґратниць, тестування структурних моделів та уточнення параметрів кристалічної структури (координати, заповнення атомових позицій, текстура тощо). Проаналізовано вплив кисню на фазовий склад продуктів розмелювання в планетарному кульовому млині. Встановлено, що в результаті механічного леґування утворюється суміш оксидів $Y_2O_3 + YCuO$. Таким чином, фазові перетворення під час розмелювання на повітрі еквіатомової шихти Y−Cu перебігають за реакцією: $Y + Cu \rightarrow YCu + YCu_2 \rightarrow YCu_2 + O_2 \rightarrow Y_2O_3 + YCuO + YCu_5$. І лише перша частина цих трансформацій реалізується у випадку синтези в атмосфері арґону.

Ключові слова: композиційний матеріял, порошкова металурґія, кристалічна структура, рентґеноструктурна аналіза.

В высокоэнергетической планетарной мельнице проведено механическое легирование эквиатомной смеси порошков меди и иттрия. Впервые эквиатомное соединение YCu с полностью упорядоченной структурой типа CsCl получено методами порошковой металлургии. Фазовые превращения, протекающие при размоле смеси Y−Cu, исследованы методами рентгеновской дифракции. Представлено расширенное описание комплекса программ, разработанного авторами для автоматического рентгеновского аппарата типа ДРОН. Это программное обеспечение предназначено для решения разнообразных задач, в частности, как для определения позиции пиков, так и интегральной интенсивности брэгговских изображений методом полнопрофильного анализа, проведения количественного и качественного фазового анализа с использованием банка данных для идентификации фазы и метода наименьших квадратов для уточнения постоянных решетки, тестирования структурных моделей и уточнения параметров кристаллической структуры (в том числе координат, заполнения атомных позиций, текстуры). Проанализировано влияние кислорода на фазовый состав продуктов размола. Установлено, что в результате механического легирования образуется смесь оксидов Y_2O_3 и YCuO. Таким образом, при размоле на воздухе эквиатомной шихты Y−Cu в ней происходят следующие фазовые превращения: $Y + Cu \rightarrow YCu + YCu_2 \rightarrow YCu_2 + O_2 \rightarrow Y_2O_3 + YCuO + YCu_5$. И только первая часть этих трансформаций реали-

зуется в случае синтеза в атмосфере аргона.

1. INTRODUCTION

Stoichiometric intermetallic compounds have always been touted for their attractive chemical, electrical, magnetic, and mechanical properties, but few practical uses have materialized because they are brittle at room temperature. Recently, considerable attention of the researchers is paid to a lot of RE–Me equiatomic compounds with CsCl-type structure (RE = Y, Dy, Er, Ho; Me = Cu, Zn, Ag), which even at room temperature characterized by a high plasticity [1].

Among these compounds, the most ductile properties are reported for YAg (>20% elongation for polycrystalline specimen tested under tension at ambient conditions) [2]. Almost as ductile as YAg is the YCu compound with reported values of tensile strength and tensile strain to fracture in the range of 175–300 MPa and (6–11)%, respectively [1, 4]. Polycrystalline YCu compound was shown to occur stress-induced martensitic transformation of the cubic phase to the orthorhombic one from room temperature (RT) down to 77 K (low temperature, LT) [5]. The lattice constants of these YCu phases are as following: $a = 0.3476$ nm (RT-phase, CsCl-type structure) [1], $a = 0.70936$ nm, $b = 0.45254$ nm, $c = 0.54030$ nm (LT, FeB-type structure) [6]. The study of the tensile deformation behaviour of an extruded YCu sample has revealed that the increasing amount of LT-phase leads to a decrease in ductility with temperature decreasing [5]. Therefore, the high ductility of YCu at RT down to 170 K is exceptional for CsCl structured intermetallic.

It is found that the Y–Cu alloys tend to amorphization. Samples completely amorphous have been synthesized by rapid solidification and copper mould casting [7]. This study has revealed that ductile YCu phase embedded in an amorphous matrix results in a low value of hardness, suggesting a possible increase in the plasticity of glassy phase. On the contrary, the presence of the additional YCu_2 phase always leads to a hardening of the materials. Besides, the presence of coarse-grained crystals decreases the hardness values [7].

Traditionally, the samples of YCu compound are produced by arc or induction melting (crystalline alloys) as well as by rapid solidification (amorphous alloys). Synthesis of the YCu samples by the mechanical alloying/milling method has not been applied yet. However, our research [8] has revealed that mechanical alloying of the Fe–Cu–carbon nanotubes powder mixture results in double increase of the tensile strength (from 900 to 1800 MPa) of the composite. This raises the pos-

sibility to obtain materials with advanced characteristics compared to alloys manufactured by the conventional techniques.

In this paper, we present the study on the phase transformation occurred at milling of the equiatomic Y–Cu powder mixture in a high-energy planetary ball mill.

2. EXPERIMENTAL DETAILS

The crushed particles of yttrium (99.8% wt. purity, particle sizes of $\cong 150$ μm) and copper powder (99.5% wt., $\cong 150$ μm) were mixed to give the desired equiatomic composition of Y–Cu. Mechanical alloying of the charge has been performed in a high-energy planetary ball mill, which is a custom made model developed at the Metal Physics and Ceramics Laboratory of the Taras Shevchenko National University of Kyiv on the basis of the 'Gidrotsvetmed' R&D Institute (Novosibirsk) technical drawing (Fig. 1). Hardened stainless steel balls (15 units of 15 mm diameter) and vial (70 mm height, 50 mm diameter) with a ball-to-powder weight ratio of 10:1 were used. The cycled milling process (5 min of treatment and 25 min of cooling time) was carried out either in the air or under an argon atmosphere. The vial temperature was held at below 375 K during 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 full complex of the X-ray diffraction methods (XRD) has been used to study the phase transformation occurred during milling of the equiatomic Y–Cu powder mixture. XRD data was collected with DRON-3 or DRON-4 automatic diffractometers (CuK_α or CoK_α radiation, respectively) for the proof samples selected after a certain milling time. The diffraction patterns were obtained in a discrete mode under
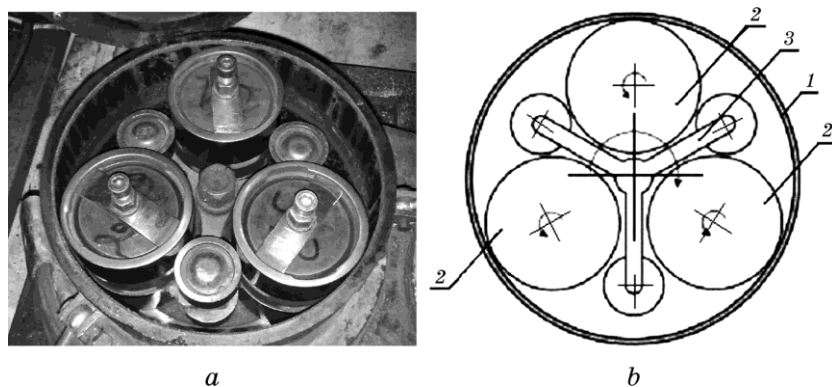

Fig. 1. Overall view (*a*) and operational scheme (*b*) of the high-energy planetary ball mill: *1*—body, *2*—vial with balls, *3*—planetary carrier.

the following scanning parameters: observation range $2\theta = 20-130°$, step scan of $0.05°$, and counting time per step at 3 s.

The original software package developed by us for the automated DRON equipment has been used for analysis and interpretation of the X-ray diffraction data obtained. This package is intended for solving different XRD tasks, namely: determination of both peak positions and integral intensities of the Bragg reflections by means of full profile analysis; carrying out the qualitative and quantitative phase analysis using PDF (Powder Diffraction File) data for phase identification and the least square method for lattice-constants' refinement; testing structure models and refining crystal structure parameters (including coordinates, atomic position filling, texture, *etc*.). The mathematical algorithms realized for these calculations are similar to those, which are used in the WinCSD software [9].

Thus, the different peak shape functions (pseudo-Voigt) are used at the full profile analysis procedure. At that, a refinement of the whole pattern or any of its part is possible. The full width at half maximum can be constrained to a single parameter that is common for all peaks within the experimental range or it may be refined for each peak individually. The asymmetry (a) and mixing parameter (q) are always common for all peaks within the fitting range. The background is refined using a polynomial function.

The parameters of the XRD peak treatment (both peak positions and integral intensities of the Bragg's reflections) are used for a qualitative phase analysis. Interpretation of the XRD data for each sample is implemented with a help of two banks of x-ray diffraction data that integrated directly into the software, namely, Standard PDF-2 Bank and the self-made working bank. The second bank contains entries obtained by calculation of the reference diffraction patterns of the inorganic and intermetallic compounds by use of available information on their crystal structures. Besides, the program of the phase analysis has completed with several graphical and analytical options. Namely, it offers graphical comparison of the experimental diffraction pattern of the sample studied with a standard diffraction pattern form the database; it proposes an analytical comparison of the interplanar distances of the sample and the standard entry; after performing comparison it is able to refine the lattice parameters of each individual phase by the least square method; it is also able to correct analytically the experimental shift of the working surface of the sample on a diffractometer. On the each stage of the interpretation process, the utilization of intensity values of the standard entry allows us to get a residual spectrum by graphical and analytical withdrawing of each well-indexed diffraction peak from the experimental diffraction pattern of the sample. Residual spectrum, which is melt into the background, is the criterion of correctness of the provided phase analysis.

The program for crystal-structure determination is a variety of software that can be used to process the 'pseudo-single crystal' experimental diffraction data represented in a form of individual structure factors or their squares. The algorithms of the most commonly used software products such as SHELXS-90 and SHELXL-97 [10] have been utilized to complete our program for Crystal structure determination. This software allows us to verify the structural models proposed and to refine the crystal structure parameters (atomic coordinates, filling of corresponding atomic positions, temperature and texture parameters, *etc.*).

The method we have developed and realized to determine the quantitative phase content in the mixture containing up to six constituents, is based on the mathematical algorithm of its refinement simultaneously with the crystal structure parameters for each phase (see below).

According to Ref. [11], the peak intensity for each phase could be presented in a form:

$$I(hkl)^i = c_i Q_i \exp[-(\bar{\mu} - \mu_i)d_i]I_0,$$

where $I(hkl)^i$ is the intensity of hkl reflection, c_i is the volume content, Q_i is the reflectivity per unit volume, μ_i is the linear absorption index, d_i is the mean size of particles for the i-th phase constituent, μ is the mean value of the linear absorption index, I_0 is the intensity of the incident beam.

In turn, the reflectivity for the i-th phase constituent could be calculated from the equation

$$Q_i = \frac{I(hkl)^{i0}}{V_i^2},$$

where $I(hkl)^{i0}$ and V_i are the reflection's intensity and unit cell volume for the i-th phase constituent, respectively.

The accuracy of the phase constituent quantity determination was better than 2% wt. when the sample is not (or weakly) textured and when the mean size of particles is small (up to 1 μm) or the linear absorption index for phases in mixture are close to one another ($\bar{\mu} - \mu_i \cong 0$). When at least one of these conditions is violated, it is very important to determine the grain sizes in the phase constituents (using optical microscopy, SEM, *etc.*). Some problems are also related with the correct accounting of texture that may lead to a rise of the errors in the quantitative phase composition determination (up to 6–10% wt.).

3. RESULTS AND DISCUSSION

In order to simplify the sampling technology, the first series of exper-

iments on mechanical milling of the equiatomic Y−Cu powder mixture was carried out under an air atmosphere. According to XRD results, a small amount of YCu phase has already been detected in the sample selected after 20 min of treatment in a ball mill (Table 1, Fig. 2). The initial components of the charge (elemental yttrium and copper) along with the milling products (YCu and YCu_2) are the phase-constitutions of the proof samples up to 40 min of milling time. The highest fraction of YCu phase has been detected in the 40 min milled sample (Fig. 3). Further treatment of the mixture in a ball mill leads to a gradual decrease of YCu phase fraction as well as to appearance of copper-rich YCu_2 phase, fraction of which steady increases up to 60 min of milling time (Table 1, Figs. 2, 3). It should be noted that the lattice constants of YCu phase formed due to mechanical alloying in the air are smaller than those, which are inherent to bulk YCu compound (Fig. 4).

The diffraction patterns of the proof samples obtained after 90 min of milling are formed by the reflections of the Y_2O_3 oxide, copper-rich YCu_5 phase and one more phase with cubic lattice ($a = 0.4863$ nm) (Table 1, Fig. 3).

TABLE 1. Phase composition of the proof samples obtained by treatment in a ball mill (phase content in wt.%).

| Milling time	Phase composition	Lattice constant of YCu, nm
Equiatomic YCu charge treated in the air		
0	Y(51) + Cu(49)	−
10	Y(54) + Cu(46)	−
20	Y(49) + YCu(25) + Cu(25)	0.34719(7)
30	YCu(26) + Y(25) + YCu_2(15) + Cu(34)	0.34725(5)
40	YCu(65) + Y(9) + YCu_2(26)	0.34728(6)
50	YCu(54) + YCu_2O_2(17) + YCu_2(29)	0.34729(8)
60	YCu_2(54) + YCu_2O_2(29) + YCu(16)	0.34729(9)
70	YCu_2O_2(55) + YCu(11) + YCu_2(34)	0.34729(9)
80	YCu_2O_2(70) + YCu_2(30)	−
90	YCu_2O_2(100)	−
100	YCu_2O_2(100)	−
110	YCu_2O_2(100)	−
120	YCu_2O_2(100)	−
Equiatomic YCu charge treated in argon atmosphere		
40	YCu(80) + Y(10) + YCu_2(10)	0.34672
120	YCu(86) + YCu_2(12) + Y_2O_3(2)	0.34771
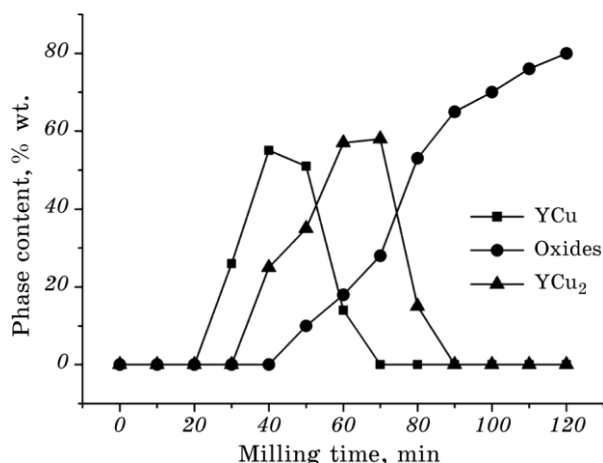
Fig. 2. Phase fractions (% wt.) of the mechanical alloying products versus milling time (equiatomic Y–Cu mixture, treatment in the air).

To check the possibility of the hardness steel wear debris effect on phase transformations studied, an energy-dispersive X-ray spectroscopy has been provided (JEOL JSM-840 microscope). It has been shown that less than 0.5% wt. of additional Fe is introduced into the sample treated of 120 min due to wear debris from the steel balls and vial. This investigation has revealed also the presence of several oxygen phases formed at the last stage of the mechanical alloying of the equiatomic Y–Cu mixture in the air.

Therefore, one more oxygen phase detected in the proof samples at the last stage of milling process in the air coexists with Y_2O_3 oxide (Fig. 3). It was shown that it is not yttrium-copper oxide such as CuO, Cu_2O, $Y_2Cu_2O_5$, YCu_2O_4, $YCuO_2$, *etc*. Taking into account the similarity of diffraction patterns, the Cu_2O-type structure has been proposed and tested for this new oxide (Table 2). Calculations performed here have revealed the stoichiometric YCuO composition for new ternary oxide detected. The fraction of YCuO oxide along with fraction of Y_2O_3 gradually increases with milling time increasing (Table 1).

It should be noted that diffraction pattern of the cubic YCuO oxide (rhombohedral lattice parameters calculated are equal to $a = 0.3439$ nm and $c = 1.684$ nm) is similar to the rhombohedral $YCuO_2$ oxide ($a = 0.3533$ nm and $c = 1.714$ nm).

Taking into account the availability of oxidation during ball milling, the second series of experiments were carried out under argon atmosphere. The diffraction patterns of two proof samples selected after 40 and 120 min of treatment are similar to each other as well as they are similar to diffraction pattern presented in Fig. 3 for the 40 min milled sample. Therefore, the main phase of the proof samples obtained
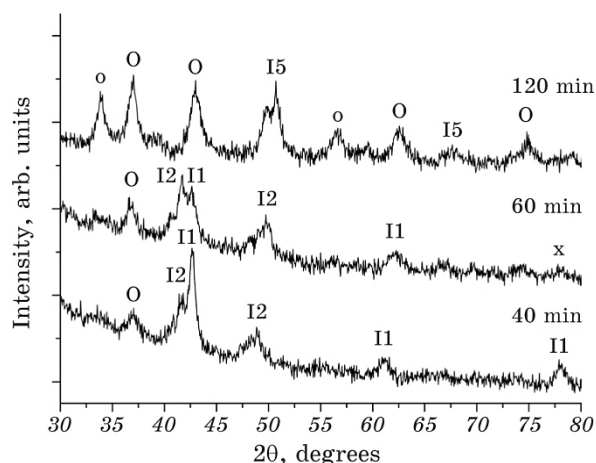
Fig. 3. X-ray diffraction patterns of the powders obtained by mechanical alloying of the equiatomic Y–Cu charge in a ball mill after **40**, **60** and **120** min of milling in the air. Y_2O_3 and YCuO oxides are marked as 'o' and 'O'; YCu, YCu_2 and YCu_5 intermetallics are pointed as 'I1', 'I2' and 'I5', respectively; radiation CoK_α.

under argon atmosphere is the YCu compound with addition of YCu_2 (up to 12% wt.).

Moreover, the crystal structure calculations have revealed that YCu compound is formed in the full ordered CsCl-type structure (Table 2) and its lattice constants (Table 1) are close to those for bulk YCu phase.

Thus, the results obtained in this study have revealed that the phase transformation during milling of the equiatomic Y–Cu charge in the air follows the reaction: $Y + Cu \rightarrow YCu + YCu_2 \rightarrow YCu_2 + O_2 \rightarrow Y_2O_3 +$
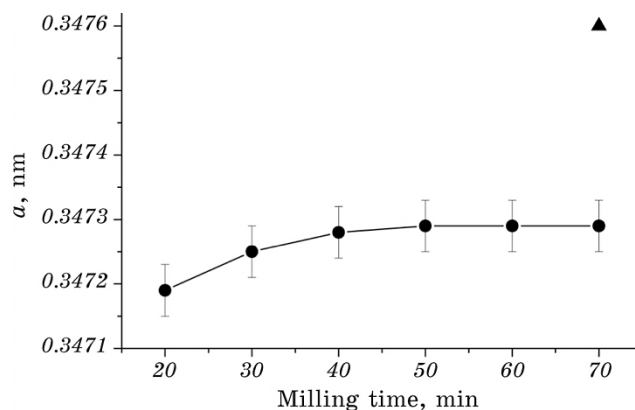

Fig. 4. Lattice parameter of YCu compound (circles) versus duration of the mechanical alloying in the air. The value for bulk YCu is plotted as triangle.

TABLE 2. Crystal data for YCu and YCu_2O_2 compounds formed at milling.

Atom	Site	Site occ.	x	y	z
YCu (CsCl type structure)					
Y	1a	1.00(1)	0	0	0
Cu	1b	1.00(1)	0.5	0.5	0.5
Space group			$Pm3m$ (No. 221)		
Lattice parameters a, nm			0.3476(1)		
Independent reflections			10		
Total isotropic B factor, nm^2			$1.06(1) \cdot 10^{-2}$		
Reliability factor			$R_I = 0.062$		
YCu_2O_2 (own type structure)					
Y	4c	1.00(1)	0.057(2)	0.25	0.791(2)
Cu(1)	4c	1.00(1)	0.254(4)	0.25	0.074(2)
Cu(2)	4c	1.00(1)	0.270(5)	0.25	0.424(3)
O(1)	4c	1.00(1)	0.787(9)	0.25	0.751(9)
O(2)	4c	1.00(1)	0.446(9)	0.25	0.270(9)
Space group			$Pnma$ (No. 62)		
Lattice parameters, a, b, c, nm			0.8408(1), 0.4161(7), 0.8957(3)		
Independent reflections			68		
Total isotropic B factor, nm^2			$3.56(1) \cdot 10^{-2}$		
Reliability factor			$R_I = 0.071$		

$+ YCuO + YCu_5$. Only the first stage of this transformation is realized in the case of synthesis under argon atmosphere.

Therefore, these results clearly demonstrate that the presence of oxygen in the reaction zone significantly affects the phase composition of the mechanical alloying products. Previously, authors of Ref. [12] have found by use of TEM method that bulk YCu compound prepared with commercial yttrium metal have revealed the existence of two impurity phases: Y_2O_3 oxide and YCu_2 intermetallic.

In our experiments, some amount of oxygen could be presented in source metal powders (Y and Cu) as well as in a ball mill reactor (even after its filling with argon). Then, at the initial stage of milling (grinding Y and Cu particles), the reaction of Y_2O_3 formation is the most thermodynamically favourable since for this phase the free energy of formation is much lower (more negative) than for CuO and Cu_2O oxides, namely: $-1816.7 \ kJ \cdot mol^{-1}$ for Y_2O_3, $-149.0 \ kJ \cdot mol^{-1}$ for Cu_2O, and $-129.7 \ kJ \cdot mol^{-1}$ for CuO. The formation of Y_2O_3 causes a deficiency of Y leading to precipitation of Cu-rich phases such as YCu_2 and, as a con-

sequence, deviations the alloy composition from YCu stoichiometry. Although XRD study has not revealed the presence of Y_2O_3 oxide, it could exist in the milling products in the form of fine-grained amorphous phase.

Therefore, our prospective researches on pure YCu material obtaining will be aimed at elimination of the oxygen influence on milling products.

4. CONCLUSION

Phase transformations taking place during mechanical alloying of the equiatomic Y–Cu mixture under an air and argon atmospheres have been studied by XRD methods. For the first time, the equiatomic YCu compound with full ordered CsCl-type structure has been synthesized in a high-energy planetary ball mill.

It has been shown that the oxygen affects significantly the phase composition of the milling products obtained under mechanical alloying in the air. Finally, it leads to the formation of the two oxides (Y_2O_3 and YCuO) mixture. So, the powders of a high purity rather than commercial ones should be used for basic research on single-phase YCu compound to avoid the incorrect results.

REFERENCES

1. K. Gschneidner Jr., A. Russell, A. Pecharsky, J. Morris, Z. Zhang, T. Lograsso, D. Hsu, C. H. C. Lo, Y. Ye, A. Slager, and D. Kesse, *Nature Materials*, **2**, No. 9: 587 (2003).
2. A. M. Russell, Z. Zhang, T. A. Lograsso, C. C. H. Lo, A. O. Pecharsky, J. R. Morris, Y. Ye, K. A. Gschneidner Jr., and A. J. Slager, *Acta Mater.*, **52**, Iss. 13: 4033 (2004).
3. Z. Zhang, A. M. Russell, S. B. Biner, K. A. Gschneidner Jr., and C. C. H. Lo, *Intermetallics*, **13**, Iss. 5: 559 (2005).
4. A. M. Russell, Z. Zhang, K. A. Gschneidner Jr., T. A. Lograsso, A. O. Pecharsky, A. J. Slager, and D. C. Kesse, *Intermetallics*, **13**, Iss. 6: 565 (2005).
5. C.-G. Oertel, R. Schaarschuch, G. H. Cao, H. N. Tian, J. Freudenberger, H.-G. Brokmeier, and W. Skrotzki, *Scr. Mater.*, **65**, Iss. 9: 779 (2011).
6. C. Ritter, M. R. Ibarra, and R. M. Ibberson, *J. Physics: Condensed Matter*, **5**, No. 4: L39 (1993).
7. M. Satta, P. Rizzi, and M. Baricco, *J. Alloys Compd.*, **483**, Iss. 1–2: 50 (2009).
8. O. Boshko, O. Nakonechna, M. Dashevskyi, K. Ivanenko, N. Belyavina, and S. Revo, *Adv. Powder Technology*, **27**, Iss. 4: 1101 (2016).
9. V. K. Pecharsky and P. Y. Zavalij, *Fundamentals of Powder Diffraction and Structural Characterization of Materials* (New York: Springer: 2009).
10. G. M. Sheldrick, *SHELX-97: Programs for Crystal Structure Analysis* (Göttingen, Germany: University of Göttingen: 1997).

11.   A. Guinier, *Theorie et Technique de la Radiocristallographie* (Paris: DUNOD: 1956) (in French).
12.   G. H. Cao, A. M. Russel, and K. A. Gschneidner Jr., *Scr. Mater.*, **64**, Iss. 9: 821 (2011).