

## **Investigation of nanocrystalline sintered W-25 wt% Cu composite**

T. Mikó<sup>1</sup>, F. Kristály<sup>2</sup>, D. Pethő<sup>1</sup>, M. Svéda<sup>3</sup>, G. Karacs<sup>3</sup>, G. Gergely<sup>1</sup>, Z. Gácsi<sup>1</sup>, A. Roósz<sup>3</sup>

<sup>1</sup>:Hungary, University of Miskolc, Institute of Physical Metallurgy, Metalforming and Nanotechnology

<sup>2</sup>:Hungary, University of Miskolc, Institute of Mineralogy and Geology

<sup>3</sup>:Hungary, University of Miskolc, MTA-ME Materials Science Research Group

Corresponding email: femdani@uni-miskolc.hu

### **Abstract**

W and Cu can be found in separate phases in the W-Cu composites since these elements do not dissolve in each other neither in liquid nor in solid phase, but with mechanical alloying it is possible to produce nonequilibrium W-Cu alloys. In this work the nanostructured W-Cu composites were produced by planetary ball milling. The nanostructured W-Cu powder was sintered on 900°C and 950°C with 50 MPa pressure applied. The meso- and microstructure of the W-Cu powder and the sintered samples, were investigated with SEM, TEM and XRD. After 50 hours of milling, the size of the W crystallites was ~ 10 nm, and about 10 % of the Cu was dissolved in the W matrix, producing a W-Cu nonequilibrium alloy layer on the surface of W nano crystallites. During sintering, the Cu atoms left from the W surface to the Cu phases, so the W-Cu nonequilibrium alloy layer disappeared. The size of the W crystallites – after 60 min of sintering on 950°C - was around 170 nm, and the relative density was ~90% of the theoretical density.

Key words: W-Cu composite, nano crystallite, planetary ball milling, pressing, sintering

### **1. Introduction**

W and Cu can be found in separate phases in the W-Cu composites since these elements do not dissolve in each other neither in liquid nor in solid phase. W has a very low coefficient of thermal expansion, a high density, and extraordinarily high strength while Cu is characterized by a very high electric- and thermal conductivity and can easily be formed [1,2]. Due to their special properties, the tungsten-copper composites are used in many different fields. Around 50% volume of W-25wt%Cu composites consists of Cu, therefore they can be used as contact material in high voltage systems; thermal extraction sheets are made from these composites for integrated circuits and they are used in microwave equipment's as well [3]. Due to their high neutron-absorptivity, they can be used as the so-called diverter sheets in the nuclear reactors [4]. These composites are often used for making arc welding electrodes.

The W-Cu composites are generally made by liquid phase sintering [4,10,11,12]. The temperature of the sintering is between 1100-1400°C (Cu is liquid at this temperature) as a consequence, the originally nano-sized crystallites within the W particles coarsen – they can even have the size of a few ten microns – practically one particle will become one grain. The

coarsening of the crystallites can be hindered by decreasing the temperature of the sintering i.e. by solid-state sintering at temperatures below the melting point of Cu [14]. However, the process of sintering (it is a diffusion process) is quite slow at low temperatures and the suitable density (at least 95-96% of the theoretical density) which is at least as important as the nanostructure, can be obtained with difficulty (only by using high pressure).

Our research work aimed to understand in detail how the W-Cu nonequilibrium alloy develops during mechanical alloying, and what happens with this nonequilibrium alloy during sintering.

## 2. Material and Methods

The Cu (APS <10 microns, 99.9 wt% Cu) and W (APS<1 micron, 99,95 wt% W)) powders were obtained from Alfa Aesar. The particle size of the as-received basic materials was determined by using a laser particle-size analyzer (Horiba LA-950V2).

The milling was performed in a hardened steel jar with a volume of 250 ml (63 HRC) with hardened steel balls (63 HRC) in a Fritsch Pulverisette 5 planetary ball mill. The mass of milled powder was 50 g (12.5 g of Cu and 37.5 g of W); the ball to powder ratio was 15:1. The milling jar was filled up with argon through the valves in order to lessen the oxidation. The milling was performed with a revolution number of 200 rpm for 50 hours. During milling, samples were taken from the milled material after 1, 10, 18, 30, 40 and 50 hours for XRD and SEM investigations.

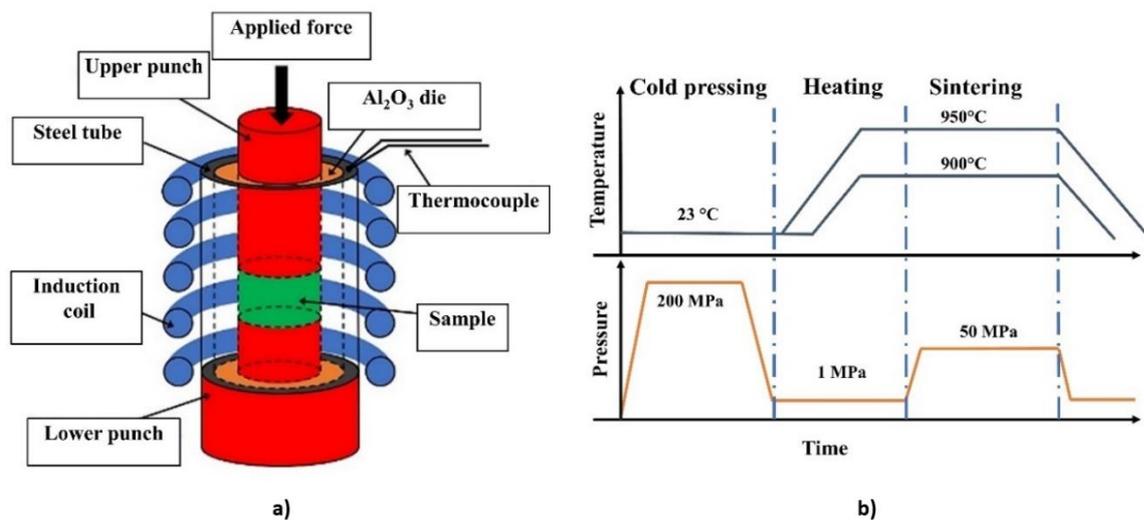


Figure 1.: The sketch of the equipment (a), the technology (b) (Coloured)

By using cold- then hot-pressing, samples with cylindric geometrical shapes were made from the W-Cu powders milled for 50 hours. Al<sub>2</sub>O<sub>3</sub> ceramic was used for making the die with an inner diameter of 6 mm, with a wall thickness of 3 mm and a height of 20 mm. The lower and upper punch was made of Al<sub>2</sub>O<sub>3</sub> ceramic material as well (Figure 1. (a)). The die is surrounded by a heat-resistant steel tube with a wall thickness of 2 mm coupled with a thermocouple controlling the induction heating in order to ensure the uniform heating of ceramic die (not only at the W/Cu mixture). An Iew5 type induction heating unit of a maximum power of 5 kW equipped with a Eurotherm 2208e type temperature controller was used to ensure the controlled heating. The powder filled in the die was pressed at a pressure of 200 MPa for 5 minutes at

room temperature. Then the pressure was decreased to 1MPa while simultaneously heating up to the sintering temperature (900 and 950°C) with the rate of 500°C/min (Figure 1 (b)). The pressure was held for 5, 10, 30 and 60 min at 50 MPa which was applied after the sintering temperature was reached. After finishing the sintering, the sample was cooled to room temperature without controlling the temperature.

The crystallite size, the lattice parameter, and the strain were determined by XRD for both the powder and bulk samples. The measurements were carried out on Bruker D8 Advance powder diffractometer (Cu-K $\alpha$ , 40 kV and 40 mA) in parallel the beam geometry was obtained by Göbel mirror equipped with Vantec1 position sensitive detector (1° detector window opening). Patterns were recorded in 2-100° (2 $\Theta$ ) range by 0.007°(2 $\Theta$ )/48 sec counting time. For the evaluation of the results, Rietveld refinement was applied in TOPAS4, with empirical instrumental parametrization (instrumental profile) on NIST SRM 640a Si standard. The background was modeled by 4<sup>th</sup> degree Tschebychev (Chebyshev) polynomial, the preferred orientation was corrected by March-Dollase function where necessary. Peak broadening was resolved by simultaneous size and strain calculation by  $\text{size(nm)} = \text{FWHM}(2\theta) \cdot \cos(\theta) / \lambda$  and  $\epsilon_0 = \text{FWHM}(2\theta) / (4 \tan \theta)$ , a dimensionless parameter which can be related to distortion of lattice parameters in percent. The two parameters were refined until the best fit, i.e. the smoothest difference curve was obtained. In cases when size-strain modeling did not resolve the measured pattern, a second structure of the same phase was implemented to distinguish between fractions defined by size range and/or strain amount.

For the TEM examinations of the powder samples, the W-Cu powder was mixed with GATAN G1 epoxy in a mold with a diameter of 8 mm and a depth of 1 mm. It was heated to 120°C and held for 10 minutes. By grinding the solidified metal powder-epoxy disk's thickness was reduced to 30-50  $\mu\text{m}$ . Molybdenum slot grids were stuck on its surface with G1 epoxy. At last, the cropped slot grids were ion polished with GATAN PIPS I system. The bulk sample's TEM measurements were performed with Tecnai T20 X-Twin Mk2. The applied acceleration voltage was constant 200 kV used with LaB<sub>6</sub> cathode. A 200  $\mu\text{m}$  thick disk was cut from the sintered W-Cu sample by Technoorg Linda's Microsaw. The obtained thin disk was prepared the same way as it was mentioned before in the case of the powder sample.

### 3. Theory

The properties of the composites are greatly influenced by their microstructure. The largest building block of a powder metallurgical product is the particle, which could consist of hundreds of grains with differing compositions. The grains can also be subdivided into subgrains, which are the crystallites, these can be detected with XRD. The properties of the bulk sample are directly correlated to the size of these crystallites.

The excellent properties of the W-Cu composites can further be increased if the tungsten – which is the base of composite – has a nanostructure, i.e. nano-size crystallites (less than 100 nm) can be found within the tungsten-grains. Due to the high number of grain boundaries, the composites with such structures have an especially high neutron-scattering ability, therefore they are planned to be used as diverters in fusion nuclear power plants. Composite base materials with nano-structure (where the size of W and Cu crystallites is between 0-10 nm) can be manufactured by the combined milling of the W and the Cu powders [5-13].

It is a well-known fact that the crystallites of solid solutions coarsen more slowly in identical circumstances (forming, temperature) than the pure elements. Due to the lattice-distortion caused by the dissolved atoms on the boundaries of crystallites (especially if their concentration is significantly higher than the average value), the atoms jump over the boundaries of the crystallites with more difficulty (the activation free enthalpy of jumping over is high), this phenomenon can hinder the coarsening of the crystallites. These crystallite-boundaries rich in dissolved atoms can be developed by two different methods. In the first case, the alloying atom is dissolved by the basic metal in an equilibrium state (e.g. Ti in W). During heat treatment (sintering), the dissolved atoms in the material containing nano-size crystallites diffuse to the crystallite-boundaries (so the system is more stable thermodynamically) [18]. The second possibility is to develop a thin non-equilibrium solid solution layer on the other element's crystallite boundaries (for example by mechanical alloying), which does not dissolve in the basic metal in equilibrium state [19]. However, in this case, it is necessary to consider that the non-equilibrium solid solution will decompose during the heat treatment (sintering) and a separate phase will develop.

Practically Cu does not dissolve in W and W does not dissolve either in liquid- or solid Cu (in equilibrium conditions) [20] so the alloying procedure (dissolution of Cu into the W crystallites) cannot be performed in the usual way. During the combined milling of W and Cu powders, the Cu-atoms are pressed into the crystal-lattice on the surface of W-crystallites due to the high local pressure caused by the milling elements (usually balls) i.e. a W-Cu non-equilibrium alloy layer develops practically on the surface of W crystallites [1-5]. Naturally, the non-alloyed Cu is alloyed with W-atoms also and by this, a non-equilibrium alloy develops [17].

The relative density of W-Cu composites should be at least 90%, in addition to the fact that W crystallites should have a nanostructure so that it can be used in the practice. Based on the reference-data, these two conditions contradict each other: a high relative density can only be obtained by sintering at a relatively high temperature (above 1000°C) however, in this case, the Cu crystallizes from the W-Cu non-equilibrium solid solution and it develops a separate phase on the grain boundary and the nano-crystallites of W coarsen.

## **4. Results and discussion**

### **4.1 Base material**

The tungsten powder has a bimodal structure (Figure 2.(c), the ratio of fine to coarse fractions is 90 to 10. The average particle size of the fine fraction of tungsten powder is  $\sim 3 \mu\text{m}$  and the average particle size of the coarse fraction of the powder is  $\sim 25 \mu\text{m}$ ; the average value of the two fractions is  $\sim 5 \mu\text{m}$  by taking into consideration the mass proportion of the two fractions. The copper powder has a monomodal structure (see Figure 2.(d), its average particle size is  $15 \mu\text{m}$ . By its crystallite sizes, the as-received W-powder could be ranged into two fractions: 20% of the powder is in the range of  $750 \pm 200 \text{ nm}$  and 80% of the powder is in range of  $250 \pm 70 \text{ nm}$ . The average size of crystallites in the Cu-powder was  $5 \mu\text{m}$ .

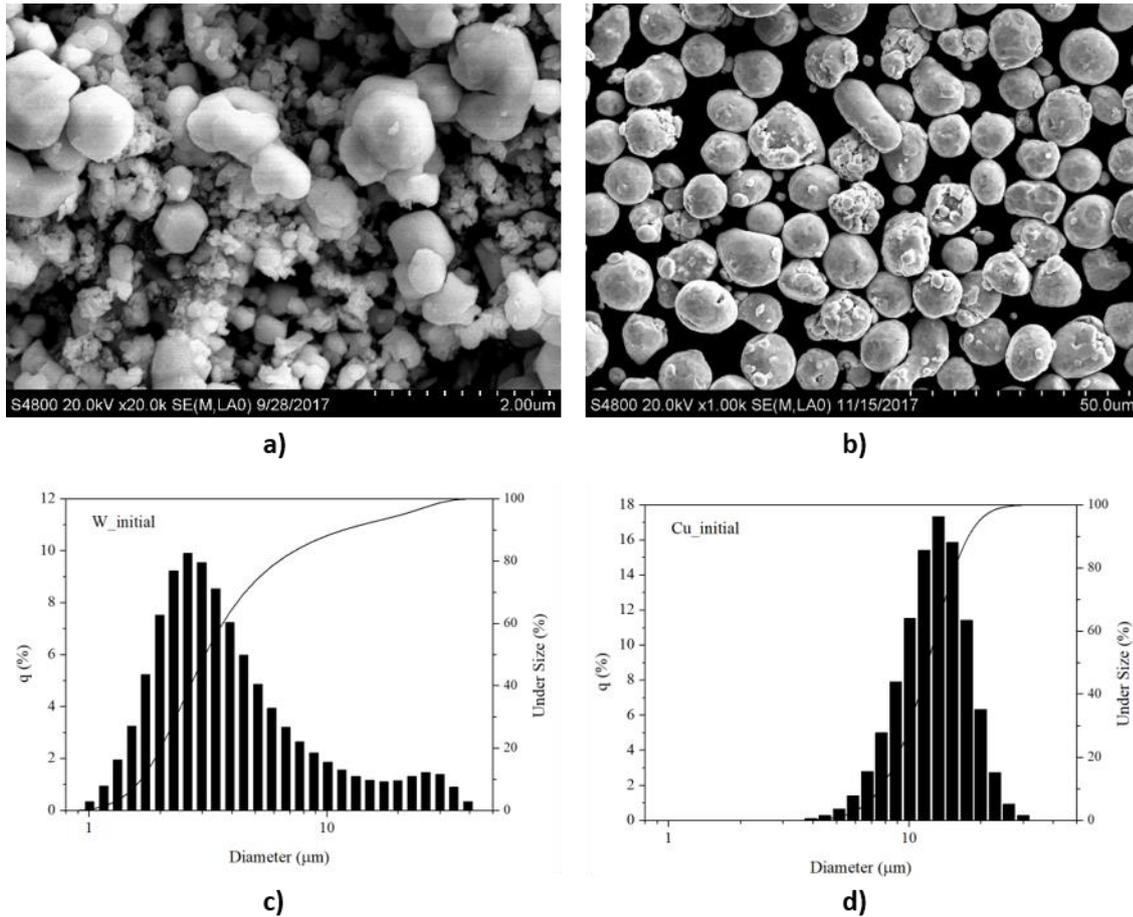


Figure 2.: Meso structure of the as-received W powder (a), Cu powder (b), the particle size distribution of W (c) and Cu (d)

## 4.2. The structure of the milled powder

### 4.2.1. SEM investigations

It was shown by the SEM investigations that the quasi-globular Cu disappeared from the W-Cu powder even after 10 hours of milling; the W particles were covered by Cu (Figure 3. (a)). Each particle consisted of many grains (Figure 3. (b)). During milling, the W particles disintegrated and coalesced repeatedly [16] and consequently, the Cu-atoms could get into the surface layer of W grains.

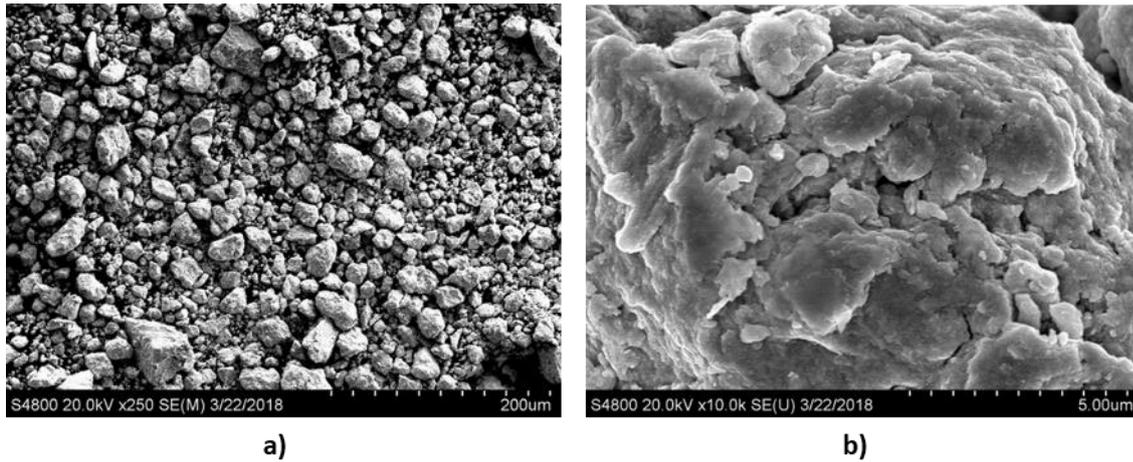


Figure 3.: The mesostructure of the milled powder after 10 hours of milling with different magnification.

The SEM image of the cross section of one particle is demonstrated in Figure 4. The black areas are Fe grains, which came from the steel balls and the steel jar during milling. The bright W grains were not mixed uniformly with the light grey Cu.

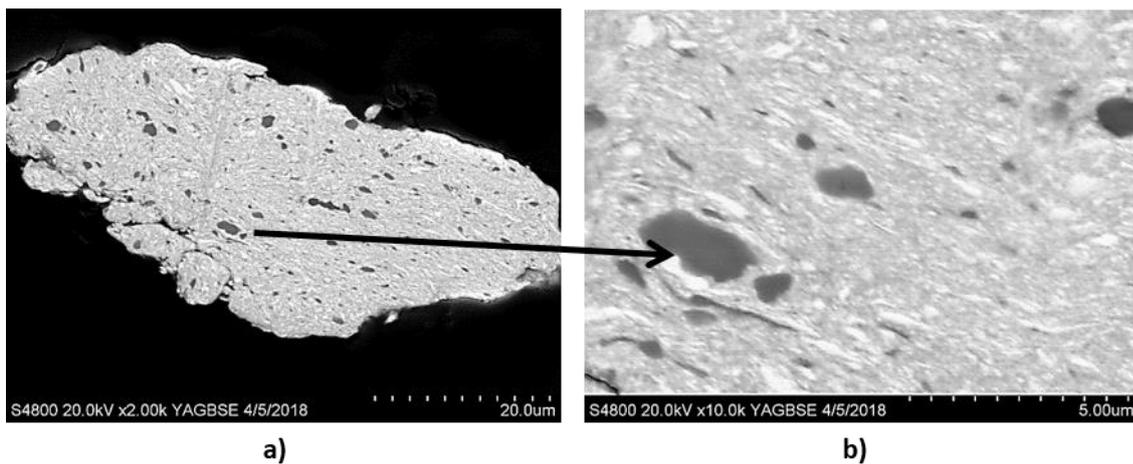


Figure 4.: Cross section of a particle milled for 50 hours

#### 4.2.2. XRD investigations

The X-ray diffraction images taken of the milled powder are demonstrated in Figure 5 (a), as a function of the different milling times. By increasing the time of milling, the intensity of both the W peak (110) and Cu-peak (111) decreased (as all the other peaks), the W-peak shifted towards the higher Bragg angle and the Cu-peak shifted towards the lower Bragg angle, the W-peak broadened significantly and it became asymmetrical (Figure 5. (b)).

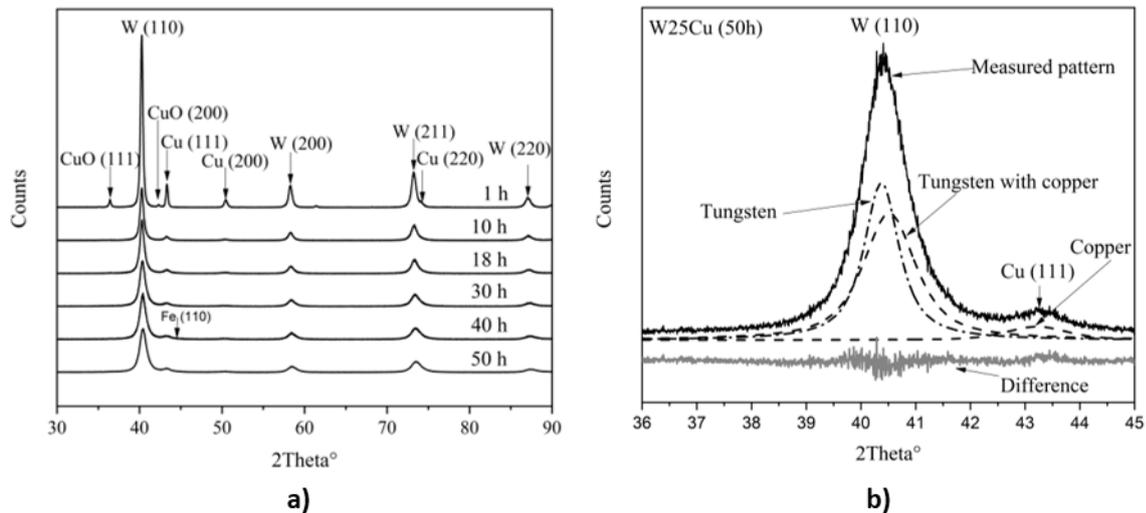


Figure 5.: XRD images of powders milled for different times (a), 50-hours milled powder (b)

The proportion of W and Cu phases can be defined from the changes of the peak intensities. After 1 hour of milling, the proportion of W and Cu was practically equal to the initial value (68% W, 24.6% Cu) and a certain percent of CuO originating from the oxygen reacting with the surfaces of powders could be detected in the system. W peak was symmetrical and neither the W-peak nor the Cu-peak shifted from the Bragg angle value characterizing the pure elements, the lattice parameter did not change either in the two different (finer, coarser) W or in the Cu fraction (Figure 5.) i.e. merely the mixing of the powders took place, no mechanical alloying could be observed. However, the width of semi-value increased due to the decrease of crystallite size. In the case of W, the average size of crystallite fraction which originally was 750 nm decreased to 110 nm and the average size of crystallite fraction which originally was 250 nm, decreased to 40 nm.

After milling for 10 hours, the W-peak became asymmetric, its intensity decreased, and the width of semi-value increased significantly. The asymmetric peak could be explained only by the fact that the Cu atoms were dissolved in the W grains and an alloyed layer with Cu appeared on the surface of grains of tungsten powder i.e. the W-powder decomposed to two fractions, namely to pure W and to metastable W(Cu) alloy. Naturally, no significant transition can be observed between the two parts, the Cu concentration changes continuously across the W grains. In this case, the W-Cu mixture contained three phases – which are the following: pure W, W(Cu) metastable alloy layer (this isn't a real phase) and Cu (Figure 6.(a)).

The shifting of W peak towards the higher Bragg angle and the shifting of Cu peak towards the lower Bragg angle indicate that both the pure W and the pure Cu contained Cu and W [17]. The shifting of the peak can be explained by the fact that the size of W atom (1,95 Å) is significantly higher than the size of Cu atom (1,35 Å) therefore the W lattice parameter decreases if the Cu atom infiltrates into the W lattice and the Cu lattice parameter increases if W infiltrates into the Cu lattice. It is interesting to note that the asymmetry of the diffraction peak cannot be observed (cannot be detected) when Cu contains W. However, it is certain that a layer rich in W develops at the Cu-boundary similar to the W-layer rich in Cu [17], but it could not be proven by the XRD. Nevertheless, the conclusion can be drawn from the fact that the lattice parameter of the Cu phase increases significantly. The W and Cu peaks broaden further to a significant extent; the grain sizes of all the three phases decrease to a great extent (10–20 nm). The difference

between the fractions having originally two different grain sizes disappeared. Due to the strong mechanical impact, the CuO phase decomposed and it could not be observed in the system in the future.

The crystallite size of all three phases decreases further to a small extent at the milling time lasting for 20 hours (Figure 6. (b)). The quantity of Cu and W phases decreases (Cu~18 wt%, W~45%) and the quantity of metastable W(Cu) phase having a high Cu-concentration increased significantly (35%). The Cu content of pure W and the W-content of pure Cu increased. Fe appeared which abraded from the steel balls and the jar due to the strong abrasive effect of W.

By increasing the milling time, the quantity of pure Cu decreased, because the Cu-atoms infiltrated into the pure W and so the W(Cu) phases increased. The W-atoms infiltrated into the pure Cu-phase, as a consequence the W-content of pure Cu increased (the lattice parameter of pure Cu phase increased) and the Fe-content of the system increased significantly as well. In contrast with the result of Qiu et al [8] where the pure Cu disappeared totally, in this case 18 wt% pure Cu remained after 40 h milling. Also, we did not find any amorphous phase after 50 h [11].

The crystallite size of three phases decreased by a small extent continuously by increasing the milling time from 20 h to 50 h with the exception that the size of pure Cu grain increased slightly after 50 hours of milling (Figure 6.b). The crystallite size of pure W phase is 12 nm at 40 h, which is very similar to the result in [8] (10,9 nm),

The value of strain is determined by two effects: (1) by the lattice-strain caused by the infiltrating foreign atom and (2) by the dislocation density. After milling for 1 hour, the strain is significantly higher in the finer W fraction than in the coarser fraction. After milling for 10 hours, only one fraction can be found in the system – here the value of strain is similar to the value of strain measured in the coarser fraction after the milling which lasted for 1 hour. The value of strain in W slightly decreases first during the further milling, then it increases. It is quite probable that the increase is caused by the infiltrating Cu atoms under the fact that the lattice parameter decreases as well (the increase of dislocation density would cause the increase of lattice parameter). The strain in Cu increases in a small extent during the milling time lasting for 30 hours as compared to the milling lasting for 1 hour then it suddenly increases in a great extent. The considerable increase of strain is probably caused by the increase of dislocation density as the W probably infiltrates into the grain boundaries only slightly.

The weight percent of the phases and the crystallite sizes measured after the 50 hour long milling are demonstrated in Figure 6 and Table 1.

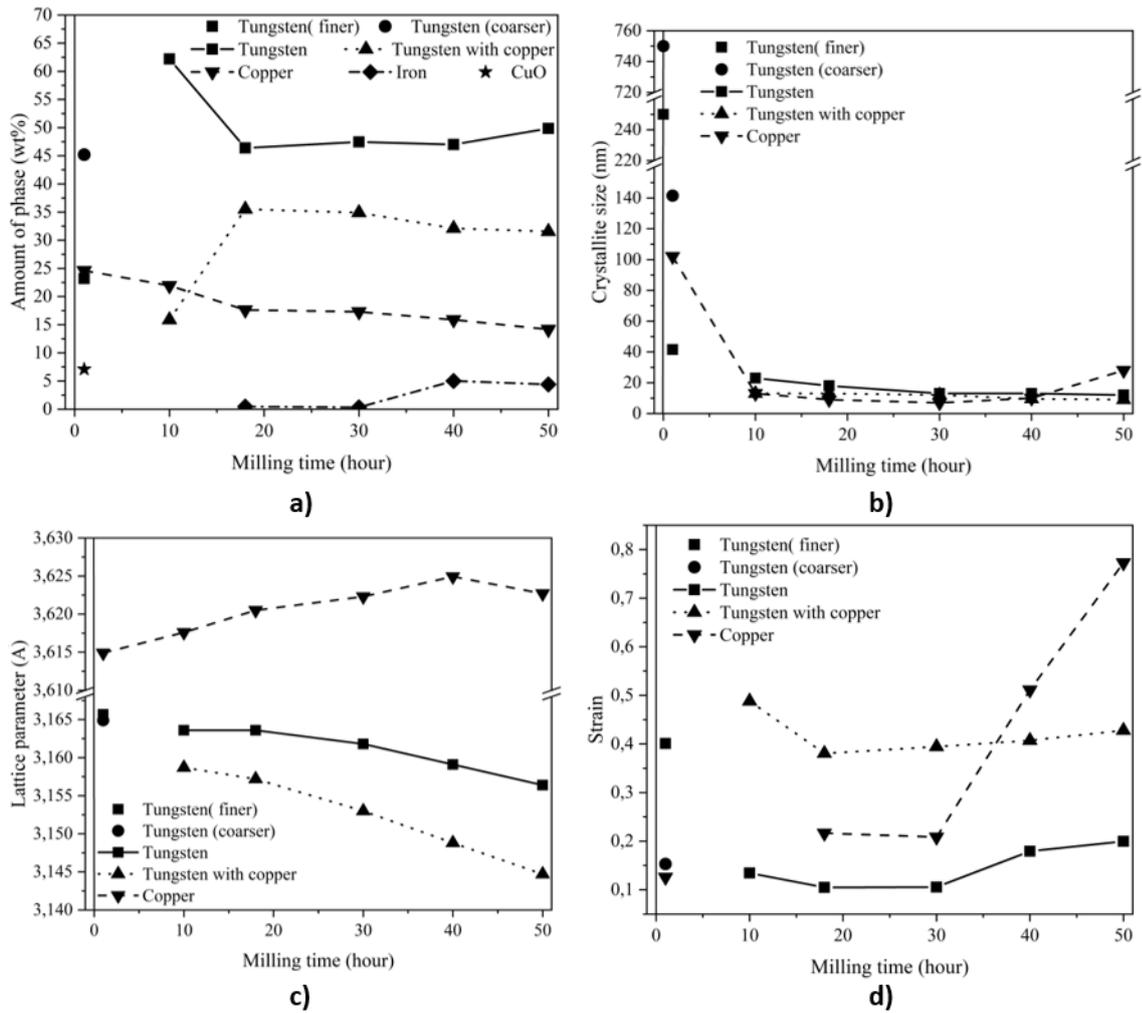


Figure 6.: Weight percentage of the phases (a), the crystallite size (b), lattice parameter (c), strain (d) as the function of milling time

Table 1.: Weight percentage, crystallite size, cell parameter and strain after 50 hours of milling

Phase	Tungsten	Tungsten with Copper	Copper	Iron
Weight percentage; wt%	49.9	31.6	14.2	4.4
Crystallite size; nm	12	9	28	8
Cell parameter; Å	3.1564	3.1447	3.6227	2.8674
Strain; -	0.1997	0.4278	0.7728	

#### 4.2.3. TEM investigation

In Figure 7. (a) the grains are shown on the TEM images and the measured grain size distribution (b). The grain size was measured on 10 images and about 200 grains were used. During the measurement, it was impossible to separate the W and Cu grains. The average grain size is about 11 nm which is nearly the same as the value measured by XRD.

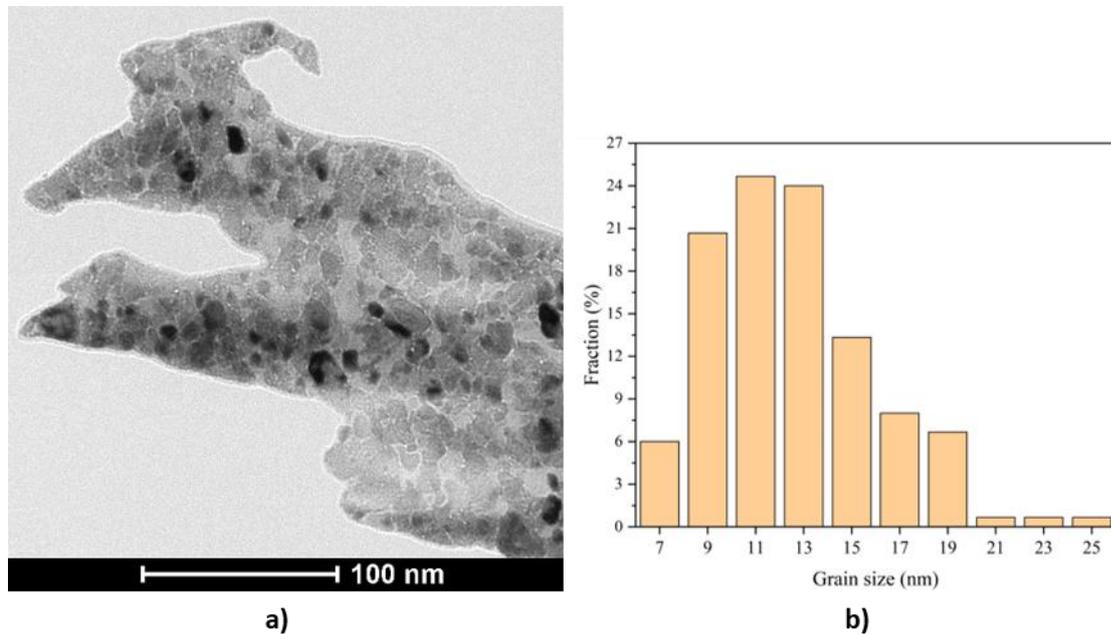


Figure 7.: TEM images of the W-Cu powder milled for 50 hours (a), grain size distribution (b)

### 4.3. The meso- and microstructure of sintered samples

#### 4.3.1. SEM investigations

With time, the particle size increased slightly and the mesostructure coarsened. No significant difference can be observed between the mesostructures of samples sintered at the 900°C and 950°C.

The mesostructure of samples sintered at a temperature of 950°C for 60 min. can be seen in Figure 8. (a). The light areas show the parts having high W and low Cu-content while the dark areas show the parts with high Cu-content. In Figure 8. (b), the composition map of this sample made by EDS is demonstrated (Cu is indicated by green color and W is indicated by red color).

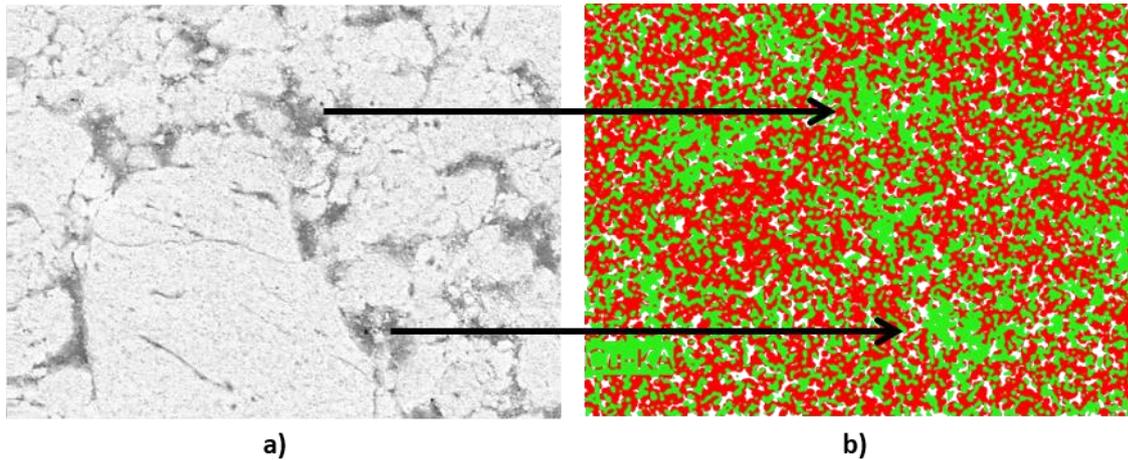


Figure 8.: Mesostructure of sample sintered at a temperature of 950°C for 60 min (a) W and Cu distribution in the sample (b) (Coloured)

#### 4.3.2. XRD investigations

The part of the X-ray diffraction images (W (110), Cu (111) peaks) taken of the sintered powder are demonstrated in Figure 9. as the function of the different sintering time at the sintering temperature of 950°C. The asymmetric W peak characterizing the milled W(Cu) mixture transforms to a sharp peak following the sintering time of 5 min, which indicates that the W-phase containing Cu disappeared, Cu precipitated from the W lattice and the original W/Cu proportion was restored in 10 min. This phenomenon also appears at 900°C. The phase content at 900°C and 950°C (Figure 10. (a) and (b)), the crystallite size (Figure 10. (c)) the lattice parameter (Figure 10. (d)) and the strain (Figure 10. (e)) were determined by the same XRD method that was used during the investigation of milled powder.

The full width at half-value decreases as the consequence of the increasing of crystallite-size moreover the intensity increases and the Bragg angle belonging to the peak decreases as the consequence of the decreasing dislocation density. Based on the XRD investigation, it cannot be stated where the precipitated Cu-atoms (which form an independent lattice) are. The quantity of pure W-phase is less than the original, as the phases containing Fe which contain W as well appear. Fe and C originated from the material of the steel crucible and balls used during milling. After the sintering procedures at the temperature of 900°C for 10 min and at the temperature of 950°C for 5 min, the proportion of the phases does not change significantly.

The average crystallite size of W was 40 nm at 900°C after the sintering time of 5 min. and it was 60 nm after 60 min. and this value changed only very slowly (Figure 10. (c)). This means that the crystallite size can presumably be kept below 100 nm by sintering the sample at this temperature. The crystallite size was 60 nm after sintering the sample at 950°C for 5 min, it was 100 nm after 30 min and 170 nm after 60 min. This value is much higher than the targeted 10-20 nm but it is much lower than the crystallite size of W-Cu composites crystallite (2000-20000 nm) used mainly during the arc welding procedure recently.

In order to examine whether the crystallite size of the sintered sample coarsens or not, the sample was sintered at the temperature of 950° for 30 min, then it was further sintered in an argon atmosphere for 10 hours without pressing. It could be stated that the size of W crystallite

increased slightly from 100 nm to 120 nm. It can be concluded from this fact that a W-Cu alloy having a crystallite-size less than 150 nm can probably be made by this technology.

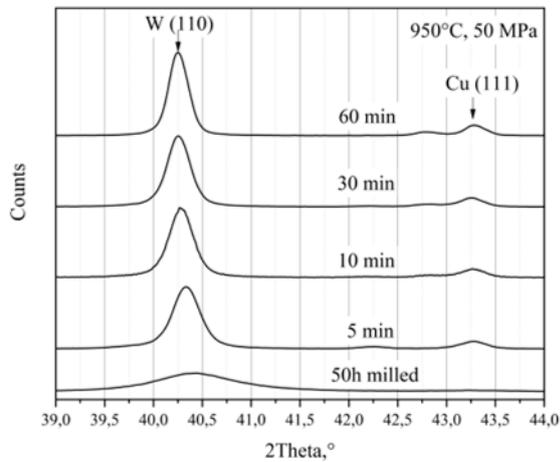


Figure 9.: Change of XRD peaks of W (110) and Cu (111) as the function of the sintering time

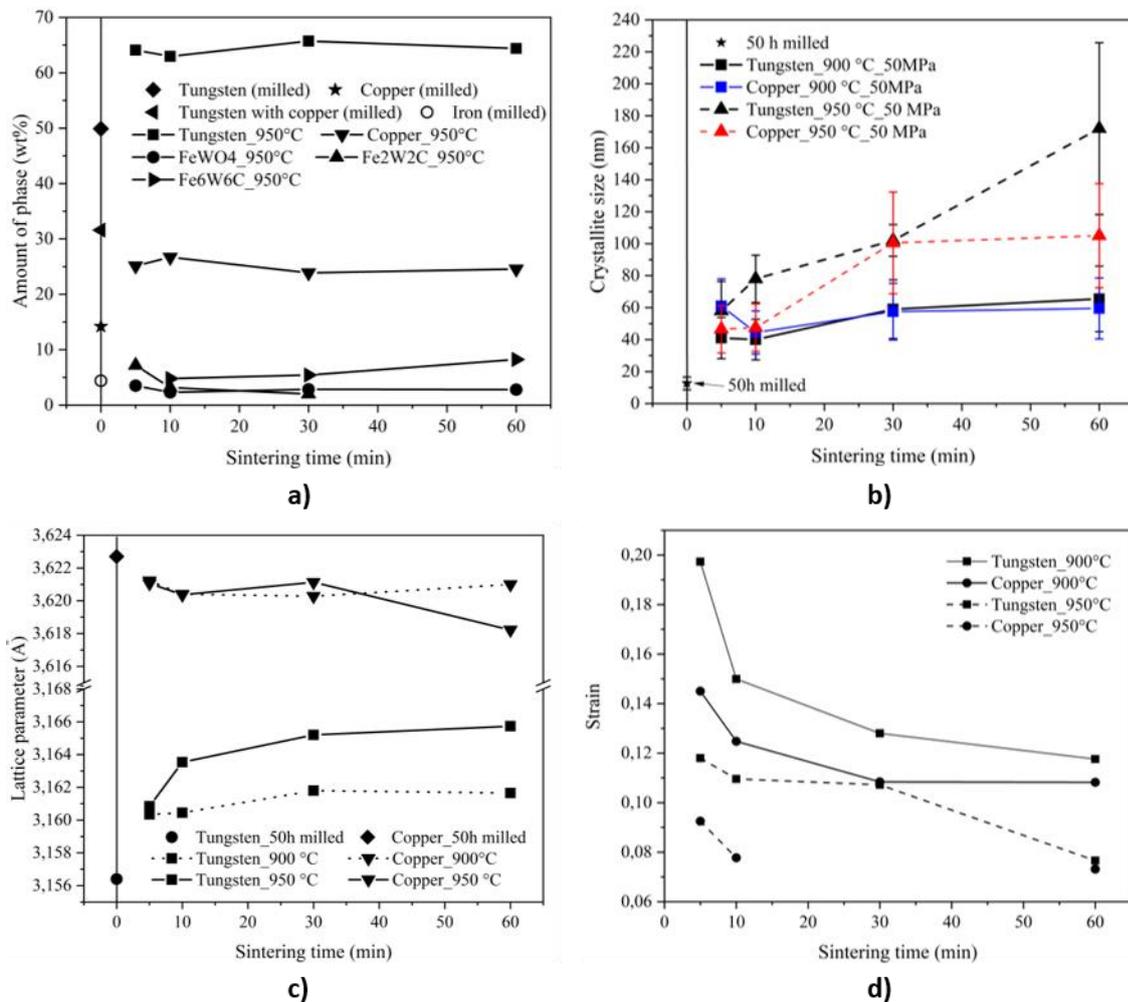


Figure 10.: Weight percentage of the phases (a), the crystallite size (b), lattice parameter (c) and strain (d) at the temperature of 900 and 950°C as the function of the sintering time (coloured)

### 4.3.3. TEM investigation

In Figure 11. the TEM images and the grain distribution are shown in the case of the sintered sample (50 h, 30 min, 950 °C). The grains were analyzed with EDS and it revealed that the light grey grains are Cu and the dark grey grains are W because of the difference between the atomic number of Cu and W. In Figure 11. (b) the grain size distribution is shown. As in the case of the milled powder, it was impossible to perform the grain size distribution of Cu and W separately. The average grain size was about 85 nm which is in a good agreement with the average determined by XRD measurement.

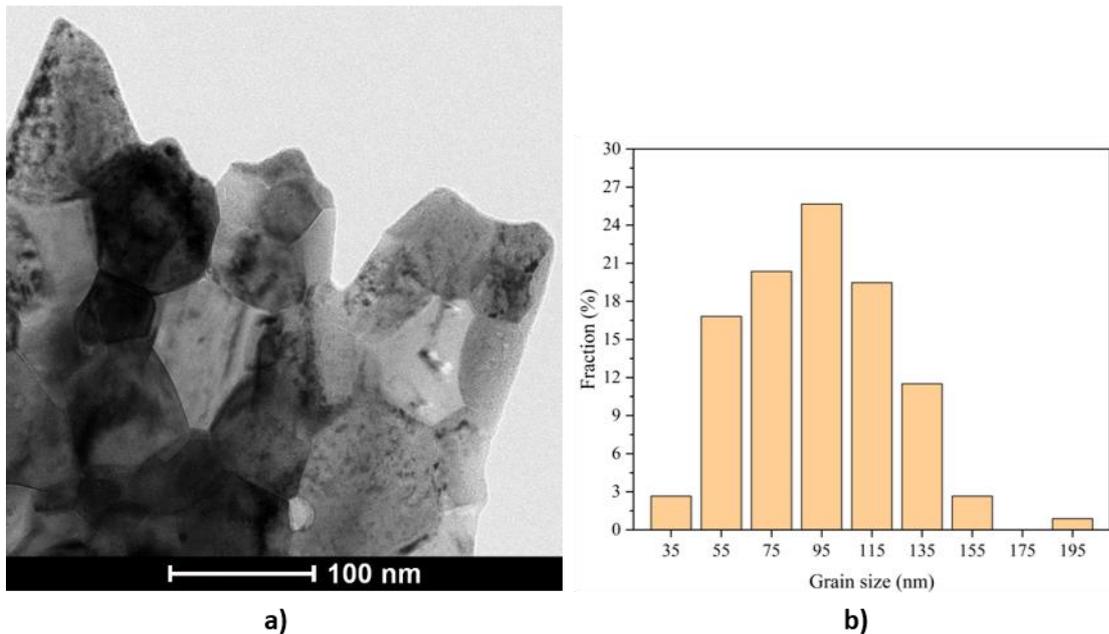


Figure 11.: TEM images (a) and grain distribution of the W-Cu powder milled for 50 hours and sintered 30 min at 950°C (b)

### 4.3.4. Effect of sintering on the density

The density of sintered samples is a very important parameter from the point of view of the usability of the product in the practice. The density of samples was determined by using the Archimedes-method. 75% of the theoretical density was obtained by sintering the sample at the temperature of 900°C for 60 min and 90% of the theoretical density was obtained at the temperatures of 950°C. This value was a little bit higher as was obtained by Qiu at al used similar technology [8].

## Summary and conclusions

The aim of this work was to examine the possibility of producing of nano-crystallite W-Cu composites with reasonable density. In order to obtain nanostructured W-Cu powder W (5  $\mu\text{m}$ ) and Cu (15  $\mu\text{m}$ ) powder was milled in argon atmosphere in a Fritsch Pulverisette 5 planetary ball mill. The mass of milled powder was 50 g (12.5 g of Cu and 37.5 g of W, ~50-50 volume%); the mass proportion of ball to powder ratio was 15:1. The nanostructured W-Cu powder was sintered at 900°C, 950°C with 50 MPa load. The meso and microstructure of the nanostructured W-Cu powder and the sintered samples were investigated with SEM, TEM and XRD.

Based on these investigations the following are stated:

(i) The quasi-globular shaped Cu disappeared from the W-Cu powder even after 10 hours of milling time. The W particles were covered by Cu. Each particle consisted of many of grains. During milling, the W particles disintegrated and coalesced repeatedly and therefore the Cu-atoms got into the surface layer of W grains.

(ii) Due to the effect of milling, the W-peak became asymmetric, its intensity decreased, and the full width half value increased significantly. The asymmetric peak could be explained only by the fact that a layer alloyed with Cu appeared on the surface of grains in the tungsten powder i.e. the W-powder decomposed to two fractions: pure W and metastable W(Cu) alloy.

(iii) The grain size of all the three phases decreased further slightly after 20 hours of milling. The weight percentage of Cu and W decreases (Cu~18 wt%, W~45%) and the weight percentage of metastable W(Cu) phase having a high Cu-concentration increased significantly (35%). The Cu content of pure W and the W-content of pure Cu increased. Fe came from the steel balls and from the jar due to the strong abrasive effect of W.

(iv) By increasing the milling time, the weight percentage of pure Cu decreased, the Cu-atoms infiltrated into the pure W, so the W(Cu) phases increased their Cu-content, also the W-atoms infiltrated into the pure Cu-phase, which increased the W-content of pure Cu, moreover, the Fe-content of the system increased significantly as well. The crystallite size decreased continuously by increasing milling time except for the size of the pure Cu grain, which increased slightly after 50 hours of milling.

(v) After 50 hours of milling the crystallite size of W was about 10 nm, and around 10% Cu was solved in the W matrix, which produced a W-Cu nonequilibrium alloy layer on the surface of the W nano crystallites.

(vi) During sintering, the Cu atoms moved out from the tungsten's surface layer and united with the Cu phase, the W-Cu nonequilibrium alloy layer disappeared even after 10 min on 900°C and after 5 min on 950°C.

(vii) Due to the Fe contamination from milling, at sintering  $\text{FeWO}_4$ ,  $\text{Fe}_2\text{W}_2\text{C}$  and  $\text{Fe}_6\text{W}_6\text{C}$  phases were formed even after 5 min, after that the content of these phases was practically constant.

(vii) The content of W and Cu after 10 min at 900°C and after 5 min on 950°C were 65 wt% and 25 wt% and it did not change afterward.

(viii) Finally, the crystallite size of W – after 60 min sintering at 950°C – remained around 170 nm, but the relative density was only ~90% of the theoretical density.

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