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INFLUENCE OF MECHANICAL-ALLOYING PARAMETERS ON THE STRUCTURE AND PROPERTIES OF $Cu_{47}Ti_{34}Zr_{11}Ni_8$

VPLIV PARAMETROV MEHANSKEGA LEGIRANJA NA STRUKTURO IN LASTNOSTI ZLITINE $Cu_{47}Ti_{34}Zr_{11}Ni_8$

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The main objective of the research was to determine the mechanical-alloying conditions that ensure the fabrication of the $Cu_{47}Ti_{34}Zr_{11}Ni_8$ amorphous alloy. The experimental work involved the following mechanical-alloying parameters: milling time (0.5 h and 1 h) to interval time (0.5 h), ratio of grinding medium to material (5:1 and 10:1), the addition of an microwax powder and the process atmosphere (argon). Their effect on the structure, the amount of material obtained after milling, the size and shape of the powders, qualitative chemical composition and microhardness of the investigated $Cu_{47}Ti_{34}Zr_{11}Ni_8$ alloy were described. The mechanical alloying (MA) of the $Cu_{47}Ti_{34}Zr_{11}Ni_8$ alloy was carried out in a SPEX 8000 high-energy ball mill. The total mechanical-alloying time of each sample was 10 hours. Each 10-hour cycle consisted of milling time (1 h or 0.5 h) and interruption 0.5 h. Microwax powders were added to selected samples. Finally, eight samples for testing were obtained. The structure of the obtained powders was examined by X-ray diffraction (XRD). The chemical compositions of the prepared powders were investigated by scanning electron microscopy (SEM) with EDS. Electron transmission microscopy (TEM) was used to confirmation the fully amorphous structure of the sample. Microhardness was measured by using a Vickers hardness testing machine. Each of the applied milling parameters had an influence on the amorphization of the $Cu_{47}Ti_{34}Zr_{11}Ni_8$ alloy. The amorphous material was obtained in two cases after 1h of milling without adding microwax. After the TEM analysis it was found that the resulting powder is not completely amorphous. In the amorphous matrix, nanocrystallites were found: $Cu_{51}Ti_{14}$ and $Cu_{5.38}Ti_{3.33}Zr_{3.29}$.The addition of microwax slowed down the amorphization. The highest microhardness was exhibited by the amorphous powders. Larger sample weights were obtained from the reactors to which microwax was added.

Keywords: parameters of mechanical alloying, $Cu_{47}Ti_{34}Zr_{11}Ni_8$ alloy, SEM, TEM, XRD, Vickers microhardness

Glavni cilji raziskave so bili določiti pogoje mehanskega legiranja za zagotovitev izdelave amorfne zlitine $Cu_{47}Ti_{34}Zr_{11}Ni_8$. Avtorji opisujejo vpliv naslednjih parametrov: intervalnega časa mletja (0,5 ure ali 1 uro) v intervalu prekinitev po 0,5 ure, razmerja med medijem za mletje in materialom za izdelavo zlitine (5:1 in 10:1), dodatek prahu mikrovoska in procesne atmosfere (argon). Nadalje v članku opisujejo analizo in rezultate vpliva parametrov na strukturo, količino dobljenega materiala po mletju, velikost in obliko prahov, kvalitativno kemijsko sestavo in mikrotrdoto preiskovane zlitine $Cu_{47}Ti_{34}Zr_{11}Ni_8$. Mehansko legiranje (MA) zlitine $Cu_{47}Ti_{34}Zr_{11}Ni_8$ so izvedli v visokoenergijskem krogličnem mlinu SPEX 8000. Celoten čas mehanskega legiranja vsakega od vzorcev je bil konstanten in sicer 10 ur. Vsak 10 urni ciklus je bil sestavljen iz časa mletja (1 uro ali 0,5 ure) in 0,5 urne prekinitve. Mikrovosek so dodajali samo določenim vzorcem. V celoti so izdelali osem vzorcev za testiranje. Strukturo preiskovanih prahov so določili z rentgensko difrakcijo (XRD). Kemijsko sestavo pripravljenih prahov so določili z vrstično elektronsko mikroskopijo (SEM) in prigrajenim EDS-detektorjem. S presevno elektronsko mikroskopijo (TEM) so potrdili popolno amorfno stanje mikrostrukture. Mikrotrdoto so določili na Vickersovem merilniku mikrotrdote. Vsak od uporabljenih parametrov mletja je imel določen vpliv na amorfizacijo (osteklenitev) zlitine $Cu_{47}Ti_{34}Zr_{11}Ni_8$. Amorfni material so avtorji dosegli v dveh primerih enournega mletja brez dodatka mikrovoska. Po TEM analizi pa so ugotovili, da izdelani prah ni bil popolnoma amorfen (steklast). V amorfni matrici so našli še nanokristalite: $Cu_{51}Ti_{14}$ in $Cu_{5,38}Ti_{3,33}Zr_{3,29}$. Dodatek mikrovoska je upočasnil tvorbo amorfne mikrostrukture. Najvišjo mikrotrdoto so imeli amorfni prahovi. Vzorci z dodatkom mikrovoska so imeli največjo maso.

Ključne besede: parametri mehanskega legiranja, zlitina $Cu_{47}Ti_{34}Zr_{11}Ni_8$, SEM, TEM, XRD, mikrotrdota po Vickersu

1 INTRODUCTION

Mechanical alloying (MA) is defined as a high-energy milling process during which particles are subjected to multiple cold welding, cracking and rewelding. The process itself is very complex and depends on many parameters.[1–5] The first time the mechanical alloying process was used was by John Benjamin and coworkers in 1966. They produced a Ni-based alloy with special properties in order to apply it to a gas turbine on an industrial scale.[1,2,6] The first amorphous material ($Ni_{60}Nb_{40}$ alloy) was obtained in 1983.[7] Currently, MA is used to produce the following materials:[1,7]

- homogeneously dispersed nanocomposites,
- metallic glasses,
- metal particles characterized by excellent combustion.

Mechanical alloying provides the possibility to obtain amorphous materials that are difficult or impossible to produce by conventional methods.[2] Moreover, modern methods of sintering (for example, spark plasma sintering) make it possible to consolidate the amorphous powders without changing their structure. As a result, it becomes possible to receive amorphous materials with a

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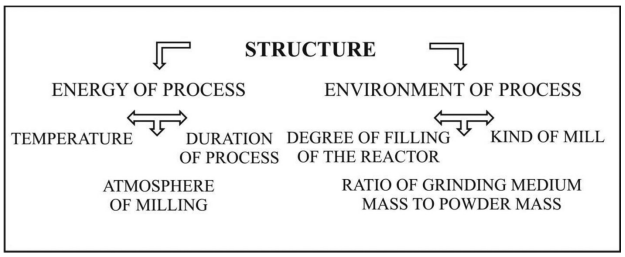

Figure 1: Schematic illustration of mechanical alloying parameters that affect the amorphous structure of the materials[6,7]

much larger size than when using a method like casting into a copper mold or melt spinning.[1]

The fabrication of an amorphous alloy by the MA method consists of a number of factors. The most important parameters which condition the formation of amorphous structure are shown in **Figure 1**. The structure of the material is dependent on the energy and the environment of the process.

For each alloy the MA process parameters must be selected individually. Most often, this is done experimentally. For example, in order to obtain an amorphous structure for $Cu_{50}Ti_{50}$[3] and $(Cu_{47}Ti_{34}Zr_{11}Ni_8)_{99}Al_1$,[5] the following parameters were used: Cr steel balls of 13 mm diameter, the weight of balls to milled material ratio was 5:1, argon atmosphere, vibratory mill type SPEX 8000 CertiPrep Mixer/Mill each hour of mechanical alloying is 30 minutes of milling and 30 minutes break. The time for which the structure for the two-component alloy was obtained lasted 8 h, and for five components it was 7 h.[3,5] M.S. Al-Assiri, A. Alolah et al.[10] studied the structure of $Cu_{45+x}Ti_{50-x}$ powders after 0 h, 2 h, 4 h and 6 h. A Spex 8000 mill was used. An amorphous structure was obtained with samples milled for 6 h. They used a ratio of balls/powder of 4.15:1. The weight of the powder samples was 4 g.[10]

In this article the basic properties of eight $Cu_{47}Ti_{34}Zr_{11}Ni_8$ powders were examined. For the preparation of the amorphous samples, different milling parameters were used.

2 EXPERIMENTAL PART

As a starting material, powders of metal of high purity (99.99 %): copper, titanium, zirconium and nickel were used. All the applied powders were characterized by the same particles size, i.e, 325 mesh (about 44 μm). Each sample was prepared with 8 grams of weighed powders. The masses of the individual elements were: Cu – 3.9252 g, Ti – 2.1389 g, Zr – 1.3187 g, Ni – 0.6170 g. The powder mixture together with the Cr steel balls were placed in an austenitic crucible in an argon atmosphere within a glove bag. Eight samples with the composition $Cu_{47}Ti_{34}Zr_{11}Ni_8$ were prepared. The exact parameters for each sample are given in **Table 1**.

Table 1: Specification of the prepared samples together with the parameters of their fabrication

Samples	A	B	C	D	E	F	G	H
Time of milling (h)	0.5	1	0.5	1	0.5	1	0.5	1
Time of interval (h)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Ratio ball to powders	5:1	10:1	5:1	10:1	10:1	5:1	10:1	5:1
Microwax	-	-	+	+	-	-	+	+

In order to produce the $Cu_{47}Ti_{34}Zr_{11}Ni_8$ amorphous alloy, different milling parameters were used. The permanent parameters were as follows: time MA – 10 h, the atmosphere – argon, and room temperature. The variable parameters were as follows: time of milling without interval – 0.5 h or 1 h, interval time: 0.5 h, microwax addition or lack thereof, weight of 40 g or 80 g of grinding media. In summary, the total amount of milling time for each of the samples was 10 h, with two different milling intervals: 0.5 h and 1 h, followed each time by a rest interval of 0.5 h. The mechanical alloying was carried out in a SPEX 8000 high-energy ball mill CertiPrep Mixer/Mill "shaker" type. The mill vibrated the balls and the material inside the container.[8,9] The particles' size and shape for the $Cu_{47}Ti_{34}Zr_{11}Ni_8$ powders were characterized using a SUPRA 25 ZEISS scanning electron microscope (SEM) with a magnification up to 200×.

An X'Pert Pro Panalytical X-ray diffractometer was used to study the structure of fabricated powders. The wavelength of the Co-K_α radiation was 0.178897 nm. The data from the diffraction lines were recorded using the "step-scanning" method in the 2θ range from 30° to 90° and with a 0.013° step. The time of the step was 40 s and the scanning speed was 0.084 °/s.

The samples for the transmission electron microscopy investigations were prepared by dispersing the powder in ethanol, placing it in an ultrasonic bath, then putting the droplets onto 3-mm copper grids coated with amorphous carbon film and drying in air at room temperature. The electron microscopy observations were made on a probe Cs-corrected S/TEM Titan 80-300 FEI microscope equipped with EDAX EDS detector. A 300-kV electron beam was used. The images were recorded in TEM-mode, using HRTEM (high-resolution transmission electron microscopy). Selected-area electron diffraction (SEAD) patters were obtained. Observations in light and dark field were used. The EDS analysis was performed using a large beam current and a convergence semi-angle of 34 mrad to amplify the signal.

The chemical compositions of the samples were analysed by means of energy-dispersive X-ray spectroscopy (EDS). The mass of the powders before and after the process was weighed on an AS 310/X analytical high-precision balance.

The microhardness of the particles was measured using a Vickers-hardness testing machine with an automatic track measurement using image analysis from FUTURETECH FM-ARS 9000. The obtained powders were prepared for microhardness testing in the form of a

microsection. The load of the micro-indenter was 0.97 N. For each of the prepared samples, ten particles were tested. Before the measurement of the microhardness, the test powders were mounted in Polyfast resin under a pressure of 250 bar, using CitoPress_20 equipment.

3 RESULTS AND DISCUSSION

3.1 Microanalysis

The composition of the research material was selected on the basis of a literature analysis. The chemical composition of the $Cu_{47}Ti_{34}Zr_{11}Ni_8$ powder selected for testing has a high ability to obtain an amorphous structure as a result of the mechanical alloying. The initial size of the powders was about 44 μm and the shape was spherical. During the mechanical synthesis the powders changed their size and shape. The average size of the particles, depending on the milling time, are shown in **Table 3**. In each sample, after the mechanical alloying the particles were larger than the size of the input powders.

Figure 2 shows the fabricated powders in the form of images taken by a scanning electron microscope (SEM) at 200× magnification. The images were displayed in the order from sample A to the powder H. As a result of analysis of the particles in the 2D image, it was observed that after milling with a higher frequency, the particles were finer (**Figure 2b, 2d, 2f** and **2h**), than when milling which was interrupted every 0.5 h (**Figure 2a, 2c, 2e** and **2g**). The powders without the addition of microwax were characterized by a spherical shape and agglomerates were formed (e.g., **Figure 2a** and **2b**).

On the other hand, powders which were milled with microwax were formed in the shape of a plate (e.g., **Figure 2b, 2d, 2e** and **2g**). Moreover, a greater mass of grinding medium, 80 g, resulted in a greater particle-size reduction (e.g., **Figure 2a, 2c, 2f** and **2h)**, than the grinding medium with a mass of 40 g. **Figure 3** presents the results of the EDS analysis of the powder E, as an example. The results of the chemical analysis for all the powders are shown in **Table 2**. The powder consisted of only starting elements and their atomic weight had moved closer to weighed mass.

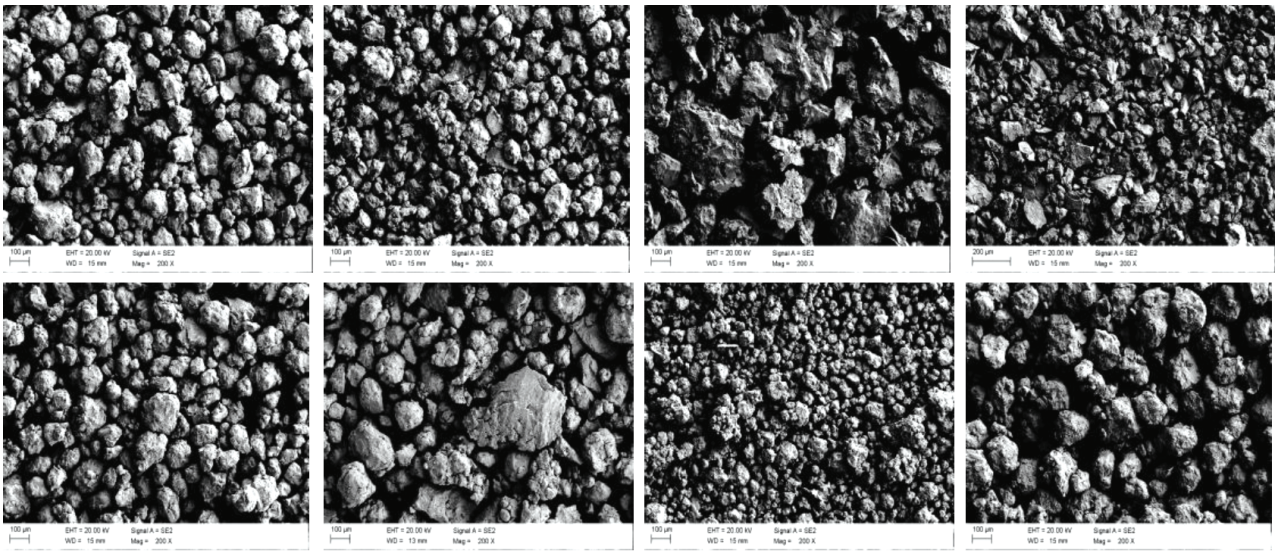

Figure 2: Shape and size of powder $Cu_{47}Ti_{34}Zr_{11}Ni_8$ after mechanical alloying from the top left to the bottom right A-H (SEM, magnifications 200×)

Table 2: Results of chemical analysis from the surface of the powder

Element	A (*a*/%)	B (*a*/%)	C (*a*/%)	D (*a*/%)	E (*a*/%)	F (*a*/%)	G (*a*/%)	H (*a*/%)
Zr	7.71	7.92	7.15	9.01	8.79	7.27	8.13	9.11
Ag	2.02	2.13	2.09	2.18	2.15	2.07	2.11	2.07
Ti	31.04	32.41	36.14	35.91	31.58	32.67	32.14	30.88
Ni	9.12	6.98	7.05	7.56	6.77	9.42	9.64	7.11
Cu	50.11	50.56	47.57	45.34	50.58	48.57	47.98	50.83

Table 3: Amount of material and particle size obtained before and after milling for individual samples

Samples	A	B	C	D	E	F	G	H	initial
Mass of powders before milling (g)	8	8	8	8	8	8	8	8	8
Weight of powders after milling (g)	4.82	4.67	6.37	6.18	4.88	4.40	6.42	6.21	x
Average particle size (μm)	85×69	81×64	213×138	68×53	101×92	172×207	51×48	256×231	44

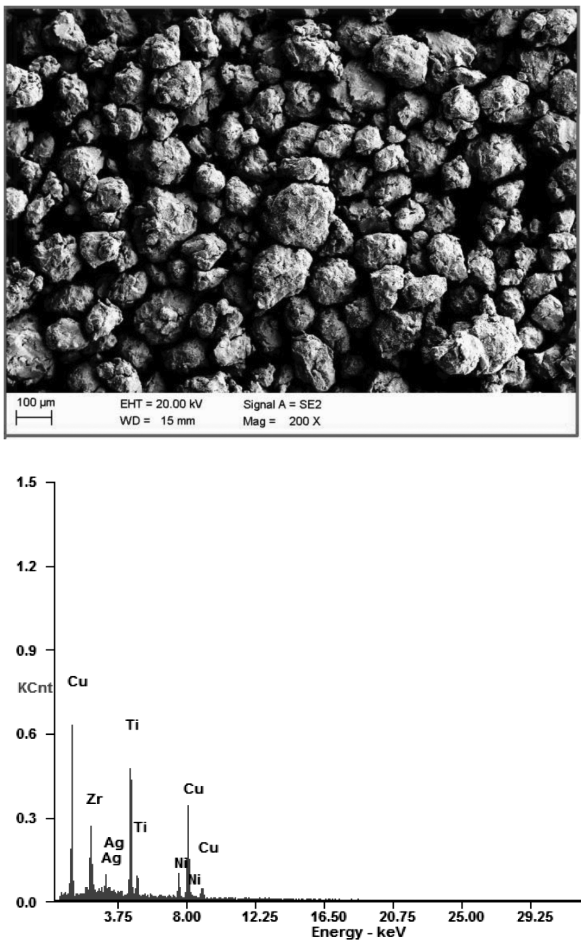

Figure 3: SEM micrographs of $Cu_{47}Ti_{34}Zr_{11}Ni_8$ powders E with marked area for energy-dispersive X-ray analysis (EDS)

3.2 XRD analysis

The XRD analysis showed that the two samples were amorphous (A and B). The diffraction pattern shows a single broad diffraction halo with the 2θ range of 42° –54° from the amorphous phase only (**Figure 4a** and **4b**). In other cases, there were peaks of crystalline phases against a background of an amorphous matrix (**Figure 4c** to **4h**). In each case, the additive microwax delayed the amorphization of the powder (**Figure 4 c, Figure 4d, 4g** and **4h**). The smaller amount of grinding medium in the reactor caused more peaks from crystalline phases on the diffractometer than in the case of samples in which the ratio by mass of grinding medium to the mass of the powder was 10:1 (e.g., **Figure 4c** and **4g**). Whereas the milling time (0.5 h or 1 h) had no effect on the structure of the powders. In the case of the fuller reactor filling, more amorphous powders came from milling for 0.5 h without interruption (**Figure 4d** and **4g**). While in the reactor, in which the ratio of balls to powder was 5:1, fewer of the crystalline peaks occurred in the powder, which was milled for 1 h without interruption (**Figure 4 c** and **4h**).

3.3 TEM analysis

TEM analysis was performed on the samples A and C. Nanocrystallites were discovered in the amorphous matrix in sample C. The following was concentrated on identifying the nanocrystallites.

Recorded selected-area electron diffraction (**Figure 5**) helped to identify the investigated phase as $Cu_{5.38}Ti_{3.33}Zr_{3.29}$. Image analysis in the light and dark

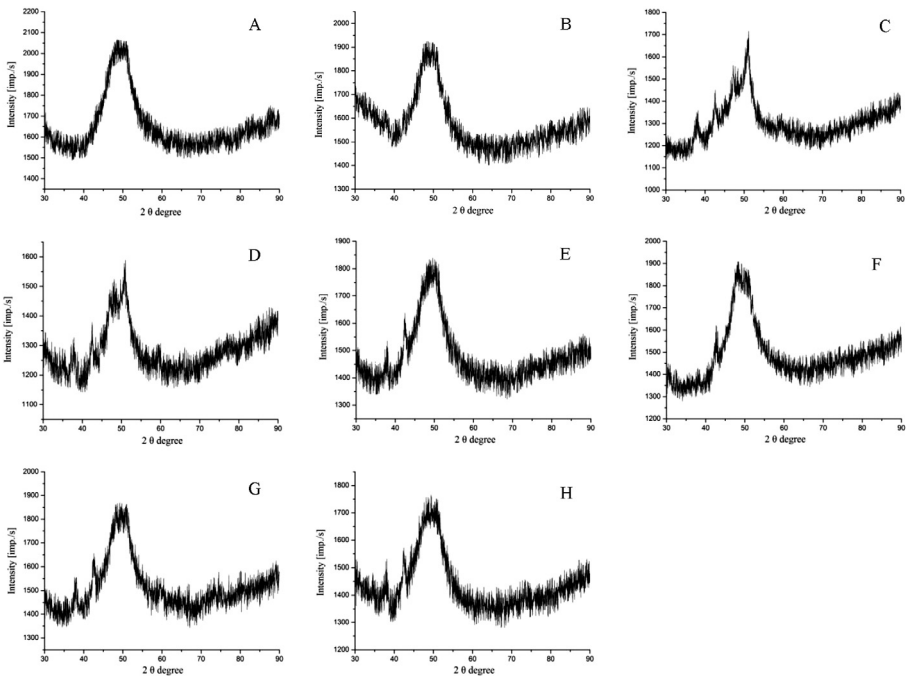

Figure 4: X-ray diffraction pattern of $Cu_{47}Ti_{34}Zr_{11}Ni_8$ powders after 10 hours of milling with different parameters of mechanical alloying: A–H (explanation of symbols shown in **Table 1**).

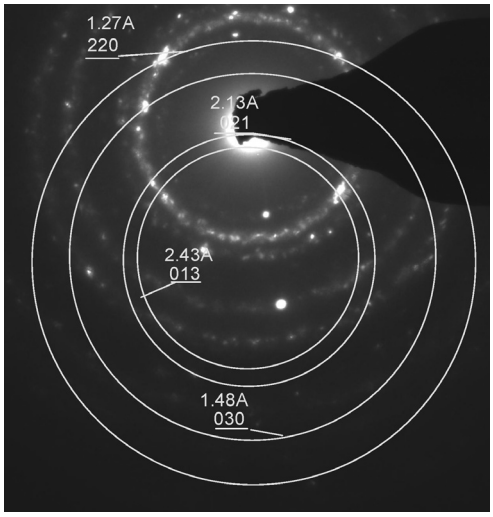

Figure 5: Selected area electron diffraction (SAED) pattern recorded from $Cu_{47}Ti_{34}Zr_{11}Ni_8$ powders C

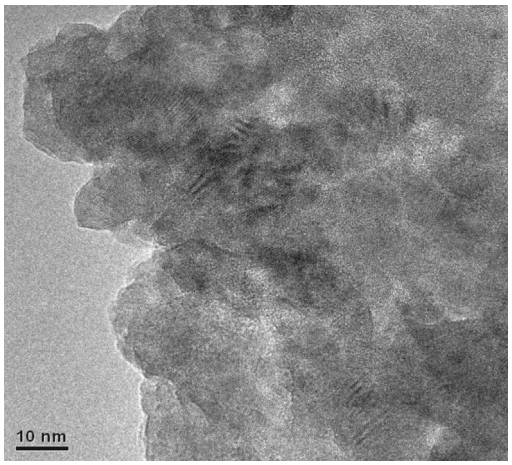

Figure 7: HRTEM images of $Cu_{47}Ti_{34}Zr_{11}Ni_8$ powders C

fields made it possible to estimate the size of the grains inside the material as about 5–10 nanometers (**Figure 6**). This confirms the very high fragmentation of grains, which can significantly improve the properties of the material.

The HRTEM images confirmed that the average grain size of the material was in the range 5–10 nm (**Figure 7**). They also allowed for confirmation of the very high homogeneity of the test material, as well as the observed grains characterized by a uniform shape.

The HRTEM image analysis allowed the implementation of a fast Fourier transform (FFT) (**Figure 8**). The solution of the FFT makes it possible to identify the analyzed grains as $Cu_{51}Zr_{14}$ in the direction of [010].

In order to confirm the fully amorphous structure of the obtained powders on the transmission electron microscope (TEM), sample A was selected (**Figure 9**). In powders A there were only continuous rings on the SAEDs (**Figure 9 b**).

3.4 The amount of material obtained after milling

In each case of milling the weights of the starting material were 8 g. The mass of grinding medium in a reactor, about ratio the material weight to the balls weight 5:1, was 40 g, and in the reactor, in which a ratio of balls weight to the material weight was 10:1, it was 80 g. The amount of material which was obtained before and after milling for the individual samples is shown in **Table 3**.

After the analysis of the results, several features were noted. From the reactors in which were placed 80 g of grinding medium, less of the milled material was obtained (more surface to deposit material), than from reactors with fewer milling balls. Also, a very high impact of a small amount of amide microwax (0.04 g) was demonstrated, for the quantity of the obtained weight of the powder after the MA process. From the reactors to which microwax was added, at least 6.18 g of material was obtained in each case. From the reactors without microwax

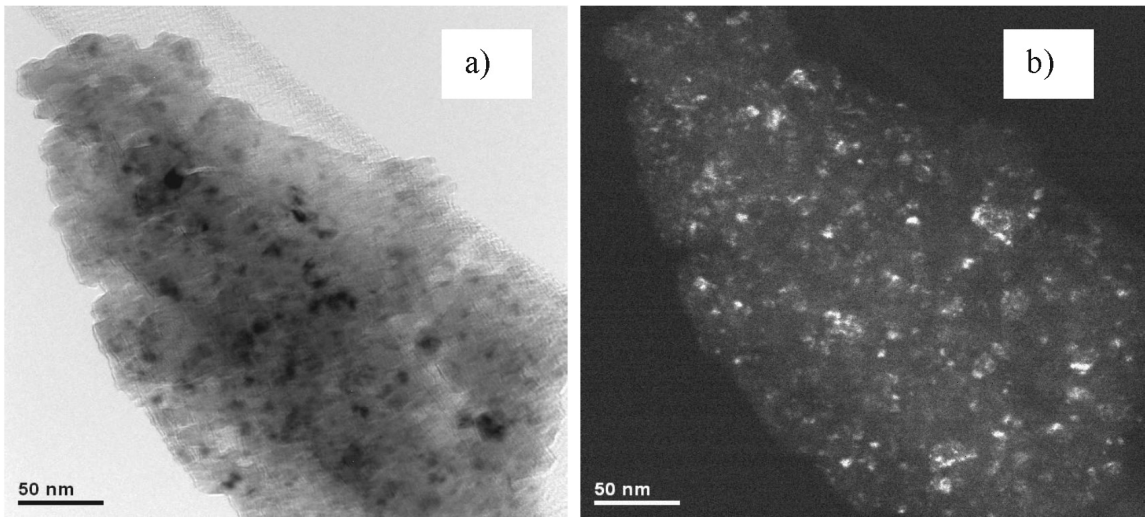

Figure 6: a) Bright-field and b) dark-field TEM image of $Cu_{47}Ti_{34}Zr_{11}Ni_8$ powders C

Table 4: Microhardness measurements (10 for each samples A-H) and the average value of received results

Number of measurement	A	B	C	D	E	F	G	H
1	479	563	482	522	527	630	585	465
2	536	613	523	521	539	545	517	526
3	557	571	447	447	496	512	475	546
4	559	535	479	481	503	516	510	570
5	587	523	538	575	561	497	538	550
6	630	606	557	547	524	524	596	528
7	492	514	517	517	598	532	521	501
8	541	567	532	521	537	515	499	516
9	568	547	498	528	512	532	511	551
10	592	553	542	532	472	542	574	583
Average	554	559	512	519	527	535	532	534

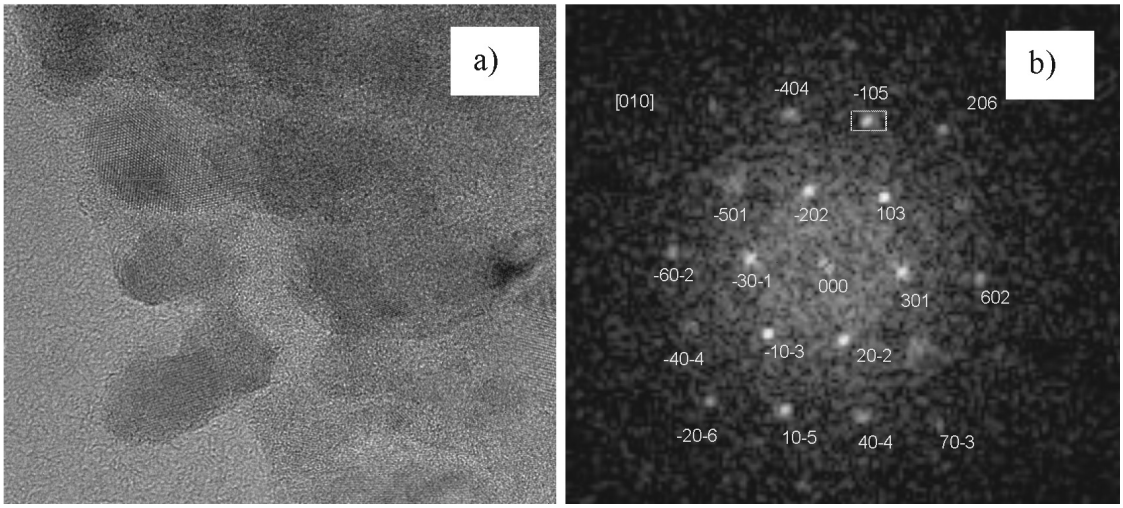

Figure 8: a) HRTEM image from $Cu_{47}Ti_{34}Zr_{11}Ni_8$ powders C and b) Fourier transform (FFT)

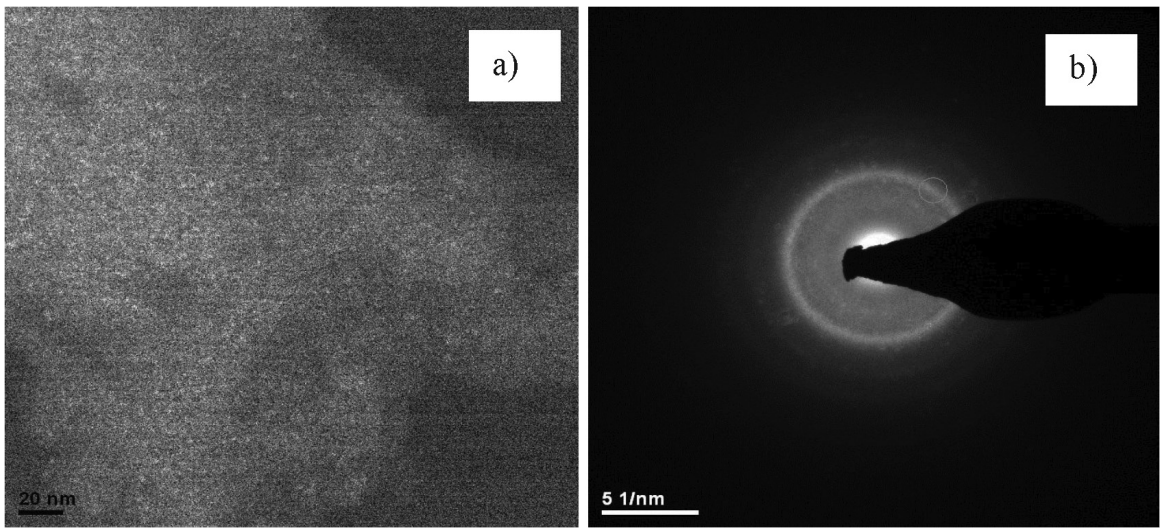

Figure 9: a) HRTEM image from $Cu_{47}Ti_{34}Zr_{11}Ni_8$ powders A and b) selected-area electron diffraction (SAED) pattern recorded from $Cu_{47}Ti_{34}Zr_{11}Ni_8$ powders A

addition, a maximum of 4.88 g milled powders were obtained. The difference between the largest quantity of generated powder from sample with and without the microwax addition was 1.79 g. This represents approximately 22 % of the total weight of the loaded material. However, there was no discernible effect of the break times (0.5 h or 1 h), for the amount of material obtained after MA.

3.5 Microhardness

The load of indenter was 100 g. The total load operating time was 15 seconds. Each of samples were examined ten times. The microhardness measurements and the average values of the results are included **Table 4**. All the microhardness measurements were very similar. As a result of the calculation of the mean value of the measurements for each sample, better results for the amorphous samples were reported. The highest microhardness was demonstrated by sample B, i.e., 559 HV. The sample A (also amorphous) showed the second highest value. Perhaps, the higher value of average microhardness was obtained for the sample B, because of longer milling time without interruption (1 h) and/or more grinding media in the reactor (10:1) was used than in sample A. For comparison, for sample A the milling time without interruption was 0.5 h, and the ratio mass of powder to the mass of grinding media was 1:5. This relationship is shown not only to amorphous samples. For other powders the average microhardness values were also higher, in cases where interruption in milling was seldom and more balls were in the reactor. The microhardness of other samples did not differ significantly from the microhardness of the amorphous powders. The lowest microhardness was obtained for powder C, i.e., 512 HV. It was found that the addition of microwax did not have an effect on the microhardness of the powders.

4 CONCLUSIONS

Based on the experiences and analysis of the obtained results, the following conclusions could be drawn:

- The parameters of the mechanical alloying had an influence on the structure, shape and size, amount of materials after milling and microhardness the $Cu_{47}Ti_{34}Zr_{11}Ni_8$ powders.
- Amorphous powder was obtained for sample A and B. This is confirmed by the XRD test, and additionally in sample A by the TEM test.
- In other cases, nanocrystallites were found in the amorphous matrix. Identification of nanocrystallites was carried out in sample C in a TEM test.
- An amorphous structure was obtained using the following parameters: the ratio of balls mass to the weight of the powder 5:1, the ratio of the milling time to the interruption 0.5 h : 0.5 h and in the second case the ratio of balls mass to the weight of the powder 10:1, the ratio of milling time to break time 1 h : 0.5 h.
- The addition of microwax caused a prolongation of the time of amorphization, larger size reduction of particles, the shape of plate and obtaining greater amount of powder material after milling.
- A longer milling time without interruption (1 h) favoured the fragmentation of grains and obtaining a higher value for the microhardness. It did not affect the structure and amount of powder after grinding.
- More balls in the reactor (80 g) caused a larger fragmentation of the particles and a higher loss of the material after milling the amount of grinding media in the reactor. The effect on the higher hardness powders was not observed.

Acknowledgments

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