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PROPERTIES AND STRUCTURE OF Cu-Ti-Zr-Ni AMORPHOUS POWDERS PREPARED BY MECHANICAL ALLOYING

LASTNOSTI IN STRUKTURA AMORFNIH PRAHOV Cu-Ti-Zr-Ni, PRIPRAVLJENIH Z MEHANSKIM LEGIRANJEM

Aleksandra Guwer, Ryszard Nowosielski, Anna Lebuda

Silesian University of Technology, Faculty of Mechanical Engineering, Institute of Engineering Materials and Biomaterials, Konarskiego Street 18A, 44-100 Gliwice, Poland
aleksandra.guwer@polsl.pl

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The method of fabrication, an investigation and a comparison of the structure, size and shape of grains of a quaternary Cu-Ti-Zr-Ni alloy were investigated. Cu-based amorphous alloys have a high strength, ductility, fracture toughness, fatigue strength and excellent corrosion resistance in solutions such as H_2SO_4, NaOH, NaCl and HNO_3. Samples of powders were prepared by mechanical alloying in a high-energy ball mill SPEX 8000. To obtain the amorphous structure of the $Cu_{47}Ti_{34}Zr_{11}Ni_8$ powder, various milling times were used. Finally, four samples for testing were obtained with pure Cu, Ti, Ni, Zr (99.99 %). The structure of the $Cu_{47}Ti_{34}Zr_{11}Ni_8$ powders was examined by X-ray diffraction (XRD) after 7 h, 8 h, 9 h and 10 h of milling time. The chemical composition, particle size and shape of the prepared powders were investigated by scanning electron microscopy (SEM). The microhardness was measured by using a Vickers hardness-testing machine with automatic track measurement. The fully amorphous powders were obtained after 10 h of milling. The prolonged time of milling resulted in an increased particle size and a changed shape of the powders. The highest microhardness was obtained for the amorphous samples.
In further work the studied amorphous powders will be consolidated using spark-plasma sintering, which is an innovative method for the production of amorphous alloys.

Keywords: mechanical alloying, Cu-based amorphous alloys, SEM, XRD, microhardness

Preiskovan je bil način izdelave, preiskava in primerjava strukture, velikosti in oblike zrn kvaternerne zlitine Cu-Ti-Zr-Ni. Amorfne zlitine na osnovi Cu imajo visoko trdnost, duktilnost, lomno žilavost, odpornost proti utrujanju in odlično odpornost proti koroziji v raztopinah H_2SO_4, NaOH, NaCl in HNO_3. Vzorci prahov so bili pripravljeni z mehanskim legiranjem v visokoenergijskem krogličnem mlinu SPEX 8000. Za zagotovitev amorfne strukture prahu $Cu_{47}Ti_{34}Zr_{11}Ni_8$ so bili uporabljeni različni časi mletja. Iz čistega Cu, Ti, Ni, Zr (99,99 %) so bili izdelani štirje preizkušanci. Struktura prahov $Cu_{47}Ti_{34}Zr_{11}Ni_8$ je bila pregledana z rentgensko difrakcijo (XRD) po 7 h, 8 h, 9 h in 10 h mletja. Kemijska sestava, velikost in oblika delcev pripravljenih prahov je bila preiskana z vrstičnim elektronskim mikroskopom (SEM). Mikrotrdota je bila izmerjena z avtomatsko napravo za merjenje trdote po Vickersu. Popolnoma amorfni prahovi so bili dobljeni po 10 h mletja. Pri podaljšanju časa mletja je narasla velikost in spremenila se je oblika delcev prahov. Najvišjo mikrotrdoto so imeli amorfni vzorci.
V nadaljevanju dela bodo preiskovani amorfni prahovi, sintrani z uporabo iskrilnega plazemskega sintranja, ki je inovativna metoda za izdelavo amorfnih zlitin.

Ključne besede: mehansko legiranje, amorfne zlitine na osnovi Cu, SEM, XRD, mikrotrdota

1 INTRODUCTION

Bulk amorphous metallic alloys exhibit many superior properties compared to crystalline alloys. Lately, it has been noted that rods and ribbons of Cu-based alloys demonstrate a high tensile strength, fatigue strength, fracture strength, ductility, relatively low cost of products, a good glass-forming ability and excellent corrosion resistance in solutions such as H_2SO_4, NaOH, NaCl and HNO_3 [1–5].

The most frequently encountered methods for the preparation of amorphous materials are casting methods. An alternative process to prepare amorphous alloys is mechanical alloying combined with the method of spark-plasma sintering. Using this production method Cu-based amorphous alloys were produced by, e.g., Kim et al.[6] and Chu et al.[7]

Mechanical alloying (MA) is defined as a high-energy milling process during which the particles are subjected to multiple cold welding, cracking and re-welding. With rapid cold deformation the specimen's temperature is increased because of the transformation of the mechanical work into heat. The MA process allows the alloying of elements that are difficult or impossible to combine by conventional casting methods. The products of MA are advanced materials, including equilibrium, non-equilibrium (amorphous, quasicrystals, nanocrystalline) and composite materials. The final material properties depend on the MA process parameters (kind of mill, size and amount of grinding media, temperature and atmosphere of milling, ratio of grinding media mass to powder mass, etc.)[8,9].

In this paper we report on the fabrication and an investigation of $Cu_{47}Ti_{34}Zr_{11}Ni_8$ alloy powder prepared by mechanical alloying. The purpose of the present work was to obtain amorphous powders that could be sintered in the future.

2 EXPERIMENTAL

2.1 Materials

Four samples with the composition $Cu_{47}Ti_{34}Zr_{11}Ni_8$ were prepared using elemental powders of copper, titanium, zirconium and nickel (99.99 % purity, < 325 mesh). Each sample was prepared with 8 g of properly weighed powders. The masses and melting points[10] of the individual elements (Cu, Ti, Zr, Ni) are shown in **Table 1**. The powder composition was weighed on an analytical high-precision balance AS/X.

Table 1: Characteristics of used elements (Cu, Ti, Zr, Ni)
Tabela 1: Značilnosti uporabljenih elementov (Cu, Ti, Zr, Ni)

Powder	x/%	m(8 g)/g	T_m/°C
Copper	47	3.9252	1085 [10]
Titanium	34	2.1389	1670 [10]
Zirconium	11	1.3187	1854 [10]
Nickel	8	0.6170	1453 [10]

x/% – amount fraction
x/% – množinski delež

2.2 Research methodology

Four different milling times were applied: (7, 8, 9, 10) h. The process of mechanical alloying was interrupted every 30 min for 30 min to lower the temperature of the crucible and the powders. Cr steel balls of 13 mm diameter were used and the ball-to-powder weight ratio was 5 : 1. The powder mixture and the Cr steel balls were placed in an austenitic crucible in an argon atmosphere inside a glove bag, as shown in **Figure 1**.

Figure 1: Schematic illustration of the cylindrical steel vessel placed in the holder inside the SPEX 8000 mill
Slika 1: Shematski prikaz cilindrične jeklene posode, postavljene v mlin SPEX 8000

A high-energy ball mill SPEX 8000 CertiPrep Mixer/Mill "shaker" type was used, which generated vibrations of the balls and the powder inside the container[11,12].

An X-ray diffractometer X'Pert Pro Panalytical and radiation (λ Co-$K\alpha$) of 0.178897 nm were used to study the structure of the obtained powders. The data of the diffraction lines were recorded using the "step-scanning" method in the 2θ range from 30 ° to 70 ° and with a 0.013 ° step. The time of the step was 40 s and the scanning speed was 0.084 ° s^{-1}.

The particles size and shape of the $Cu_{47}Ti_{34}Zr_{11}Ni_8$ powders were assessed using the microscope SEM SUPRA 25 ZEISS with a magnification up to 500-times

The chemical compositions of the samples were measured with energy-dispersive X-ray spectroscopy (EDS) with an EDS analyzer as part of the SEM. The values of the characteristic radiation energy allow a qualitative analysis in the test sample, and the intensity (peaks height) allows for a quantitative analysis.

The microhardnesses of the particles were measured by the Vickers tester with automatic track measurement using image analysis FUTURETECH FM-ARS 9000. The microhardness measurements were made under a load of 0.97 N. In each of the prepared samples, seven particles were tested.

3 RESULTS AND DISCUSSION

3.1 XRD analysis

Figure 2 demonstrates the XRD patterns of the $Cu_{47}Ti_{34}Zr_{11}Ni_8$ powders after different milling times (7 h, 8 h, 9 h, 10 h). After 7 h of mechanical alloying there is no significant change in the position of the diffraction peaks and the slightly diminished intensity of those peaks is observed. After 8 h and 9 h of processing the broadening and intensity reduction of the crystalline diffraction lines were observed and a maximum broad diffuse diffraction started to form, and after 10 h of milling the samples were amorphous. The diffraction pattern shows a single broad diffraction halo with the 2θ range of 43–54 ° from the amorphous phase without simple peaks (**Figure 2d**).

The same alloy was tested by Shengzhong et al.[13] The team of researchers used different process parameters for a QM-1SP planetary high-energy ball miller and pure elemental powders, i.e., 99.9 %. The process of mechanical alloying was interrupted every hour for 30 min. They obtained an amorphous phase after 8 h, 9 h, 10 h and 12.5 h of milling time.

The amorphous structure of the $Cu_{50}Ti_{50}$ powders was obtained after 8 h of mechanical alloying by using identical parameters to those indicated in this article[14].

3.2 Microstructure

Figure 3 shows the powders after: a) 7 h, b) 8 h, c) 9 h, d) 10 h of milling time. The initial size of the powders

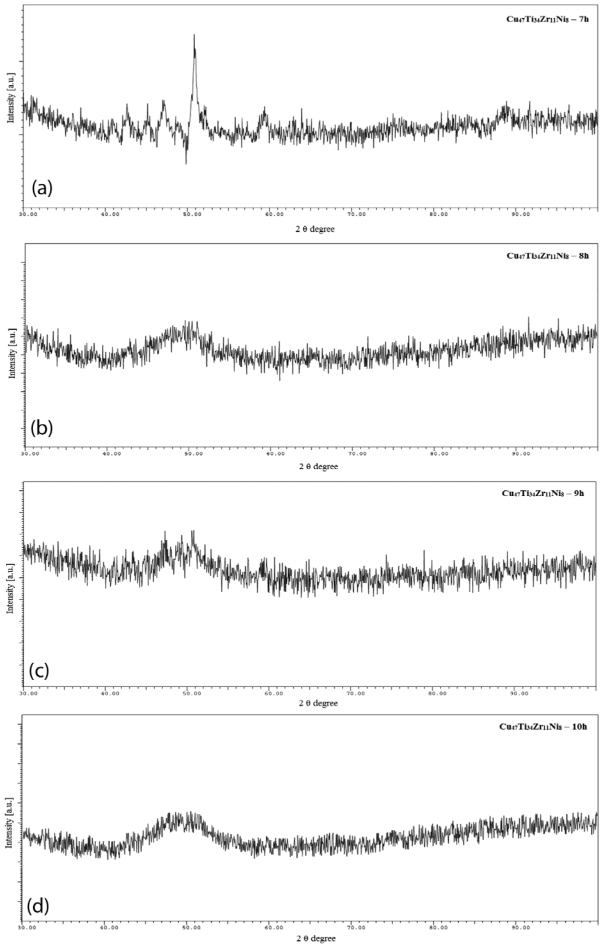

Figure 2: X-ray diffraction pattern of $Cu_{47}Ti_{34}Zr_{11}Ni_8$ powders after: a) 7 h, b) 8 h, c) 9 h, d) 10 h of mechanical alloying

Slika 2: Posnetek rentgenske difrakcije prahov $Cu_{47}Ti_{34}Zr_{11}Ni_8$ po: a) 7 h, b) 8 h, c) 9 h, d) 10 h mehanskega legiranja

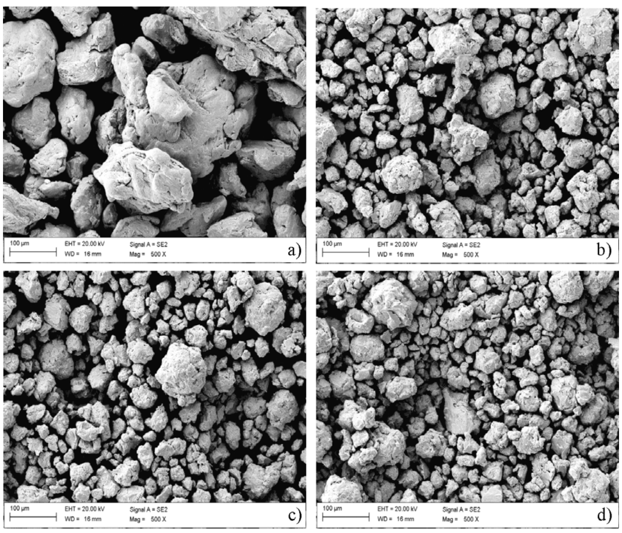

Figure 3: Shape and size of $Cu_{47}Ti_{34}Zr_{11}Ni_8$ powder after: a) 7 h, b) 8 h, c) 9 h, d) 10 h of mechanical alloying, (SEM, magnifications 500-times)

Slika 3: Oblika in velikost prahu $Cu_{47}Ti_{34}Zr_{11}Ni_8$ po: a) 7 h, b) 8 h, c) 9 h, d) 10 h mehanskega legiranja, (SEM, povečava 500-kratna)

was about 44 μm. As a result of the mechanical synthesis the powders changed their size and shape. The largest particles were found after 7 h of milling time (238 μm × 143 μm). During this milling time, the particles were stuck to large agglomerates, then after 8 h of milling time the particles disintegrated, because after 8 h of milling the particles were crushed to a smaller average of 47 μm × 25 μm. By using longer milling times (9 h, 10 h), the particles size was increased and their shape became more homogeneous and spherical. However, their size was below that after 7 h of milling time. The average size of the particles after the milling time is listed in **Table 2**.

Table 2: Average particle size (μm) of the MA powders

Tabela 2: Povprečna velikost delcev (μm) MA-prahov

Time of mechanical alloying (h)	7	8	9	10
Average particle size (μm)	238 × 143	47 × 25	63 × 41	87 × 62

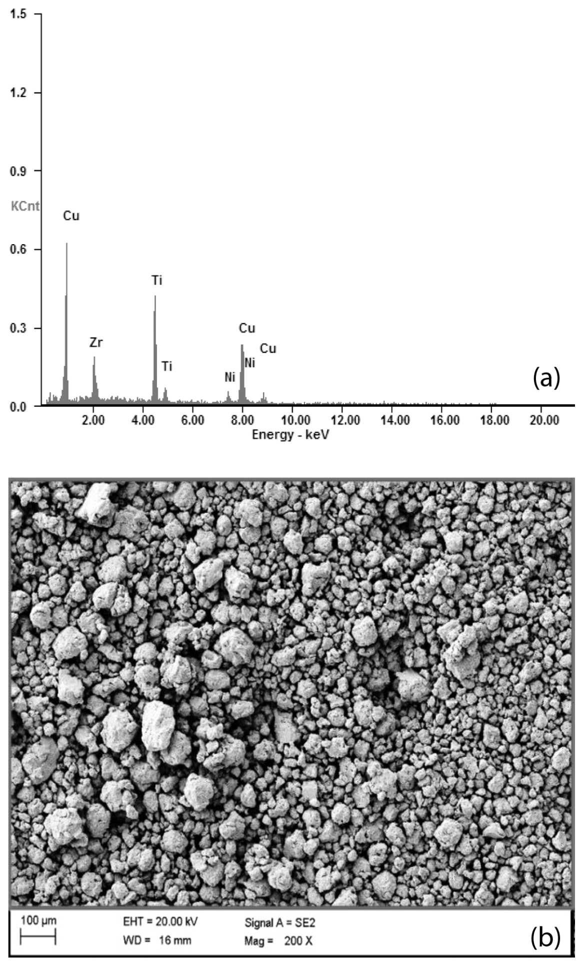

Figure 4: a) EDS spectrum with marked EDS X-ray lines and b) SEM micrographs of $Cu_{47}Ti_{34}Zr_{11}Ni_8$ powders after 10 h of mechanical alloying with 30 min interruption

Slika 4: a) EDS-spekter z označenimi EDS rentgenskimi linijami in b) SEM-posnetek prahov $Cu_{47}Ti_{34}Zr_{11}Ni_8$ po 10 h mehanskega legiranja s prekinitvijo 30 min

Figure 4 depicts the XRD spectrum and the analyzed area of the $Cu_{47}Ti_{34}Zr_{11}Ni_8$ powder after 10 h of milling. Energy-dispersive X-ray analysis (EDS) shows the X-ray lines of copper, titanium, zirconium and nickel elements in the sample. The amount of Cu, Zr, Ni and Ti depends on the time of milling. **Table 3** presents the detailed results of the chemical analysis for every sample. The particles contain the basic components (Ti, Cu, Zr and Ni). The initial atomic percentage of Cu equals 47 %, for Ti it is 34 %, for Zr it is 11 % and for Ni it is 8 %. The results indicate that the obtained powder particles after the alloying process have a very similar atomic composition compared to the initial weighed composition. The chemical composition of the milled powders confirms the existence of the metals identified from the XRD spectra.

Table 3: Chemical composition of the powders surface
Tabela 3: Kemijska analiza površine prahov

Milling Time (h)	Element	*x*/%
0	Cu	47
	Ti	34
	Zr	11
	Ni	8
7	Cu	50.61
	Ti	32.89
	Zr	09.23
	Ni	07.27
8	Cu	49.58
	Ti	33.02
	Zr	9.82
	Ni	7.58
9	Cu	48.73
	Ti	33.43
	Zr	10.02
	Ni	7.82
10	Cu	51.50
	Ti	30.94
	Zr	08.98
	Ni	08.57

3.3 Microhardness

The microhardness was measured on pressed powders with ten indentations for each sample and are shown in **Figure 5**. The deduced average microhardness after milling times (7 h, 8 h, 9 h, 10 h) is shown in **Table 4**. The highest average microhardness was obtained for the powders after 10 h of milling time (553 HV), i.e., for the powders with the fully amorphous structure. The average microhardness increases with the milling time. The difference between the lowest 334 HV, after 7 h of milling, and the highest (518 HV), after 10 h of milling, was 184 HV. This indicates the great heterogeneity of the obtained particles. The average microhardness of the amorphous powder $Cu_{47}Ti_{34}Zr_{11}Ni_8$ (553 HV) is higher than that of the amorphous powders $Cu_{50}Ti_{50}$ (542 HV).[14]

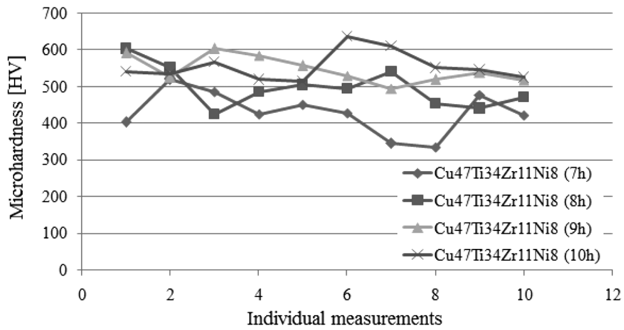

Figure 5: Powders microhardness after different milling times
Slika 5: Mikrotrdote prahov po različnih časih mletja

4 CONCLUSIONS

The result of the tests and the examination of the $Cu_{47}Ti_{34}Zr_{11}Ni_8$ powders lead to the following conclusions:

- It is possible to obtain an amorphous structure for a four-component alloy $Cu_{47}Ti_{34}Zr_{11}Ni_8$ by using mechanical synthesis in a SPEX 8000 mill.
- An amorphous structure was obtained for the 10 h milling-time sample.
- The largest particles are obtained after 7 h milling and the smallest after 8 h milling. The largest shape and the best size regularity were obtained for the amorphous powders.
- The presence of the initial elements Cu, Ti, Zr, Ni in the milled particles was confirmed. The content of elements in the milled powders corresponds to the initial weighed composition.
- The average microhardness value increases with the milling time and the highest hardness is achieved in the amorphous sample (553 HV).

Acknowledgments

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Table 4: Average microhardness after different mechanical-alloying times
Tabela 4: Spreminjanje povprečne mikrotrdote pri različnem trajanju mehanskega legiranja

Samples	$Cu_{47}Ti_{34}Zr_{11}Ni_8$ (7 h)	$Cu_{47}Ti_{34}Zr_{11}Ni_8$ (8 h)	$Cu_{47}Ti_{34}Zr_{11}Ni_8$ (9 h)	$Cu_{47}Ti_{34}Zr_{11}Ni_8$ (10 h)
The average microhardness (HV)	428	496	545	553

5 REFERENCES

[1] P. Lee, C. Yao, J. Chen, L. Wang. R. Jeng, Y. Lin, Preparation and thermal stability of mechanically alloyed Cu–Zr–Ti–Y amorphous powders, Materials Science and Engineering A, 375–377 (**2004**), 829–833, doi:10.1016/j.msea.2003.10.107

[2] C. Suryanarayana, A. Inoue, Bulk Metallic Glasses, CRC Press, Boca Raton, London, New York 2011, 313–322

[3] H. Kim, K. Sumiyama, K. Suzuki, Formation and thermal stability of nanocrystalline Cu-Ti-Ni prepared by mechanical alloying, Journal of Alloys and Compounds, 239 (**1996**), 88–93, doi:10.1016/0925-8388(96)02274-8

[4] C. Hu, H. Wu, Formation of Cu–Zr–Ti amorphous powders with Band Si additions by mechanical alloying technique, Journal of Alloys and Compounds, 434–435 (**2007**), 390–393, doi:10.1016/j.jallcom.2006.08.219

[5] A. Inoue, B. Shen, A. Takeuchi, Fabrication, properties and applications of bulk glassy alloys in late transition metal-based systems, Materials Science and Engineering A, 441 (**2006**), 18–25, doi:10.1016/j.msea.2006.02.416

[6] C. K. Kim, H. S. Lee, S. Y. Shin, J. C. Lee, D. H. Kim, S. Lee, Microstructure and mechanical properties of Cu – based bulk amorphous alloy billets fabricated by spark plasma sintering, Materials Science and Engineering A, 406 (**2005**), 293–299, doi:10.1016/j.msea.2005.06.043

[7] Z. H. Chu, H. Kato, G. Q. Xie, G. Y. Yuan, W. J. Ding, A. Inoue, Consolidation and mechanical properties of $Cu_{46}Zr_{42}Al_7Y_5$ metallic glass by spark plasma sintering, Journal of Non-Crystalline Solids, 358 (**2012**), 1263–1267, doi:10.1016/j.jnoncrysol.2012.02.027

[8] C. Suryanarayana, Recent developments in mechanical alloying, Reviews on Advanced Materials Science, 18 (**2008**), 203–211

[9] M. Adamiak, Mechanical alloying for fabrication of aluminium matrix composite powders with Ti-Al intermetallics reinforcement, Journal of Achievements in Materials and Manufacturing Engineering, 31 (**2008**), 191–196

[10] The Engineering ToolBox /cited 2014-07-10/. Available from World Wide Web: http://www.engineeringtoolbox.com/melting-temperature-metals-d_860.html

[11] R. Nowosielski, R. Babilas, G. Dercz, L. Pajak, J. Wrona, Structure and properties of barium ferrite powders prepared by milling and annealing, Journal of Achievements in Materials and Manufacturing Engineering, 22 (**2007**), 45–48

[12] R. Nowosielski, R. Babilas, G. Dercz, L. Pająk, Microstructure of composite material with powders of barium ferrite, Journal of Achievements in Materials and Manufacturing Engineering, 17 (**2006**), 117–120

[13] K. Shengzhong, F. Liu, D. Yutian, X. Guangji, Synthesis and magnetic properties of Cu-based amorphous alloys made by mechanical alloying, Intermetallics, 12 (**2004**), 1115–1118, doi:10.1016/j.intermet.2004.04.007

[14] A. Guwer, R. Nowosielski, A. Borowski, R. Babilas, Fabrication of copper-titanium powders prepared by mechanical alloying, Indian Journal of Engineering & Materials Sciences, 21 (**2014**), 265–271