Volume 70 • Issue 1 • May 2015

Journal of Achievements in Materials and Manufacturing Engineering

International Scientific Journal published monthly by the World Academy of Materials and Manufacturing Engineering

$Cu_{47}Ti_{34}Zr_{11}Ni_8$ amorphous alloy fabricated by the pressure die casting method

R. Nowosielski, A. Guwer*, A. Gawlas-Mucha

Division of Nanocrystalline and Functional Materials and Sustainable Pro-ecological Technologies, Institute of Engineering Materials and Biomaterials, Silesian University of Technology, ul. Konarskiego 18a, 44-100 Gliwice, Poland

* Corresponding e-mail address: aleksandra.guwer@polsl.pl

ABSTRACT

Purpose: The aim of present work is characterization of the pressure die casting, fabrication and testing of structure and properties $Cu_{47}Ti_{34}Zr_{11}Ni_8$ ingot and amorphous and crystalline alloys prepared in the form of rods.

Design/methodology/approach: The preliminary ingot was prepared by using the method of arc melting. Rods were fabricated by the pressure die casting method. The melting point and liquidus temperatures of the ingot were determinated in the thermal analysis DTA. Analysis of the microstructure of a pre-alloy was carried out by using the EDS method. X-ray diffraction was used to study structure of fabricated ingot and rods. Hardness was measured by using the Vickers method and compression tests were also performed.

Findings: Modernization of the pressure die casting station in the form of housing, which was made from the plexiglass, allowed to keep a protective atmosphere during casting, after that alloys did not oxidate. The X-ray diffraction investigations were indicated that the examined quaternary rods with 2 mm and 3 mm diameters had amorphous structure. The rod with diameter of 4 mm had crystalline structure. The phases occur in ingot and crystalline rods were identified by using X-ray card. Rod about 4mm diameter demonstrated the highest hardness. The rod with diameter of 3 mm demonstrated the highest compressive strength - 1798 MPa.

Research limitations/implications: In the future, the research of mechanical properties of $Cu_{47}Ti_{34}Zr_{11}Ni_8$ amorphous rod will be performed. Moreover, further attempts of a fabrication of the $Cu_{47}Ti_{34}Zr_{11}Ni_8$ amorphous rod about diameter higher than 3 mm, will be prepared.

Practical implications: A manufactured housing enables the production of bulk metallic glasses about different chemical compositions, by preventing possible oxidations of elements.

Originality/value: Modernization of position for the pressure die casting into copper mould. A comparison of properties of $Cu_{47}Ti_{34}Zr_{11}Ni_8$ amorphous and crystalline rods.

Keywords: Amorphous materials; Bulk metallic glasses; Pressure die casting method

Reference to this paper should be given in the following way:

R. Nowosielski, A. Guwer, A. Gawlas-Mucha, $Cu_{47}Ti_{34}Zr_{11}Ni_8$ amorphous alloy fabricated by the pressure die casting method, Journal of Achievements in Materials and Manufacturing Engineering 70/1 (2015) 5-12.

MATERIALS

1. Introduction

Amorphous materials have better properties than the corresponding crystalline materials. Amorphous matrix is a solid which not having a periodic arrangement of atoms characteristic for the crystal and resulting of it the property. In this solid occurs only the short-range order. The molecules are arranged in a chaotic manner, more similar to the one found in liquid, so often is encountered the term "supercooled liquid" [1, 2]. Glass is a solid about amorphous structure formed by melting of certain materials such as silica or a mixture of suitably selected materials and followed by sufficient cooling of the material. Among the glasses are distinguished oneself metallic glasses, which are formed by the rapid cooling. This kind of materials are prepared from metal and non-metal alloys. A special type of such materials are bulk metallic glasses materials about amorphous structure and a diameter greater than 1mm [3].

Structure of amorphous materials ensure among others production methods which involve the very rapid discharge of heat from the heated starting material. Methods of manufacture of metallic glasses include among others: splat-cooling, double-roll casting, melt-spinning, laser melt-spinning. The methods of producing bulk metallic glasses include: water-quenching, squeeze casting process, electromagnetic vibration, high-pressure die casting, copper mold casting, cap cast technique, suction-casting, arc-melting and unidirectional melting zone. Depending on the choice of method of manufacturing, samples were obtained in various forms such as: ribbon, rod, thin sheet, plate, drop. The Figure 1 shows a casting area for fabrication bulk metallic glasses in form of rods [4].

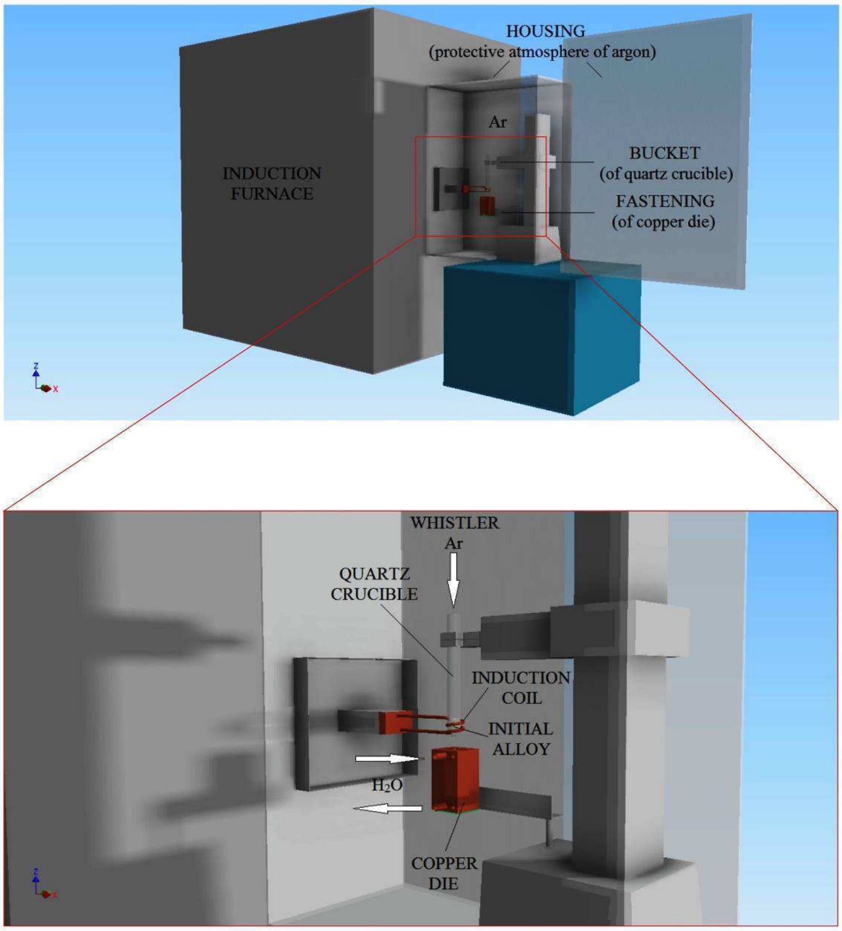

Fig. 1. The scheme of area for casting of bulk metallic glasses by using the pressure die casting method

The pressure die casting method consists in pouring in the molten pre-alloy into copper mold. Pre-alloy is placed in a quartz crucible mounted in the induction coil over the copper mold. The fusion of material is ensured by inductive current. The molten material is pushed out from the crucible using a blowing of inert gas-argon. The molten material fills of copper die, which rapidly absorbs heat from the material and causes changes of the material state from liquid to solid [4-6]. If the rod is formed from oxidizable metal (for example at elevated temperature), it is necessary to provide a protective atmosphere during casting [7-10]. In order to produce a sealed atmosphere, it was made the plexiglas housing of position for casting rods. Scheme of modernized position is given in Figure 1.

Execution of the housing was necessary because the $Cu_{47}Ti_{34}Zr_{11}Ni_8$ alloy which is the subject of research has in its composition the elements strongly react with oxygen at elevated temperature. Titanium is inflammable at a temperature of 1200°C in air and in pure oxygen in 610°C [11], and zirconium reacts violently with oxygen in approx. 700°C [11].

The main advantage of Cu-based alloy, which allows their commercial application is a relatively low cost of these alloys [12]. The $Cu_{47}Ti_{34}Zr_{11}Ni_8$ amorphous alloy was developed by Johnson et al. in 1995 [12-14]. Maximum thickness of cast rod was 4 mm by a critical cooling rate of about $250Ks^{-1}$ [14, 15]. Ribbons of this four component alloy can by welding by resistance spot welding [16]. Jian et al. in article "Strengthening bulk metallic glasses with minor alloying additions" reported that they fabricated sheets with a length of 50mm and cross section of 1mm x 5mm [17].

Therefore, the article describes a modernization of the area for casting of rods by using pressure die casting method, designed to provide a sealed argon atmosphere. Pre-alloy was prepared and the rods having a diameter of 2, 3 and 4mm were cast. Their structures and hardness were examined.

2. Experimental procedure

The production of specimen was run in two stages. First, the pre-alloy was prepared. The resulted ingot was remelted and casted into a copper die to obtain a sample in the form of rod. The structure and some mechanical properties were examined.

2.1. Material

Approximately 3 g of polycrystalline $Cu_{47}Ti_{34}Zr_{11}Ni_8$ were fabricated by arc melting (Compact Arc Melter MAM-1, Edmund Buhler GmbH, Germany) in a high purity (5N) argon atmosphere using high purity (Cu, Ti, Zr and Ni-99,99%) elements in form of powders about particle size <325 mesh. The amount of each element (Cu, Ti, Zr, Ni) attributable per 3g of the alloy and the melting point are listed in Table 1. The compounds were re-melted six times to achieve a homogeneous composition. In order to obtain sufficient quantity of material for the preparation of samples in form of rods were prepared several ingots.

Table 1.
Characteristics of used elements (Cu, Ti, Zr, Ni) to prepare the pre-alloy

Powder	at. [%]	mass per 3 [g]	T_m [°C]
Copper	47	1,47195	1085 [18]
Titanium	34	0,8021	1670 [18]
Zirconium	11	0,4945	1854 [18]
Nickel	8	0,2314	1453 [18]

2.2. Research methodology

The X-ray diffraction measurement of the prepared pre-ingot was performed at ambient temperature using a Rigaku MiniFlex 600 diffractometer (Rigaku Corporation, Tokyo, Japan) with Cu Kα radiation (λ =1,5406Å), a tube voltage of 40kV, and a current of 15mA using a D/teX Ultra silicon strip detector.

Examination of the structure of the fabricated rods were performed on X-ray diffractometer X'Pert Pro Panalytical. The length of radiation (λ CoKα) was 0,178897nm. The data of diffraction lines were recorded by "step-scanning" method in 2θ range from 30° to 90° and with 0,026° step. Time of step was 25,5s and scanning speed 0,26°/s.

X-ray microanalysis of ingot was carried out on JXA 8230 of JEOL company.

DTA measurements were performed on a device STA 449 F3 Jupiter (Netzsch). The process of heating and cooling were made after earlier pumping out the working chamber and rinsing by using Ar. During the process, the protective gas (Ar) flew through the chamber at a rate of 50ml/min. Heating rate was 40 K/min. The samples were placed in Al_2O_3 crucibles.

Microhardness of the ingot and rods were measured by using the Vickers hardness testing machine with automatic track measurement using image analysis FUTURE-TECH FM-ARS 9000. Hardness measurements were made under load 500g. Each of the samples were tested seven times.

Compression test was performed on testing machine Zwick roll z020.

3. Description of results

3.1. Research of pre–alloy

DTA measurements

Figure 2 presents DTA curves for $Cu_{47}Ti_{34}Zr_{11}Ni_8$ crystalline alloy. In result of melting the $Cu_{47}Ti_{34}Zr_{11}Ni_8$ pre-alloy with heating rate 40 K/min was obtained curves, which shows picture 2a. On this curve arose a clear endothermic peak, which allowed to determine the onset point (melting temperature) - 832.1°C. The figure on the right (Figure 2b) displays a curve, which was obtained during cooling the $Cu_{47}Ti_{34}Zr_{11}Ni_8$ pre-alloy by cooling rate 40K/min. From the curve was read endset point (crystallization temperature), whose value equals 852.3°C.

For comparison, X.H. Lin et al. reported in 1995 that solidus temperature for $Cu_{47}Ti_{34}Zr_{11}Ni_8$ crystalline alloys equals 831.9°C and liquidus temperature is 886.9°C [19]. The results are similar to obtained in this paper. The difference in melting points between the value obtained in the DTA test in this article and value, which was determined by X.H. Lin equals 0.2°C. Slightly larger difference in values between the temperature of crystallization - 34.6°C was noted. Unfortunately, in the article wasn't defined the heating and cooling rate, which were used in the DTA research by X.H. Lin. Perhaps the difference in crystallization temperature of the alloy is a result of using of different cooling rate of the alloy. Moreover, in the current article the pre-alloy was prepared by arc-melting method whereas in the cited article by using induction melting. In the next step, the microanalysis studies were performed. Outcomes were described below.

X-ray microanalysis

In the first step of chemical microanalysis four areas of the fracture surface of the ingot were examined. Selected zones of the study is indicated in Figure 3a. The starting material included the following elements: Cu, Ti, Zr, Ni about of percentage, which was respectively 47 at.%, 34 at.%, 11 at.% and 8 at.%. Investigated amounts of the individual elements in the areas of the sample were summarized in Table 2. The average value for Cu from selected zones amounted 48,375 at.%, Ti - 33,825 at.%, Zr - 9,425 at.% and Ni - 8,375 at.%. The obtained values were slightly different from the amount of starting elements.

Then performed X-ray microanalysis for a larger area. The area tested was indicated in Figure 4a. The results of the analysis are given in Figure 4b. The presence of only starting elements was confirmed. Quantitative chemical analysis was showed the following amounts of elements in the test area of the surface: Cu - 47.8 at. % Ti - 33.7 at. % Zr - 11.64 at. % and Ni - 7.86 at. %. The results obtained are closer to the output values than the results obtained from the quantitative analysis of small surface of sample.

X-ray analysis

Studies X-ray powder diffraction pattern for the obtained master alloys were carried out at room temperature. The sample in the form of powder from the alloy obtained previously was prepared by hand grinding in an agate mortar. The resulting pattern has many peaks from crystalline phases (Fig. 5a). In order to identify the peaks occurring on the diffraction patterns was consulted of the database ICSD Database FIZ Karlsruhe 2014-1. Identified the following phases: Cu_3Ti, CuTi and CuNi. Only the Cu_3Ti phase appeared three times. It was used the next cards about ICSD collection code: 103127, 103131 and 103063. Other peaks were appeared on the background level.

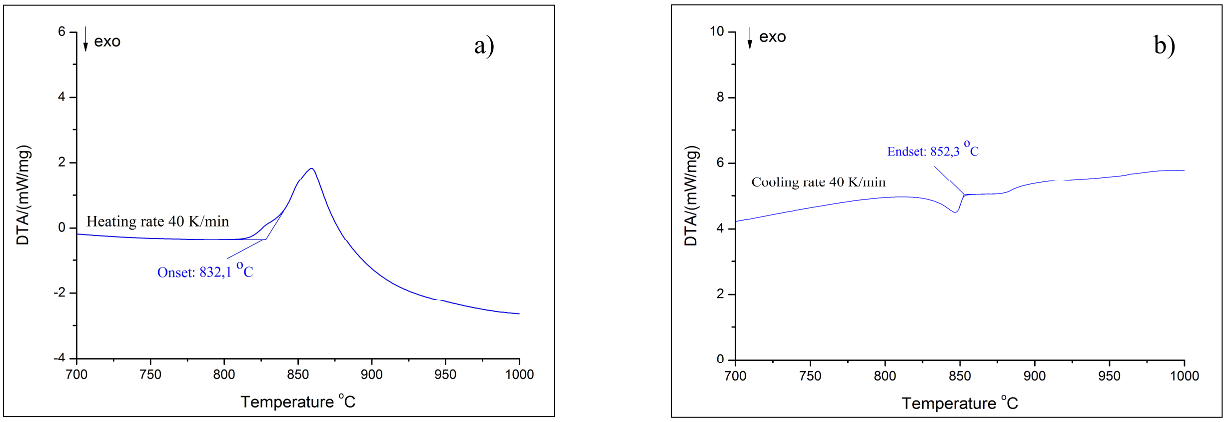

Fig. 2. DTA traces obtained from the $Cu_{47}Ti_{34}Zr_{11}Ni_8$ crystalline pre-alloy with marked a) onset point for heating rate 40°C K/min and b) endset point for cooling rate 40°C K/min

Table 2.
Results of chemical analysis from the surface of marked areas: 001 - 004 in picture

Element	Initial element [At %]	Area 001 [At %]	Area 002 [At %]	Area 003 [At %]	Area 004 [At %]
Cu	47	47.3	48.4	47.4	50.4
Ti	34	34.7	33.4	34.2	33.0
Zr	11	9.2	9.9	10.1	8.5
Ni	8	8.8	8.3	8.3	8.1

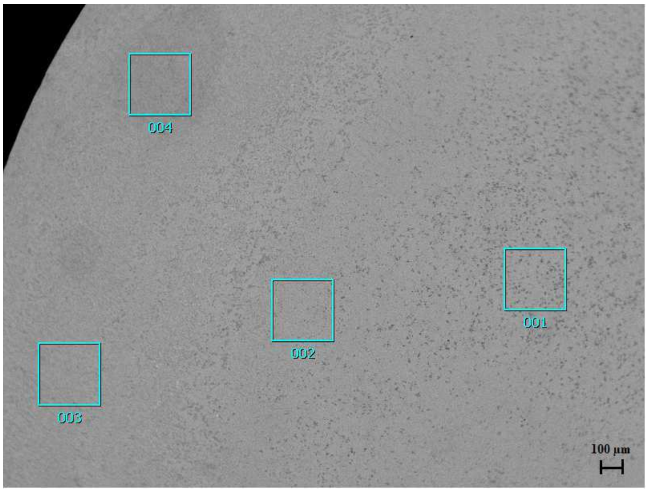

Fig. 3. SEM micrographs of $Cu_{47}Ti_{34}Zr_{11}Ni_8$ ingot on magnification 40x with marked areas for which energy dispersive X-ray analysis (EDS) was made and result

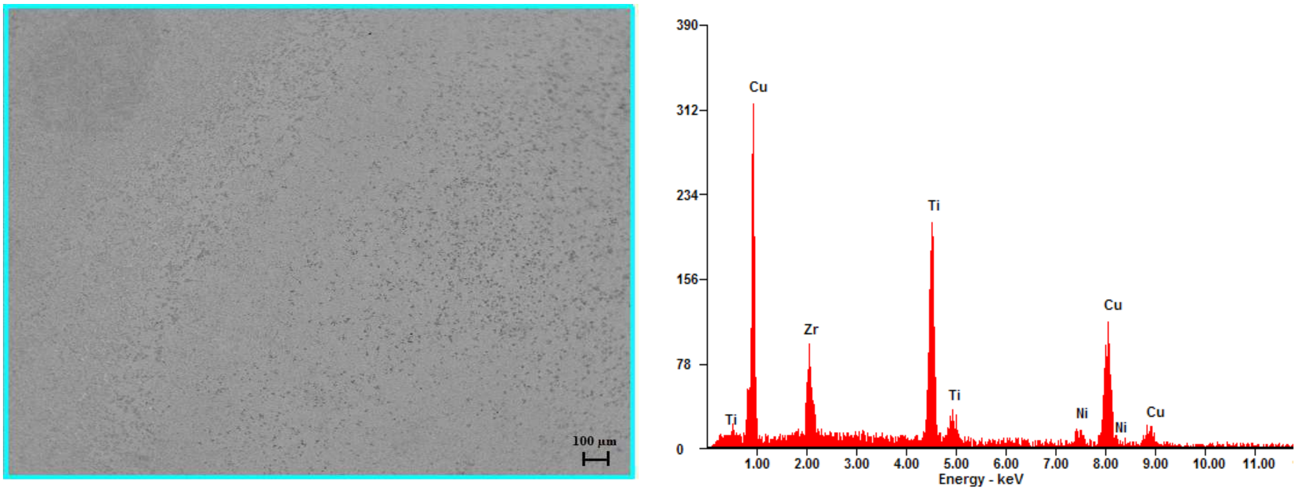

Fig. 4. Result of energy dispersive X-ray analysis (EDS) of $Cu_{47}Ti_{34}Zr_{11}Ni_8$ ingot for the marked area

3.2. Research of Rods

X-Ray analysis

Figure 5b and 5c show X-ray diffraction analysis of rod with 2mm and 3mm were amorphous. The diffraction patterns show a single broad diffraction halo with the 2θ range of 43º-57º from the amorphous phase only (without any peaks). In Figure 5d is illustrated X-ray diffraction analysis for rod about 4mm of diameter. The obtain X-ray diffraction photograph is characterized a lot of peaks, so the structure of rod is crystalline. The identification of individual phases was performed by using the ICSD Database FIZ Karlsruhe 2014-1. For peaks were identified the following phases: $Cu_{51}Zr_{14}$ and CuTi. Phases occurred three times each, so these definitely can be found in the sample. In addition to these phases were also identified CuZr and CuNi. In aim to solve X-ray pattern the cards with following ICSD collection code were used: 103163, 103127, 103063 and 629471.

Hardness

The Vickers hardness test was carried out under a load of 500g, namely during low load which constituted 4.85N. In the first instance the pre-alloy was tested. Its average hardness was 569HV. The difference between the highest measured value of hardness and the lowest was 30N. All prepared rods (amorphous and crystalline) characterized by a greater hardness than the pre-alloy, from which they were fabricated. The highest average hardness showed crystalline rod with a diameter of 4 mm - 671. Amorphous rods had very similar hardness to each other, but lower than the crystalline rod. Amorphous rod having a diameter of 2 mm - 618N, and rod with a diameter of 3mm - 62N. The difference between the largest and the smallest value of the hardness for each of the tested rods amounted to more than 50N (Φ 2mm - 53N, Φ 3mm - 54N, and Φ 4mm - 55N). Each of the recorded measurements of hardness of the tested samples and their average values shown in Table 3.

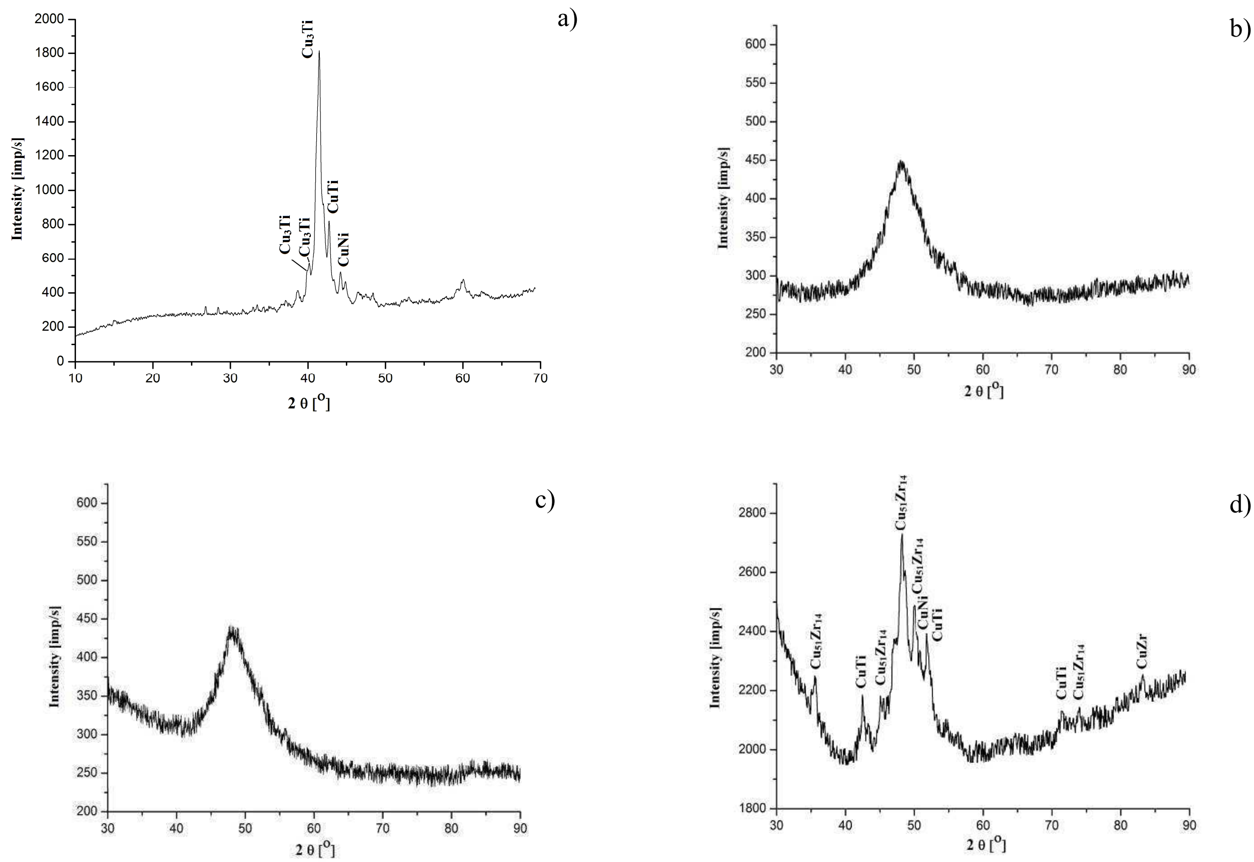

Fig. 5. X-ray diffraction patterns of $Cu_{47}Ti_{34}Zr_{11}Ni_8$ a) pre-alloy, b) amorphous rod with diameter of 2mm, c) amorphous rod with diameter of 3mm, d) crystalline alloy with diameter of 4mm

Table 3.
The results of Vickers hardness for pre-alloy and fabricated rods

SPECIMEN	1	2	3	4	5	6	7	AVERAGE
Ingot	570	557	565	563	574	570	587	569
Rod φ 2 mm	620	642	589	635	598	609	632	618
Rod φ 3 mm	599	653	602	638	624	621	632	624
Rod φ 4 mm	672	702	655	688	658	647	675	671

Compression test

Figure 6 shows compressive stress-strain curve for the tested $Cu_{47}Ti_{34}Zr_{11}Ni_8$ amorphous rods. Rod with diameter of 3mm exhibited elastic elongation in the range up to 1.55%, plastic elongation of about 1.68%, and fracture elongation of about 1.8%. The compressive strength equals about 1798MPa and Young's modulus about 110GPa. Whereas the rod about diameter of 2mm is characterized the higher elongations values but the lower values of stresses and Young's modulus. The elastic elongation, plastic elongation, fracture elongation, compressive strength and Young's modulus are 1.8%, 1.9%, 2.1%, 1775MPa and 90.6GPa.

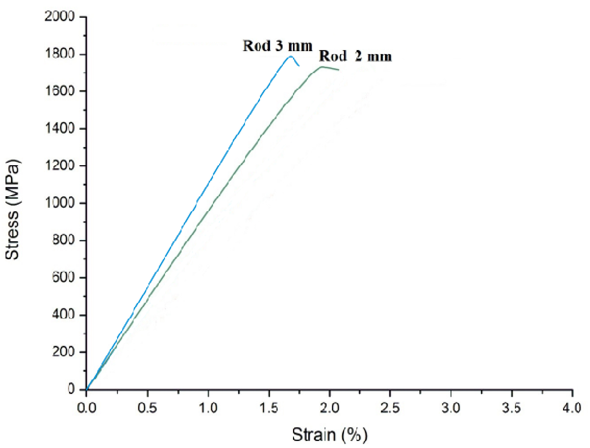

Fig. 6. Stress-strain curves obtained from the uniaxial compression test for $Cu_{47}Ti_{34}Zr_{11}Ni_8$ amorphous rods

4. Conclusions

As result of provided researches of $Cu_{47}Ti_{34}Zr_{11}Ni_8$ ingot and rods the following conclusions were stated:

- it is possible to fabricated $Cu_{47}Ti_{34}Zr_{11}Ni_8$ pre-alloy by arc-melting method,
- as a result of DTA the onset point - 832.1°C with heating rate 40K/min and endset point - 852.3°C with cooling rate 40K/min were determined;
- in result of EDS analysis, the of pre-alloy occurrence of initial elements Cu, Ti, Zr, Ni was confirmed. Quantitative composition of the elements wasn't changed significantly in relation to initial weighed composition;
- prepared housing of station allowed for keeping protective atmosphere of argon and the cast rods weren't oxidized;
- X-ray analysis revealed that the structure of rods with a diameter of 2mm and 3mm were amorphous. Rod with a diameter of 4mm was crystalline. In the structure were identified the following phases: $Cu_{51}Zr_{14}$ and CuTi;
- the hardness test of pre-alloy and rods by Vickers method showed that each of the fabricated rods (amorphous and crystalline) are characterized by greater hardness than the pre-alloy (569HV).

Acknowledgements

The research was partially supported by the National Science National Science Centre under research Project No.: 2012/07/N/ST8/03437.

Part of the research was developed in cooperation with the Institute of Non-Ferrous Metals, Sowinskiego 5, 44-100 Gliwice, Poland.

References

[1] L. A. Dobrzański, Fundamentals of materials science and physical metallurgy. WNT Press, Gliwice, 2006.
[2] K. Brzózka, Examination of the structure and properties of amorphous and nanocrystalline alloys based on iron by Mössbauer spectroscopy. First Edition, Technical University of Radom, Radom, 2003.
[3] R. Zallen, Physics of amorphous bodies. PWN Press, Warsaw, 1994.
[4] C. Suryanarayana, A. Inoue, Bulk Metallic Glasses. CRC Press, Taylor&Francis Group, Boca-Raton-London-New York, 2011.

[5] R. Nowosielski, R. Babilas, A. Guwer, A. Gawlas-Mucha, A. Borowski, Fabrication of $Mg_{65}Cu_{25}Y_{10}$ bulk metallic glasses, Journal of Archives of Materials Science and Engineering 53 (2012) 77-84.

[6] A. Borowski, A. Guwer, A. Gawlas-Mucha, R. Babilas, R. Nowosielski, Fabrication of Mg-based bulk metallic glasses by pressure die casting method, Indian Journal of Engineering And Materials Sciences 21 (2014) 259-264.

[7] S. Lesz, Preparation of Fe-Co-based bulk amorphous alloy from high purity and industrial raw materials, Archives of Materials Science and Engineering 4 (2011) 77-88.

[8] S. Lesz, S. Griner, R. Nowosielski, Influence of geometry of rapidly solidified rods on properties of Fe-Co-based alloy, Journal of Achievements in Materials and Manufacturing Engineering 1 (2010) 16-25.

[9] S. Lesz, R. Babilas, R. Nowosielski, Influence of Copper Addition on Glass Forming Ability, Thermal Stability, Structure and Magnetic Properties of Fe-Co-Based BMGs, Solid State Phenomena 6/203-204 (2013) 296-301.

[10] R. Nowosielski, A. Borowski, A. Guwer, R. Babilas, Fabrication of ternary Ca-Mg-Zn bulk metallic glasses, Journal of Achievements in Materials and Manufacturing Engineering 56 (2013) 67-74.

[11] R. Singh, Applied Welding Engineering, Processes, Codes and Standards, Second Edition, BH, Elsevier Inc, 2016.

[12] N. Baca, R. Conner, S. Garrett, Corrosion behaviour of oxide-covered $Cu_{47}Ti_{34}Zr_{11}Ni_8$ (Vitreloy 101) in chloride-containing solution, Materials Science and Enginering B 134 (2014) 105-112.

[13] B. Liu, L. Liu, The effect of microalloying on thermal stability and corrosion resistance of Cu-based bulk metallic glasses, Materials Science and Engineering A 415 (2006) 286-290.

[14] E. Park, H. Chang, D. Kim, Improvement of glass-forming ability and phase separation in Cu-Ti-rich Cu-Ti-Zr-Ni-Si bulk metallic glasses, Journal of Alloys and Compounds 504S (2010) 27-30.

[15] L. Liu, B. Liu, Influence of the micro-addition of Mo on glass forming ability and corrosion resistance of Cu-based bulk metallic glasses, Electrochimica Acta 51 (2006) 3724-3730.

[16] N. Baca, T. Ngo, R. Conner, S. Garrett, Small scale resistance spot welding of $Cu_{47}Ti_{34}Zr_{11}Ni_8$ (Vitreloy 101) of bulk metallic glass, Journal of Materials Processing Technology 213 (2013) 2042-2048.

[17] K. Jian, X. Dang-sheng, Y. Qun-xing, Y. Zhi-tao, Strengthening bulk metallic glasses with minor alloying additions, Transactions of Nonferrous Metals Society of China (2006) 598-602.

[18] The Engineering ToolBox /cited 2014-07-10/. Available from World Wide Web: http://www.engineeringtoolbox.com/meltingtemperaturemetalsd_860.html

[19] X. Lina, W. Johnson, Formation of Ti-Zr-Cu-Ni bulk metallic glasses, Journal of Applied Physics 78 (1995) 6514-6519.