CRITICAL CASTING THICKNESS OF $Cu_{60}Zr_{30}Ti_{10}$ AT.% BULK METALLIC GLASS INVESTIGATED BY SYNCHROTRON RADIATION

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Abstract

Since the discovery, metallic glasses (MS) and bulk metallic glasses (BMG - metallic glasses with a minimum diameter of 1 mm) have opened up a novel engineering field in the world of metallic materials. These types of glassy metals with good glass forming ability have excellent mechanical, magnetic and corrosion resistance properties, that are dissimilar to properties of conventional crystalline materials. Particularly, Cu - based BMG have attracted much attention due to their excellent mechanical properties, exhibiting compressive strength of over 2200 MPa and great ductility values (up to 18 % for $Cu_{47.5}Zr_{47.5}Al_5$ at.% at room temperature) coupled to large critical casting thicknesses (up to 12 mm for $Cu_{42}Zr_{42}Ag_8Al_8$ at.%). Conical ingot of the composition of $Cu_{60}Zr_{30}Ti_{10}$ at.% of diameter 1 - 5 mm was prepared by suction casting method at the Institute of Materials Research in Košice. In order to investigate critical casting thickness of the alloy, conical shape ingot was transmitted by monochromatic synchrotron radiation of the wavelength of 0.020671 nm (59.9799 keV) and X-ray diffraction patterns were recorded by 2D detector. Passing from the amorphous to crystalline part of sample, critical casting thickness (CCT) was determined as largest diameter, where the structure remains still amorphous. In order to demonstrate the difference between the amorphous and crystalline state of the same alloy, ingots of critical (ø ~ CCT), subcritical (ø < CCT) and supercritical (ø > CCT) diameters were cast. Compression test was performed and strength of the materials was compared.

Keywords: Metallic glasses, BMG, $Cu_{60}Zr_{30}Ti_{10}$, critical casting thickness, synchrotron radiation

1. INTRODUCTION

The future of metallurgy lies in mastering disorder. If our future is to master disorder, then amorphous metals will certainly point the way. In particular, metallic glasses (i.e. amorphous metals produced from the melt) are formed by intentionally stabilizing the disordered liquid structure, and the rules for doing so become better understood with each passing year. Their properties are not limited by the presence of lattice defects; they promise a suite of genuinely exceptional properties. Extreme values of strength, fracture toughness, magnetic properties, corrosion resistance, and other properties have been recorded in amorphous metals. In some cases, these come not individually, but in combinations unparalleled by any other material known as humankind [1]. Among metallic glasses, there is a group called Bulk Metallic Glasses (BMG) which are amorphous metals with section thickness of at least 1 mm (some researchers classify a glass as BMG with the requirement of minimum section thickness of 10 mm). Metallic glasses are attractive for engineering, especially for high - tech applications. Usually, despite of attractive physical and mechanical properties, monolithic bulk metallic glasses undergo inhomogeneous plastic deformation and exhibit poor ductility (< 1 %) at room temperature what restricts them as a structural material for the variety of applications. During deformation, BMGs do not show strain hardening, but instead upon yielding, they tend to form shear bands in which plastic deformation occurs in a highly localized manner. Cu based BMG have attracted much attention not only due their excellent mechanical and corrosion properties, but also due to great ductility values at high strength (up to 18 % above 1800 MPa for $Cu_{47.5}Zr_{47.5}Al_5$ at.% at room temperature - this remarkable value is attributed to special microstructural features at the atomic scale, which enable homogeneous nucleation of the shear bands and continuous multiplication during deformation) [2, 3]. These properties predetermine such types of glasses for applications as different kinds of construction materials or sensors, where deformation can be converted into measurable units such as electric signals [4]. In recent years Cu based glassy alloys have been synthesized in various forms [5]. They possess excellent mechanical properties with a tensile strength of about 2100 MPa, compressive plastic strain up to 2 % and compressive fracture strength of about 2200 MPa (Cu-Zr-Al) [6]. The reduced glass transition temperature was reported to be 0.62 for the $Cu_{60}Zr_{20-30}Ti_{10-20}$ glassy alloys, thus good glass forming ability is expected [7]. The authors [8-10] have previously reported formation of nanocrystals dispersed in a glassy matrix in the as - quenched alloys of the composition of $Cu_{60}Zr_{30}Ti_{10}$ at.% as well as in the form of bulk rods. They conclude that prepared materials (as the thin ribbons and thick rods of several mm) are a nanocomposite, i.e. nanocrystals embedded in an amorphous matrix. The maximum diameter of the rod with a glassy structure was reported to be 4 mm [7], Park et al. reported that the maximum diameter of the same composition is 2 mm [11]. In the study we present our own results focused on determination of critical casting thickness (CCT) of the $Cu_{60}Zr_{30}Ti_{10}$ at.% bulk metallic glass. The scientific equipment at the Laboratory of Progressive Alloys at the Institute of Materials Research in Košice - Slovakia allowed us to passed through the entire process of the experiment - from preparation of the material to characterization of the entire volume in form of as - quenched ribbon (verification of the amorphous character) and as - cast rod (considered for CCT determination of the alloy). We performed unique experiment with synchrotron radiation in transmission (Debye - Scherrer) geometry so we were able to find out CCT undoubtedly! In order to demonstrate the difference in mechanical properties between amorphous and crystalline states of the alloy, ingots of critical (ø ~ CCT), subcritical (ø < CCT) and supercritical (ø > CCT) diameters were cast, compression test was performed and results were compared.

2. EXPERIMENTAL PROCEDURE

Master alloy of the composition of $Cu_{60}Zr_{30}Ti_{10}$ at.% was prepared by arc-melting of high purity Cu (99.999%), Zr (99%) and Ti (99.98%) under a titanium - gettered argon atmosphere. The alloys were remelted several times in order to achieve homogeneous chemical composition over the whole cast. The amorphous ribbon thick ~ 30 μm was prepared by melt-spinning technique under an argon atmosphere. In order to prepare materials for CCT determination, copper mould of conical shape with continuously changing diameter from 1 - 5 mm was prepared (**Figure 1**).

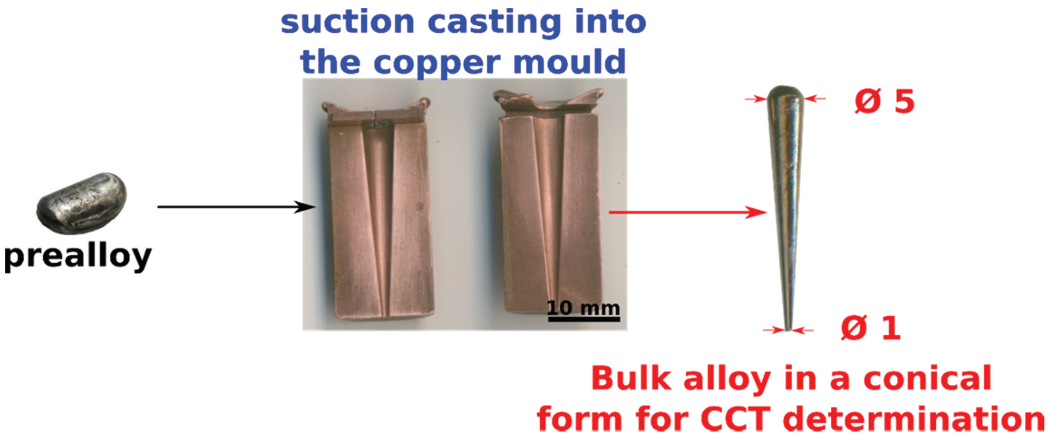

Figure 1 Copper mould and conical bulk alloy for CCT determination

Bulk alloy in a conical form was prepared in suction casting facility attached to the arc melting, where remelted master alloy was suck into the copper mould cooled with water. There were several attempts to find appropriate suction parameters until ingots of desired shape were prepared. Chemical composition of the samples was verified by SEM EDX Jeol JSM 7000 F. Initial evaluation of the amorphous structure of the ribbon was verified by laboratory X-Ray diffractometer (Philips X´Pert Pro) with Cu Kα radiation (wavelength of 0.15405 nm), locally with transmission electron microscopy (Jeol 2100 F) and finally confirmed with hard XRD measurement at beam line P02.1 at DESY. In order to determine CCT of the bulk conus, in-situ hard XRD measurement was carried out in transmission (Debye-Scherrer) geometry at the beam line P02.1 [12] - PETRA III [3] synchrotron facility in Hamburg, Germany using monochromatic synchrotron radiation of the energy of 59.9799 keV (λ = 0.020671 nm).

Bulk conical alloy was scanned shot-by-shot along a straight path with the step size of 0.5 mm, passing from the amorphous to crystalline part of the ingot while XRD patterns were recorded simultaneously by 2D detector. We were able to localise, where the structure of the cast ingot starts to be crystalline. Or by other words we found the largest diameter, where the structure still remains amorphous - the critical casting thickness of the alloy (**Figure 2**). After CCT identification, conical ingots of critical, subcritical and supercritical diameters were prepared and mechanical (compression) tests performed to fracture at room temperature on 200 kN Zwick to determine and compare compression strength of the amorphous, semi - crystalline and crystalline rods of the same composition.

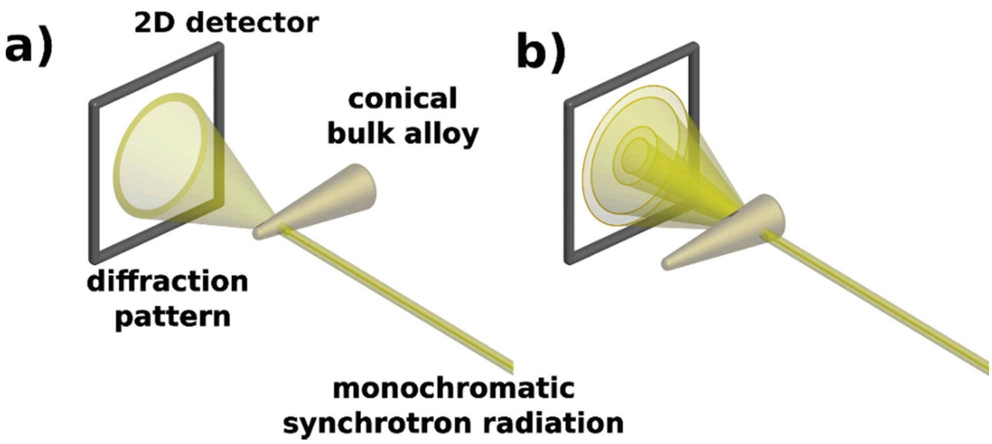

Figure 2 Layout of the experiment with synchrotron radiation. Conical bulk alloy is transmitted by monochromatic synchrotron radiation of the wavelength of 0.02067 nm (59.98 keV) while X-ray diffraction patterns are recorded by 2D detector. Passing from the amorphous - a), to crystalline section - b), critical casting thickness (CCT) was determined as the largest diameter, where the structure still remains amorphous

3. RESULTS

After preparation of the alloy in the form of ribbon and conical bulk rod, chemical composition and chemical homogeneity was examined by EDX. The quantitative analysis proved good (within 2 at.%) agreement to required composition. Verification of the sample amorphous character was performed at synchrotron beam line P02.1 using hard monochromatic X-rays and locally by TEM. X-ray diffraction pattern and TEM electron diffraction pattern (SAED) are depicted in **Figure 3**. Bulk conical alloy was scanned shot-by-shot along a straight path with the step size of 0.5 mm, passing from the amorphous to crystalline part of the conical ingot and XRD patterns were recorded by the plate detector. XRD patterns from individual points were analysed. At a diameter of about 2.8 mm, there was a clear change in the character of analysed XRD patterns. The broad diffuse diffraction maxima - characteristic feature for the glassy structures were transformed to the distinct Bragg's peaks representing crystalline structure. We were able to localise critical thickness starting from which the sample is partially crystalline.

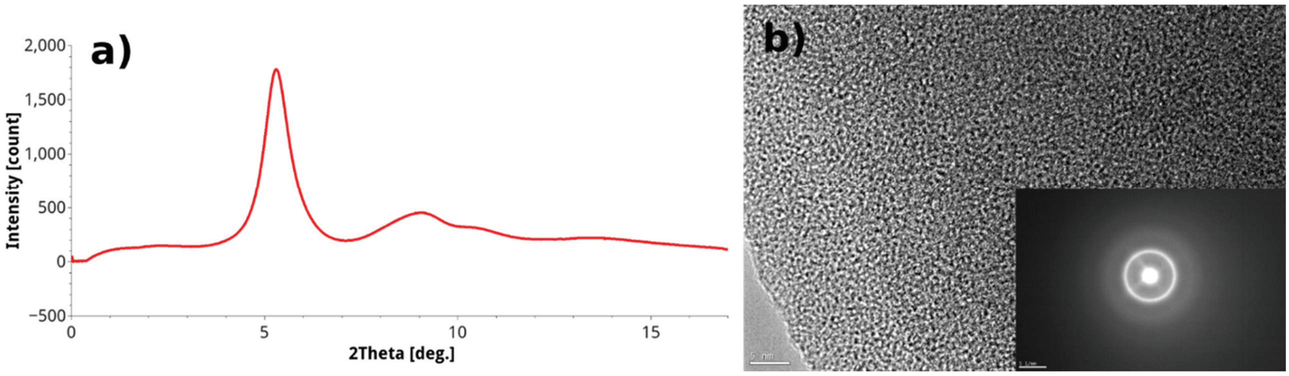

Figure 3 Verification of the amorphous character confirmed by XRD measurement performed at synchrotron beam line P02.1 using hard monochromatic X-rays of wavelength 0.020671 nm and locally by TEM. a) X-ray diffraction pattern from beam line P02.1 - DESY, b) TEM electron diffraction pattern

Critical casting thickness of the alloy of the $Cu_{60}Zr_{30}Ti_{10}$ at.% alloy was found to be 2.8 mm (**Figure 4**). After CCT identification, cylindrical ingots of critical (ø = 3 mm), subcritical (ø < 1 mm) and supercritical (ø > 4 mm) diameters were prepared by suction casting method at Laboratory of Progressive Alloys [17] and mechanical (compressive) tests at room temperature were realized on 200 kN Zwick. The main purpose of mechanical testing was to compare compression strength of amorphous (ø < 1 mm), partially - crystalline (ø = 3 mm) and crystalline (ø > 4 mm) alloys of the same composition. Results of the compression test are shown in **Table 1**. It is evident that the highest value of compression strength has the rod with a fully amorphous structure (ø < 1 mm), exceeding 3500 MPa. The lowest values of compression strength possess the rod of the diameter of 4 mm, which structure is completely crystalline, what has been proved by synchrotron radiation.

4. CONCLUSION

Despite the number of reports on the formation of nanocrystals embedded in the glassy matrix of the ribbons prepared from $Cu_{60}Zr_{30}Ti_{10}$ at.% bulk metallic glass [8 - 10], our investigation demonstrated and confirms the ability to quench the alloy to fully amorphous state. By investigation of critical casting thickness of the conical bulk alloy we identified section, from which the alloy begins to be crystalline. Critical casting thickness of the $Cu_{60}Zr_{30}Ti_{10}$ at.% alloy is 2.8 mm. Our result is in quite good agreement with study of Park et al. [11], they localized CCT of the alloy between 2 and 3 mm (without having conical specimens with continuously changing parameter). Different results of CCT from individual authors are probably result of different material preparation (parameters of melt spinning and suction casting methods) and method of analysis (techniques used to analyze alloys that not always allowed to pass through the entire volume of the sample, e.g. XRD diffraction with laboratory diffractometer, or techniques which could have affect the amorphous sample during preparation, e.g. transmission electron microscopy). Compressive strength of fully amorphous $Cu_{60}Zr_{30}Ti_{10}$ at.% alloys excess 3.5 GPa exceeding crystalline counterparts by more than three times.

Table 1 Compression strength of the $Cu_{60}Zr_{30}Ti_{10}$ (at.%) alloy in the form of as - cast rods with critical (ø = 3 mm), subcritical (ø < 1 mm) and supercritical (ø > 4 mm) diameters prepared by suction casting technique

Diameter of the as - cast rod of the $Cu_{60}Zr_{30}Ti_{10}$ alloy (mm)	Compression strength (MPa)
4.1.1. **1**	4.1.2. 3581
4.1.3. **3**	4.1.4. 1705
4.1.5. **4**	4.1.6. 994

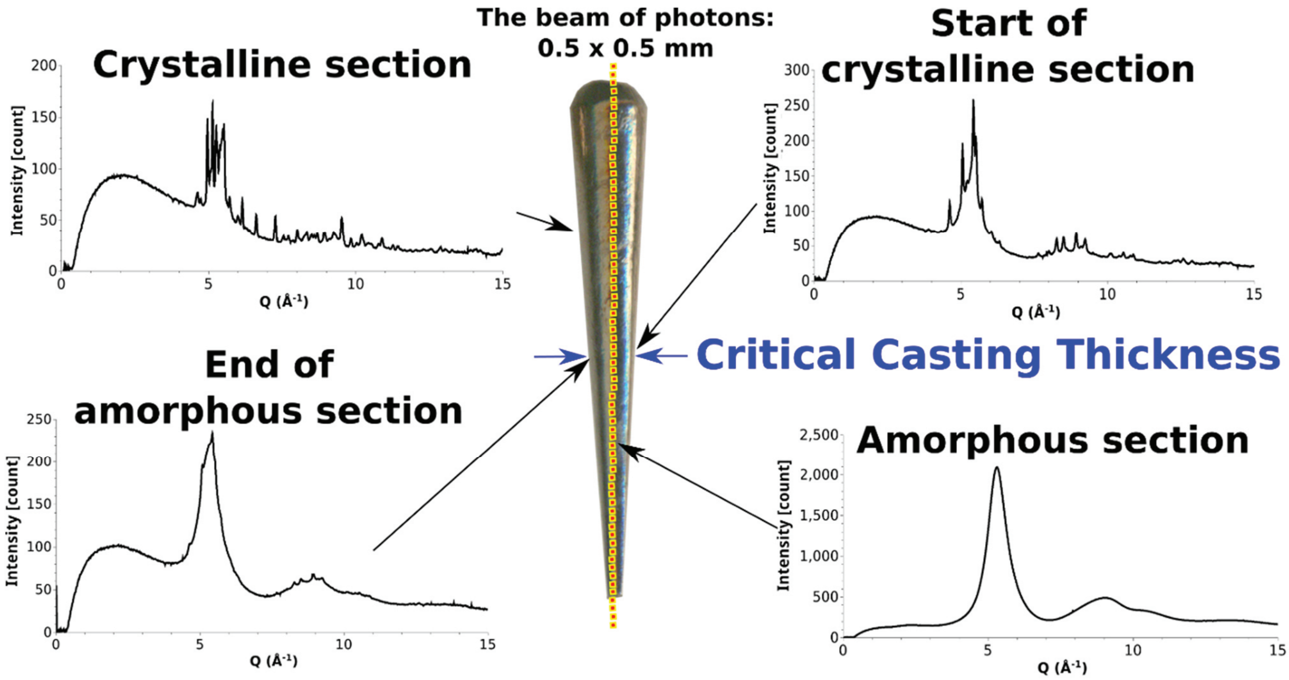

Figure 4 Critical casting thickness determination using monochromatic synchrotron radiation of the wavelength of 0.020671 nm (59.9799 keV) at beam line P02.1 at DESY, Germany. Bunch of photons with cross section of 0.5 x 0.5 mm was transmitted through the conical sample along a straight path with the step size of 0.5 mm. At a diameter of about 2.8 mm, there was a distinct difference in XRD pattern. Critical casting thickness of the $Cu_{60}Zr_{30}Ti_{10}$ at.% alloy was found to be 2.8 mm

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REFERENCES

[1] SURYANARAYANA, C., INOUE, A. *Bulk Metallic Glasses*. CRC Press: Boca Raton, 2011.

[2] SCHROERS, J., JOHNSON, W. L. Ductile bulk metallic glass. *Physical Review Letters*, 2004, vol. 93, pp. 255506-1-4.

[3] DAS, J., TANG, M. B., KIM, K. B., THEISSMANN, R., BAIER, F., WANG, W. H., ECKERT, J. "Work - hardenable" ductile bulk metallic glass. *Physical Review Letters*, 2005, vol. 94, pp. 205501-1-4.

[4] ĎURIŠIN, J., BALGA, D., SAKSL, K., PIETRIKOVÁ, A. Atomic structure of Cu-Zr-Ti metallic glasses subjected to high temperature annealing. *Journals of Alloys and Compounds*, 2014, vol. 608, pp. 241-246.

[5] ZHANG, W., ZHANG, Q. S., QIN, C.L., INOUE, A. Synthesis and properties of Cu-Zr-Ag-Al glassy alloys with high glass-forming ability. *Materials Science and Engineering: B*, 2008, vol. 148, pp. 92-96.

[6] INOUE, A., ZHANG, W. Formation, thermal stability and mechanical properties of Cu-Zr-Al bulk glassy alloys. *Materials Transactions*, 2002, vol. 43, pp. 2921-2925.

[7] INOUE, A., ZHANG, W., ZHANG, T., KUROSAKA, K. High-strength Cu-based bulk glassy alloys In Cu-Zr-Ti and Cu-Hf-Ti ternary systems. *Acta Materialia*, 2001, vol. 49, pp. 2645 - 2652.

[8] KASAI, M., SAIDA, J., MATSUSHITA, M., OSUNA, T., MATSUBARA, E., INOUE, A. Structure and crystallization of rapidly quenched Cu-(Zr or Hf)-Ti alloys containing nanocrystalline particles. *Journal of Physics: Condensed Mater.*, 2002, vol. 14, pp. 13867-13877.

[9] JIANG, J. Z, SAIDA, J., KATO, H., OHSUNA, T., INOUE, A. Is Cu60Ti10Zr30 a bulk glass-forming alloy? *Applied Physics Letters*, 2003, vol. 82, pp. 4041.

[10] KASAI, M., MATSUBARA, E., SAIDA, J., NAKAYAMA, M., UEMATSU, K., ZHANG, T., INOUE, A. Crystallization behaviour of $Cu_{60}Zr_{30}Ti_{10}$ bulk glassy alloy. *Materials Science and Engineering: A*, 2004, vol. 375-377, pp. 744-748.

[11] PARK, E. S., CHANG, H. J., KIM, D. H., KIM, W. T., KIM, Y. C., KIM, N. J., KIM, Y.W. Formation of amorphous phase in melt-spun and injection - cast $Cu_{60}Zr_{30}Ti_{10}$ alloys. *Scripta Materialia*, 2004, vol. 54, pp. 221-224.

[12] Unified Data Sheet - P02.1 *Hard X-Ray Diffraction Beam Line*. Deutsches Elektronen-Synchrotron A Research Centre of the Helmholtz Association. Available on: http://photon-science.desy.de/facilities/petra_iii/beamlines/P02.1_hard_x_ray_diffraction_beamline/unified_data_sheet/index_eng.html>

[13] BALEWSKI, K., BREFELD, W., DECKING, W., FRANZ, H., ROHLSBERGER, R., WECKERT, E. *A Low Emittance Synchrotron Radiation Source*. Technical Design Report. Hamburg: DESY, 2004. Available on: http://petra3-project.desy.de/general/tdr/index_eng.html oponenta

[14] ID22 - High resolution powder diffraction beam line. ESRF - The European Synchrotron. Available on: http://www.esrf.eu/id22

[15] TOBY, B. H. CMPR - a powder diffraction toolkit. *Journal of Applied Crystallography*, 2005, vol. 38, pp. 1040-1041.

[16] KRAUS, W., NOLZE, G. Powder cell - a program for the representation and manipulation of crystal structures and calculation of the resulting X-ray powder patterns. *Journal of Applied Crystallography*, 1996, vol. 29, pp. 301-303

[17] Laboratory of Progressive Alloys. Institute of Materials Research, Slovak Academy of Sciences in Košice. Website of the Laboratory: http://www.imr.saske.sk/en/7-65/laboratories-laboratory_of_progressive_alloys.