

THERMAL STABILITY OF Cu₆₀Zr₃₀Ti₁₀ at.% BULK METALLIC GLASS

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Abstract

 $Cu_{60}Zr_{30}Ti_{10}$ at. % metallic glass was prepared in two forms: as an ingot of diameter 3 mm and length of 26 mm and as a thin ribbon wide 5 mm and thick 35 µm. Chemical composition of the alloys were ascertain by Scanning Electon Microscopy (SEM) coupled with EDX analysis. Phase composition was evaluated by X-ray diffraction (laboratory and high-energy XRD at synchrotron). Thermal stability of ingot and ribbon samples were investigated by Differential Scanning Calorimetry (DSC) – where thermal characteristics such as glass transition temperature, crystallisation temperature and subsequent supercooled liquid region were compared for the two materials. Based on performed in-situ high temperature X-ray diffraction experiment we were able to determine changes in phases composition of the $Cu_{60}Zr_{30}Ti_{10}$ at. % amorphous alloys upon an anealing.

Keywords: bulk metallic glasses (BMG), Cu₆₀Zr₃₀Ti₁₀, suction casting, melt spinning, thermal stability

1. INTRODUCTION

Metallic glasses exhibit superior properties (high hardness and strength values, excellent corrosion resistance, large elongation limit, good combination of magnetic properties, etc.) which renders them unique for engineering and high-tech applications. Among metallic glasses, there is a group of noncrystalline solids called Bulk Metallic Glasses (BMG), which can be obtained by continuous cooling from the liquid state with section thickness of at least 1 mm (nowadays there's a tendency among researchers to designate a glass as BMG with the requirement of the minimum diameter value to be 10 mm) [1]. To form a BMG, an alloy must fulfill 3 emphirical rules formulated by Inoue [2]. Several exceptions to these emphirical rules have been noted and one of these exceptions is connected to the ternary system of Cu-Zr-Ti. Cu - based glassy alloys have been synthetised in recent years in various forms (ribbons, bulk rods) and maximum diameter of the Cu - based BMG alloys was reported to be 12 mm in Cu₄₂Zr₄₂Ag₈Al₈ alloy [5]. Great ductility, which is uncommon for the vast majority of metallic glasses, predetermines Cu-based glasses for applications where deformation can be converted into measurable units such as fluid flow rate or electric signals and in this way they can be applied for different kinds of construction materials or sensors [6]. Cu - based systems (Cu-Zr-Ti, Cu-Hf-Ti, Cu-Zr-Ti-Hf) can be produced in a fully glassy state with a critical thickness of 4 mm. They can be used for structural applications - they have excellent mechanical properties with a tensile strength of about 2100 MPa, compressive plastic strain of 0,8 - 1,7 %, compressive fracture strength of 2200 MPa (Cu-Zr-Al) and a plastic strain of 0,2 % [7]. Das et al. has reported work – hardenable ductile bulk metallic glass of the composition of Cu_{47,5}Zr_{47,5}Al₅, which exhibits hight strength of up to 2265 MPa together with extensive work hardening and a large ductility of 18% measured by uniaxcial compression tests. This remarkable ductility is attributed to special microstructural features at the atomic scale, which enable easy and homogeneous nucleation of the shear bands and continuous multiplication during deformation [8]. Ternary system of the composition of Cu₆₀Zr₃₀Ti₁₀ at.% belongs to the family of Cu – based bulk glassy alloys formed by Inoue et al. and is one of the exceptions to the Inoue emphirical rules for high glass-forming ability (nanocrystalline microstructure of the BMG). This bulk metallic glass exhibits a large compressive plastic



strain of 1.6 % with a high tensile and compressive strength of 2000 MPa. The supercooled liquid region was reported to be 37 °C. Since the reduced glass transition temperature $(T_{rg}=T_g/T_g)$ is relatively high (it was reported to be 0.62) and good glass forming ability is excepted, nanocrystalline microstructures with a size of 3 – 5 nm were always observed from the as-quenched state. Park et al. reported single phase amorphous state of the Cu₆₀Zr₃₀Ti₁₀ ribbon. These observations suggest that the crystallisation occurs when cooling rate is not fast enough to supress the crystallisation and relatively high plastic strain observed from the as-cast bulk Cu-Zr-Ti alloy is probably due to in-situ formed nanocrystals [10].

The main aim of this paper is to present the results of our own work on the ternary alloy of the composition of $Cu_{60}Zr_{30}Ti_{10}$ at.%. Equipment of the Laboratory of Progressive Alloys of Materials and the Laboratory of Thermal Analysis of Institute of Materials Research allowed us to pass through the entire process - from the preparation of the material to the characterization with focus on thermal stability of the melt-spun ribbon and as-quenched ingot.

2. EXPERIMENTAL PROCEDURE

Cu₆₀Zr₃₀Ti₁₀ alloy was prepared by arc-melting of the pure elements under a zirconium – gettered argon atmosphere. The alloys were remelted several times due to homogeneity (problem of evaporation was neglected because of low vapour pressure of the elemenets) and finally cylindrical rods of the diameter of 3 mm and the length of 26 mm were prepared in suction casting facility attached to the arc melter. There were several efforts until the ingot was quenched because of chosing the appropriate suction parameters like temperature of the water - cooled copper crucible, argon overpressure and optimal weight of the sample... The amorphous ribbon of the thickness of 35 µm was prepared by melt-spinning technique under an argon atmosphere. Chemical composition of both samples was verified by SEM coupled with EDX microanalyser and the quantitative analysis proved good agreement with specified composition The amorphous nature of the specimens was verified by X-Ray diffraction using Philips X'Pert Pro diffractometer with Cu Kα radiation. In order to investigate phase composition of the material upon an annealing, in-situ hard XRD measurement was carried out in transmission (Debye-Scherrer) geometry at the BW5 wiggler beamline [15]. Monochromatic synchrotron radiation of the energy of 100 keV (λ = 0.0124 nm) was used. The beam of photons illuminating sample had cross-section of 0.5 x 0.5 mm, diffracted X-rays were recorded by a 2D image plate detector Perkin Elmer XRD 1621 (2048 pixels x 2048 pixels, size of a pixel: 200µm x 200µm). In this experiment the Cu₆₀Zr₃₀Ti₁₀ amorphous ribbon was cut into small pieces and put into a quartz capillary of the inner diameter of 0.8 mm. The capillary was mounted into a Linkam THMS600 resistive heater furnace with a maximal operating temperature of 600 °C. The temperature in the sample's vicinity was measured by a thermocouple. The samples were heated up from the room temperature up to their crystallisation point at a heating rate of 10 °C/min. After reaching the required temperature, the glasses were illuminated by the X-ray beam for 20 s and 2D XRD patterns were recorded by the detector. Additionally, a time of about 15 s was needed for data transfer from the detector to a computer, to relax the detector and to stabilize the temperature. The XRD intensity was radially integrated to 20 by using the Fit2D software. From the diffraction patterns we identified phases using the CMPR [16] toolkit. Thermal stability and characteristic temperatures were examined also by differential scanning calorimetry (Perkin Elmer DSC 8500) at a heating rate of 10 °C/min in an argon atmosphere. The compositional analysis was performed by energy – dispersive X-ray spectroscopy analysis installed in a field emission scanning electron microscope (Jeol JSM – 7000 F). Mechanical (compressive) tests has been realized on cylindrical specimen of the diameter of 3 mm and the length of 6 mm at room temperature using 200 kN Zwick – Extensometer.



3. RESULTS

As it is evident from Fig. 1 the X-ray diffraction patterns of the ingot (a) as well as the ribbon (b) exhibit broad diffraction maxima – characteristic feature for the glassy structures. XRD measurement indicating that the $Cu_{60}Zr_{30}Ti_{10}$ alloy can be quenched as a single amorphous phase material with the diameter of 3 mm and more.



Fig. 1 X-Ray diffraction pattern obtained from the ingot (a) and the ribbon (b) samples. Measurements were carried out on diffractometer Philips X'Pert Pro with Cu-K radiation, position sensitive detector and the scan step of size 0.03342 degree



Fig. 2 DSC curves normalised to sample weight for the as-cast ingot (red) and the as-spun ribbon (blue) measured at the heat rate of 10 K/min show clear endothermic glass transition and exothermic crystallisation peaks

Fig. 2 shows DSC curves of the as-cast rod and from the melt-spun ribbon obtained upon continuous heating with a rate of 10 °C/min, all performed in an argon protective atmosphere. Both the curves exhibit a distinct glass transition, followed by a supercooled liquid region and strong exothermic reactions caused by crystallisations. The values of glass transition temperatures and crystallisation temperatures slightly differ as can be seen on Fig. 2 and in the Table 1. Supercooled liquid region increased from the value of 32 °C for as-cast ingot to the value of 36 °C for as-spun ribbon. For the as-spun ribbon there are three exothermic peaks, the first with maxima at 489 °C (enthalpy of the exothermic reaction is 17.79 J/g), the second – twin peak has a maxima at 535 °C (enthalphy is 31.89 J/g) and the third one has a maxima at the position of 690 °C with the enthalpy of 3.79 J/g. In the case of as-cast ingot, the first exothermic peak has a maxima at the



temperature of 481 °C (enthalpy is 10.49 J/g) followed by a twin peak with the maxima at 530 °C (enthalpy 13.81 J/g) and the third crystallisation peak with the maxima at 645 °C and the enthalpy of 3.76 J/g.

Table 1 Values of significant temperatures of the $Cu_{60}Zr_{30}Ti_{10}$ ribbon and the ingot obtained from DSC curves at a heating rate of 10 °C/min in an argon atmosphere

sample	Tg [°C]	T _{x1 onse} t [°C]	T _{x1} [°C]	Enthalpy [J/g]	T _{x2} [°C]	Enthalpy [J/g]	Tx₃ [°C]	Enthalpy [J/g]	ΔT _x =T _x -T _g [°C]
ribbon	443	479	489	17.79	535	31.89	690	3.79	36
ingot	435	467	481	10.49	530	13.81	645	3.76	32

The ribbon seems to be more glassy than the ingot because of higher value of the magnitude of heat produced by the exothermic transformations – it's known that sample having a higher value of the magnitude of heat has more volume fraction of the amorphous phase. Uneven widths of the supercooled liquid regions and different values of the significant temperatures are presumabely features of unidentical glassy structure after casting / spinning of the rod and the ribbon. The observed differences indicate that structure of ingots contains some amount of nanocrystals (not detected by the XRD) acting as nucleation centers facilitating crystallisation of this alloy. This assumption need to by verified by transmission electron microscopy or by the other similar unambiguous technique.



Fig. 3 XRD patterns of the ribbon with pase evolution for various temperatures: in the glassy state, after 1st and after 2nd crystallisation

Fig. 3 shows XRD patterns taken from the ribbon samples at different temperatures.. In the picture we can see 4 distinct curves belonging to 4 various temperatures – temperature at which the ribbon is still in the glassy state followed by 3 temperatures after 1st and 2nd crystallisation peaks. At the temperature of 150 °C, the ribbon is preserving the glassy structure manifested by the broad and diffuse peaks. Once the temperature increases and reaches the value of 514 °C, we can see distinct change of its character. We identified products of the glassy phase transfomation as hexogonal Cu_{1.35}Zr_{0.825}Ti_{0.825} and two face centered cubic phases having significantly different lattice parameters - Cu_{0.92}Ti_{0.08} and a new – CuZr phases. As the temperature continuous to increase, above the second crystallisation peak 553 °C, hexagonal



 $Cu_{1.35}Zr_{0.825}Ti_{0.825}$ phase begins to disolve and transforms into the two fcc phases - $Cu_{0.92}Ti_{0.08}$ and a a new - CuZr phase which. Space groups and lattice parameters of all the identified phases are listed in Table 2.

Formula	Space Group	a [Å]	c [Å]	Reference
$Cu_{1.35}Zr_{0.825}Ti_{0.825}$	P63/mmc (194)	5.1775	8.3673	[18]
Cu _{0.92} Ti _{0.08}	Fm-3m (225)	5.08	-	[19]
CuZr	Fm-3m (225)	3.65	-	-

Table 2 Lattice parameters of the identified phases in Cu₆₀Zr₃₀Ti₁₀ at.% ribbon

The room temperature compressive stress-strain curve obtained from ingot of nominal composition of $Cu_{60}Zr_{30}Ti_{10}$ at. % is shown in Fig. 4. The ingot exhibits an elastic regime of 7.5 % before yielding, which occurs at about 1640 MPa stress. After yielding the stress increases with increasing strain up to the fracture, which takes place at 1790 MPa stress and a strain of 8.4 %. This results in a plastic strain of 0.9 %.



Fig. 4 Room temperature compressive stress – strain curve for the ingot of nominal composition of Cu₆₀Zr₃₀Ti₁₀ with aspect ratio of 2 (6mm length and 3 mm diameter) prepared from the cast rod

CONCLUSION

In this work thermal stability, phase analysis and compression characteristics of $Cu_{60}Zr_{30}Ti_{10}$ at. % BMG were examined. Thermal parameters of the ingot and the ribbon were evaluated and compared. Characteristic temperatures differ manifesting unequal glassy structure of the samples. Phase evolution of the ribbon was described in relation to distinct temperatures at which the sample was heated. Hexagonal $Cu_{1.35}Zr_{0.825}Ti_{0.825}$ and two cubic - $Cu_{0.92}Ti_{0.08}$ and new - CuZr phases with enhanced lattice parameters were identified. The yield strength, the elastic and plastic deformation and the compression fracture strength were evaluated.

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REFERENCES

- [1] SURYANARAYANA C., INOUE A. Bulk Metallic Glasses. CRC Press: Boca Raton, 2011.
- [2] INOUE A. Recent progress of Zr-based bulk amorphous alloys. Science Reports of the Research Institutes, Tohoku University. Series A, Vol. 42, 1996, pp. 1–11.
- [3] INOUE A. Stabilization of supercooled liquid and opening-up of bulk glassy alloys. Proceedings of the Japan Academy. Series B, Vol. 73, 1997, pp. 19–24.
- [4] INOUE A. Bulk Amorphous Alloys: Preparation and Fundamental Characteristics. Materials Science Foundations, Vol. 4. Trans Tech Publications: Zürich, 1998.
- [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, Vol 148, 2008, pp. 92-96.
- [6] 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, Vol. 608, 2014, pp. 241-246
- [7] INOUE A., ZHANG W. Formation, thermal stability and mechanical properties of Cu–Zr–Al bulk glassy alloys. Materials Transactions, Vol. 43, 2002, pp. 2921–2925.
- [8] 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, Vol. 94, 2005, pp. 205501- 1-4.
- [9] INOUE A., ZHANG W., ZHANG T., KUROSAKA K. Cu-based bulk glassy alloys with high tensile strength of over 2000 MPa. Journal of Non-Crystalline Solids, Vol. 304, 2002, pp. 200-209.
- [10] NAGAHAMA D., OHKUBO T., MUKAI T., HONO K. Characterisation of nanocrystal dispersed Cu₆₀Zr₃₀Ti₁₀ metallic glass. Materials Transactions, Vol. 46, No. 6, 2005, pp. 1264-1270.
- [11] 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, Vol. 49, 2001, pp. 2645 – 2652.
- [12] KASAI M., MATSUBARA E., SAIDA J., NAKAYAMA M., UEMATSU K., ZHANG T., INOUE A. Crystallisation behaviour of Cu₆₀Zr₃₀Ti₁₀ bulk glassy alloy. Materials Science and Engineering A. Vol 375-377, 2004, pp. 744-748.
- [13] 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 Cu₆₀Zr₃₀Ti₁₀ alloys. Scripta Materialia, Vol. 54, 2004, pp. 221-224.
- [14] INOUE A., ZHANG W., SAIDA J. Synthesis and Fundamental Properties of Cu-Based Bulk Glassy Alloys in Binary and Multi-component Systems. Materials Transactions, Vol. 45, No. 4, 2004, pp. 1153 - 1162
- [15] BOUCHARD R., HUPFELD D., LIPPMANN T., NEUEFEIND J., NEUMANN H.-B., POULSEN H.F., RUTT U., SCHMIDT T., SCHNEIDER J.R., SUSSENBACH J., VON ZIMMERMANN M. Journal of Synchrotron Radiation, Vol. 5, 1998, pp. 90–99.
- [16] TOBY B.H. CMPR a powder diffraction toolkit. Journal of Applied Crystallography, Vol. 38, 2005, pp. 1040-1041.
- [17] QIU X., THOMPSON J. W., BILLINGE S. J. L. PDFgetX2: a GUI-driven program to obtain the pair distribution function from X-ray powder diffraction data. Journal of Applied Crystallography, Vol. 37, 2004, pp. 678 678.
- [18] Yan X., CHEN X.Q., GRYTSIV A., ROGL P., PODLOUCKY R., POMJAKUSHIN V., SCHMIDT H., GIESTER G. Crystal structure, phase stability and elastic properties of the Laves phase ZrTiCu₂. Intermetallics, Vol. 6, No. 5, 2008, pp. 651-657
- [19] KRULL W.E. The lattice parameter of the alpha copper-titanium solid solution. Journal of Applied Crystallography. Vol. 3, 1970, pp. 519-521.