

# Pressure-assisted Crystallization of Cu-Zr-Ti Glass-forming Alloys

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## Abstract

*Alloy powders with nominal composition  $Cu_{60}Ti_{20}Zr_{20}$  were investigated by in-situ X-ray diffraction at the B2 powder diffraction beamline (HASYLAB/DESY, Hamburg, Germany) and by X-ray diffraction experiments during continuous heating under uniaxial pressure at the F2.1/MAX80 beamline in HASYLAB. The structural phase transitions in the nanocrystalline  $Cu_{60}Zr_{20}Ti_{20}$  were investigated for continuous heating at three different pressures, namely 0.6 GPa, 1.0 GPa and 1.7 GPa. The pressure dependence of the phase transition temperatures was obtained.*

**Key words:** bulk metallic glasses; mechanical alloying; synchrotron radiation, X-ray diffraction

## Introduction

Bulk metallic glasses (BMGs) are modern metallic materials which hold great promises for a broad variety of technological and industrial applications [1]. During the past few decades, bulk glass-forming compositions were reported for Pd- [3,4], La- [5], Fe- [6], Ni- [7], Ti- [8], Zr- [2,9], Co- [10], Mg- [11] and Al-based [12] multicomponent alloys. The primary interest in BMG materials stems from their outstanding mechanical properties like high strength, high resistance to fatigue, large elastic deformation, low wear but also soft magnetic properties or high corrosion resistance [12-15].

Copper-based BMGs were recently discovered in the Cu-Zr-Ti alloy system [16], with excellent mechanical properties: Young modulus 114-134 GPa, yield strength close to 2 GPa, fracture strength (in compression) 2150-2160 MPa, and elastic deformation of up to 2%. The combination of low cost, excellent mechanical behaviour and good glass-forming ability (GFA) makes the Cu-Zr-Ti BMGs suitable for advanced engineering applications. The alloy composition range favourable for the synthesis of Cu-Zr-Ti BMGs was initially identified at Cu-rich compositions between  $Cu_{60}Zr_{30}Ti_{10}$  and  $Cu_{60}Zr_{20}Ti_{20}$  [16]. Further attempts to refine the BMG alloy composition using the e/a variant line criterion [17] were recently reported [18]. The e/a criterion specifies a straight composition line in the Cu-Zr-Ti ternary phase diagram linking a specific binary alloy (Cu-Zr) composition with high GFA (either near a deep eutectic point or at a binary cluster position) to a third alloying element (here Ti). The suggested optimal alloy composition for glass-formation is  $Cu_{64}Zr_{28.5}Ti_{7.5}$  (at.%), situated on the  $(Cu_9Zr_4)_{1-x}Ti_x$  variant line. It is interesting to notice that the  $Cu_9Zr_4$  composition corresponds to an icosahedral cluster

structure and is not associated with any eutectic composition of the Cu-Zr binary alloy [18]. A *new* composition range suitable for bulk glass formation was recently reported to exist around  $\text{Cu}_{52}\text{Zr}_{40}\text{Ti}_8$  [19], which correlates with the presence of  $\text{Cu}_{10}\text{Zr}_7$ -like nanoclusters. It is well known that the mechanical properties of BMGs and of composites derived thereof depend strongly on their microstructural features. The formation of nanocrystalline phases upon heating and their stability under various pressure-temperature conditions is of fundamental importance for understanding the mechanisms leading to a superior glass-formation ability, but also for defining the operational limits of BMGs as engineering materials. In this study we examine the high-pressure high-temperature stability of nanocrystalline phases in a  $\text{Cu}_{60}\text{Zr}_{20}\text{Ti}_{20}$  alloy using in situ synchrotron radiation powder diffraction.

## Experimental

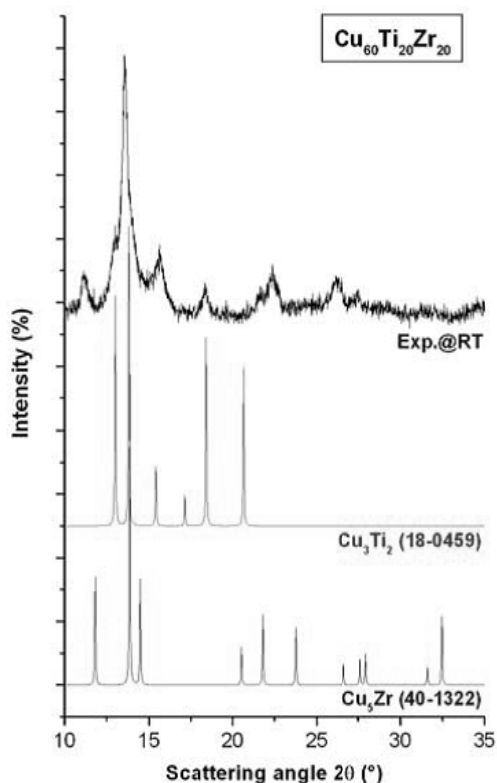
Bulk metallic glasses are usually prepared by slow copper-mould casting at cooling rates between 1-100 K/s [1]. However, other synthesis methods like ball-milling have often been employed, e.g. for multicomponent Cu-Zr-Ti alloys [20-24]. High-purity elemental powders of copper (99.9%, 200 mesh), zirconium (98%, 100 mesh) and titanium (99.9%, 100 mesh) were mixed to get the desired nominal composition  $\text{Cu}_{60}\text{Zr}_{20}\text{Ti}_{20}$  (at.%). Mechanical alloying was carried out on a high energy ball-mill using a planetary ball-mill Retsch PM-400. The powders mixtures were placed into chromium-steel vials together with 10mm and 20mm diameter chromium-steel balls and ball-milled for 50 hours at 250 rotations per minute (rpm). The ball-to-powder mass ratio was equal to 139/10. Hexane was added to prevent oxidation events. No other additives were employed in the present wet-milling experiments.

For the high-temperature X-ray diffraction experiments, the powder samples were filled into a quartz capillary (0.3 mm) mounted on a rotating sample holder. The heating was performed by a STOE furnace under Ar atmosphere. The high-resolution diffraction patterns were collected using an OBI image-plate detector which allows for fast data acquisition [25]. The pressure-temperature evolution the  $\text{Cu}_{60}\text{Zr}_{20}\text{Ti}_{20}$  ball-milled powders was determined by *in situ* synchrotron radiation X-ray diffraction. The experiments were performed in energy dispersive mode at the MAX80 beamline at HASYLAB/DESY (Hamburg, Germany). Pressure and temperature were applied by a multi-anvil press and an electrical-current heating system. The alloy powders were mounted into a boron/epoxy resin container, with graphite and copper ensuring electrical conduction for sample heating [26]. The sample is further embodied in boron nitride powder for chemical inertness. Sodium chloride was used as a standard for pressure calibration. The temperature was monitored using a thermocouple embedded in the central boron nitride layer.

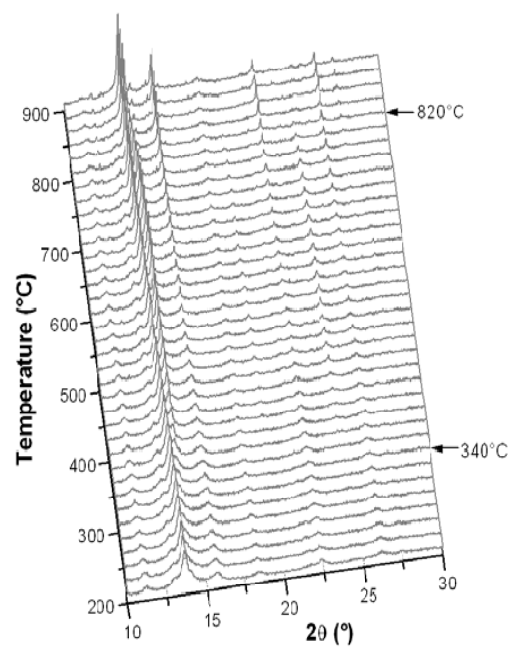
## Results and Discussion

In spite of the long-term high-energy milling conditions (50 hours at 250 rpm), the Cu-Zr-Ti alloy powders could not be rendered amorphous. The X-ray powder diffraction pattern taken at room temperature on the as-milled specimens is shown in Fig. 1. The as-prepared alloy powders consist most probably of a mixture of tetragonal  $\text{Cu}_3\text{Ti}_2$  (space group 129, P4/nmm, PDF 18-0459) and face-centered-cubic  $\text{Cu}_5\text{Zr}$  (space group 216, F-43m, PDF 40-1322) nanocrystals. Some other phases appear to have marginally formed during high-energy mechanical alloying, as suggested by a few small yet unidentified Bragg peaks. Several authors have previously dealt with the crystallization of amorphous Cu-Zr-Ti alloys [27-30] and with the ternary alloy phase diagram [18, 19, 31]. Most of these studies however started with an initial amorphous alloy, so the results cannot be directly compared with the present investigation. We first observe that the  $\text{Cu}_5\text{Zr}$  composition lies near to the hexagonal  $\text{Cu}_{51}\text{Zr}_{14}$  (space group 175, P6/m, PDF 42-1185), often reported as the primary crystallization phase for the  $\text{Cu}_{60}\text{Zr}_{20}\text{Ti}_{20}$  alloy [30,31]. The  $\text{Cu}_5\text{Zr}$  and  $\text{Cu}_{51}\text{Zr}_{14}$  phases coexist well in intermetallic layers formed by interdiffusion during

heating of ternary diffusion couples [31]. The  $\text{Cu}_5\text{Zr}$  phase has a limited solubility for Ti [31]. The tetragonal  $\text{Cu}_3\text{Ti}_2$  is a stable phase of the Cu-Zr-Ti alloy system. The evolution of the ball-milled alloy nanopowders during non-isothermal heating is shown in Fig. 2.



**Fig. 1.** Room-temperature X-ray diffraction pattern of as-prepared Cu-Zr-Ti alloy powders.



**Fig. 2.** X-ray diffraction patterns collected during non-isothermal heating of  $\text{Cu}_{60}\text{Zr}_{20}\text{Ti}_{20}$  powders.

A first change in the diffraction patterns is seen at  $340^\circ\text{C}$  (Fig. 2). This is due to the different thermal expansion of the constituent phases. The mixed nanocrystalline nature of the as-milled powders is thus confirmed.

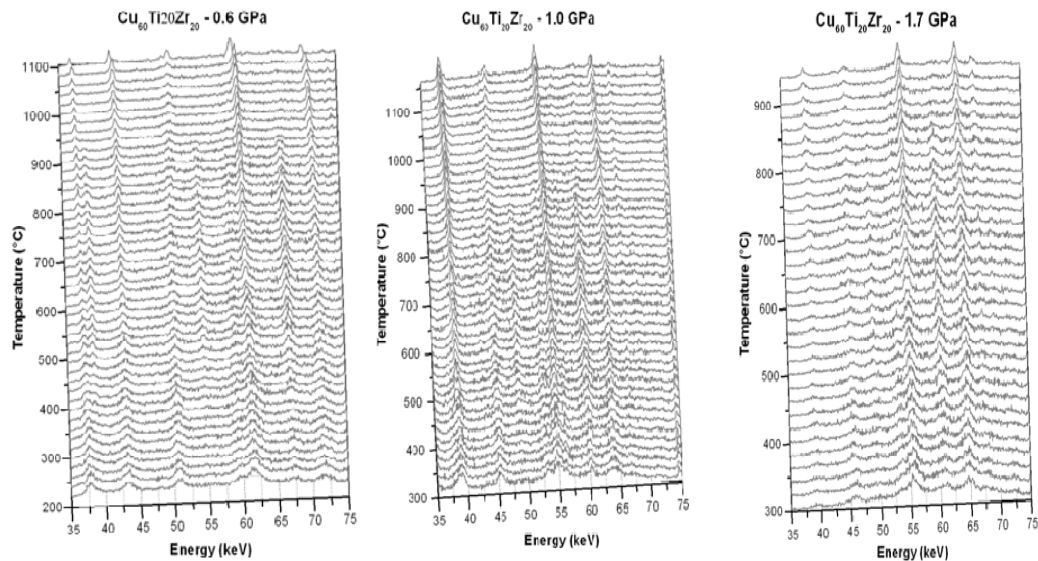
An intermediate metastable nanocrystalline phase seems to form between  $420\text{--}820^\circ\text{C}$ , as indicated by the additional Bragg peaks at  $20$  and  $25$  degrees  $2\theta$ . Above  $820^\circ\text{C}$ , the metastable phase dissolves and a high-temperature alloy phase is formed instead.

The so formed high-temperature phase is presumably the ternary  $\text{Cu}_2\text{ZrTi}$  phase, which is in equilibrium with most binary phases of the ternary alloy [31].

The formation of the ternary  $\gamma\text{-Cu}_2(\text{Zr},\text{Ti})$  phase by a high-temperature solid-state reaction at  $T_R=820^\circ\text{C}$  is in good agreement with the Cu-Zr-Ti alloy phase diagram [19].

The volume fraction of the  $\text{Cu}_3\text{Ti}_2$  phase decreases accordingly, pointing out that the  $\gamma$ -phase formation is largely due to the easier diffusion of the Ti atoms into the neighbouring phases. The high-temperature solid-state reaction leading to the formation of the stable ternary  $\gamma\text{-Cu}_2(\text{Zr},\text{Ti})$  phase from the initial  $\text{Cu}_5\text{Zr}$  and  $\text{Cu}_3\text{Ti}_2$  constituents was followed also under the application of uniaxial pressure (Fig. 3).

The reaction temperature  $T_R$  decreases with increasing applied pressure, signalling the eventual lowering of the energy barriers for the  $\gamma$ -phase formation under pressure application. Further experimental research efforts are planned for clarifying this effect in more detail.



**Fig. 3.** Energy-dispersive X-ray diffraction patterns collected under pressure at 0.6 GPa (left), 1 GPa (middle) and 1.7 GPa (right) for temperatures up to 1150°C.

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## Cristalizarea sticlelor metalice Cu-Zr-Ti asistată de presiune

### Rezumat

Aliajele sub formă de pulbere având compoziția  $\text{Cu}_{60}\text{Ti}_{20}\text{Zr}_{20}$  au fost investigate folosind radiație de sincrotron la liniile B2-difracție de pulberi (HASYLAB/DESY) și F2.1/MAX80- încălzire continuă în prezența presiunii aplicată uniaxial. Tranzițiile de fază pentru aliajul nanocristalin  $\text{Cu}_{60}\text{Ti}_{20}\text{Zr}_{20}$  au fost investigate în condiții de încălzire continuă la diferite presiuni și anume: 0.6 GPa, 1.0 GPa, 1.7 GPa. Au fost obținute dependențele tranzițiilor de fază de temperatură și presiune.