



## Full length article

# Transient nucleation and microstructural design in flash-annealed bulk metallic glasses



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## ABSTRACT

Due to their inherent metastability, metallic glasses crystallize upon thermal activation, which involves nucleation and growth. It is debatable, however, whether steady-state kinetics of crystal nucleation and growth apply when glasses are heated quickly. We partially devitrified a CuZr-based bulk metallic glass at heating rates in the range of 0.08–180 K s<sup>-1</sup>. Immediate quenching after heating preserves the partially transformed microstructure and allows direct observation of crystallite sizes and numbers. The crystallization reaction changes from eutectic to polymorphic at high heating rates and uniformly dispersed metastable shape-memory crystals precipitate in the glass. A beneficial side effect of this microstructure is a strongly enhanced room-temperature deformability. The analysis of crystal populations suggests that the nucleation rate on fast heating is effectively lower than in the steady state. At the later stage of crystallization by flash-annealing, the glass sample is traversed by a thermal front that migrates almost ten times faster than the crystal-liquid interface in levitation experiments. This phenomenon is related to the high population of crystals already present. Flash-annealing, thus, not only permits tailoring of BMG composites to overcome the intrinsic brittleness of monolithic BMGs, but also permits study of the fundamental crystallization processes in highly undercooled melts.

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## 1. Introduction

The high cooling rates required for vitrification of metallic melts guarantee that the structure of the liquid is preserved while the melt gradually transforms into a solid [1,2]. As a result of their disordered structure, metallic glasses generally possess an intrinsic brittleness limiting their applicability [3]. One solution to overcome this deficiency is to incorporate ductile crystals into the glass [4,5]. Particularly interesting in this respect are BMG-matrix composites containing B2 CuZr shape-memory crystals [6–8]. Such CuZr-based composites not only exhibit a pronounced plastic strain but also work hardening due to a deformation-induced martensitic transformation in the crystals [9,10].

When it comes to deliberately precipitating crystals in a

supercooled liquid in order to produce a glass-matrix composite, nucleation and growth have to be controlled. Both are also key processes to consider in understanding glass formation and a comprehensive theory was developed almost half a century ago [11]. Experience, in turn, suggests that crystal sizes and the distribution of crystals can be only manipulated to some extent in conventional experiments involving quenching of metallic melts. For exceptionally good glass formers, the low growth velocities just below the liquidus temperature [12] can be exploited to design the composite microstructure during a semi-solid process [13]. But in the case of the aforementioned CuZr-based glass-forming alloys, it is very difficult to precipitate relatively small and uniformly dispersed B2 CuZr shape-memory crystals in a reproducible fashion during solidification [6,8,14]. For the intermediate glass former Cu<sub>50</sub>Zr<sub>50</sub>, the maximum growth rate is relatively high ( $u_{\max} = 23 \text{ mm s}^{-1}$ ) [15,16] and it is necessarily crossed on cooling to room temperature [12]. When a few nuclei grow in a thermally controlled manner [17] at such a relatively high velocity, large crystals heterogeneously distributed in the glassy matrix are the outcome [9]. In contrast, below 0.73  $T_m$  ( $T_m$ : melting temperature)

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crystal growth in an undercooled  $\text{Cu}_{50}\text{Zr}_{50}$  melt becomes diffusion-controlled and at the glass-transition temperature, the growth rate is seven orders of magnitude lower than at its maximum [16]. If the liquid is quenched to a glass, which is then heated, the maximum growth rates are avoided and one might control the crystal sizes more effectively owing to lower growth velocities.

The B2 CuZr crystals precipitate polymorphically from the melt whereas the glass devitrifies into the low-temperature equilibrium phases,  $\text{Cu}_{10}\text{Zr}_7$  and  $\text{CuZr}_2$  [18]. This should render the synthesis of shape-memory BMG-matrix composites starting from bulk metallic glasses impossible. Interestingly, on reheating a CuZr-based metallic glass at intermediate heating rates (e.g.  $8.33 \text{ K s}^{-1}$ ), the B2 phase is formed in a temperature regime where it is still metastable, but unfortunately next to other phases [18,19]. The presence of B2 CuZr crystals in the glassy matrix improves the ductility of the material [8,20]. Still, the details of how the microstructure evolves, i.e. how it depends on the annealing temperature and the heating rate, have not been addressed yet.

Our expectation is that only B2 CuZr would form in the glass if the heating rate is significantly increased and the alloy is immediately quenched at a sufficiently high rate to suppress the eutectoid decomposition of the B2 CuZr crystals. During this thermal treatment, (i) crystal growth must be slow enough and (ii) the time available for growth must be small enough to avoid substantial impingement of the crystals or even complete crystallization of the supercooled liquid [21]. This suggests that fast heating of a glass to temperatures smaller than  $T_{\text{max}}$ , where the growth rate is maximum, followed by instantaneous quenching, i.e. a flash-anneal, is the most promising approach to fulfill these requirements for bulk metallic glasses. More importantly, if the flash-annealing process is controlled properly, it could open up a route for measuring isochronal nucleation kinetics. By analyzing crystal populations after different anneals, one can deduce the number of critical nuclei in the glass as a function of the heating rate [22].

The term ‘flash-annealing’ is used in a broad context in the literature and does not refer to a specific heating technique (inductive or resistive) [23–27] or heating rate ( $10 \text{ K s}^{-1}$  up to  $10^7 \text{ K s}^{-1}$ ) [28,29]. It has been applied to modify the magnetic properties of metallic glasses [30,31], to micro-form metallic-glass surfaces [23] and to thermoplastically form BMGs [32]. But to-date, the potential of flash-annealing for studying fundamental nucleation and growth processes as well as to tailor the phase formation and the microstructure to improve mechanical properties has remained largely unexplored.

While transient nucleation is known to occur in metallic glasses during isothermal annealing [22,33–35], theoretical considerations predict a heating-rate dependent transient nucleation phenomenon during fast isochronal heating based on the dissolution of subcritical clusters [36]. The critical cluster size increases with temperature, as we will discuss below, and the assumption of steady-state nucleation kinetics being applicable to fast heating of glasses fails [36] because the nucleation rates are effectively reduced. This has been measured for silicate glasses [37], yet, this hypothesis has never been directly verified for metallic glasses by experiments. The present experiments are hence conducted to (i) analyze heating-rate-dependent transient effects in metallic glasses heated at high rates and to (ii) assess the potential of flash-annealing for optimizing composite microstructures and thereby the resulting deformation behaviour.

## 2. Experimental

$\text{Cu}_{44}\text{Zr}_{44}\text{Al}_8\text{Hf}_2\text{Co}_2$  pre-alloys were obtained by mixing high-purity elements (min. 99.99%) in a Ti-gettered Ar atmosphere

in an arc melter (Edmund Bühler). Rods with diameters of 3 and 4.5 mm were prepared by suction casting in the arc melter. The flash-annealing was carried out in a custom-made device developed in-house. A Siemens Simatic control unit receives the sample-temperature signal from a high-speed Lumasense pyrometer (sampling rate: 5 ms) and triggers the clamping system to eject the sample at a predefined temperature. The heating is realized by means of a water-cooled induction coil around the sample. A 10 kW, medium-frequency generator (10–100 kHz, Trumpf Hüttinger) induces the currents in, and heats, the rod-shaped specimens. A beaker with water is placed directly underneath the sample to quench it. To minimize oxidation, the sample is flushed in argon during the entire heating process.

The skin depth of the current set-up was estimated using [38]:

$$s = \frac{1}{\sqrt{\mu_r \mu_0 \kappa \pi f}} \quad (1)$$

where  $\mu_r$  and  $\mu_0$  are the relative permeability and the permeability of vacuum, respectively,  $\kappa$  is the electrical conductivity and  $f$  is the frequency of the experimental set-up (RCL circuit). With a room-temperature resistivity ( $\rho = \kappa^{-1}$ ) for  $\text{Cu}_{44}\text{Zr}_{44}\text{Al}_8\text{Hf}_2\text{Co}_2$  of  $1.66 \times 10^{-6} \Omega \text{m}$  (measured with a Quantum Design PPMS Model 6000 equipped with a AC transport controller 7100), a relative permeability,  $\mu_r$ , of 1, a permeability of vacuum,  $\mu_0$ , of  $4\pi \times 10^{-7} \text{ N A}^{-2}$  and a frequency of 80 kHz, the skin depth amounts to 2.3 mm. The glassy samples used in the present study to determine the CHT diagram had diameters of 4.5 mm. Taking the skin depth of about 2.3 mm into account, we can conclude that the entire sample volume is heated during flash-annealing and that the heating should be relatively uniform.

For an estimation of the typical cooling rate, the eutectic alloy Al–33Cu (at.%, Al<sub>82.7</sub>Cu<sub>17.3</sub>) was melted inductively in the device and the molten drop was subsequently quenched in water. The solidified drop had a typical diameter of 4–5 mm. The inter-lamellar spacing is known to depend on the applied cooling rate [39,40] and the method outlined in Ref. [39] was applied. About five independent measurements were conducted and the microstructures evaluated. The cooling rate is estimated to be at least of the order of  $10^3 \text{ K s}^{-1}$ . The achievable cooling rate should be sufficient to avoid pronounced crystallization of the glassy matrix during cooling since it exceeds the critical cooling rate for the present alloy [41,42].

The structure of selected flash-annealed  $\text{Cu}_{44}\text{Zr}_{44}\text{Al}_8\text{Hf}_2\text{Co}_2$  glasses was investigated at the ID11 beamline at the ESRF in Grenoble using high-energy X-rays ( $\lambda = 0.013 \text{ nm}$ ) and using a STOE STADI P diffractometer (MoK $_{\alpha 1}$  radiation). A Perkin-Elmer Diamond differential scanning calorimeter (DSC) was employed to determine  $T_g$  and  $T_x$  at low heating rates (0.083 up to  $5 \text{ K s}^{-1}$ ). The liquidus temperature ( $1194 \pm 5 \text{ K}$ ), melting temperature ( $1159 \pm 5 \text{ K}$ ) and the eutectoid transformation peak temperature were measured in a DSC 404 C (Netzsch) at  $0.33 \text{ K s}^{-1}$ .

The flash-annealed cylindrical rods were cut in half along their longitudinal axis (Struers Accutom), ground with sandpaper down to 4000 grit, and polished using a diamond suspension (1  $\mu\text{m}$ , MetaDi, Buehler) and Mastermet2 (Buehler). The microstructure along these longitudinal sections was then analyzed. The micrographs were recorded in a Zeiss Gemini 1530 scanning electron microscope (SEM) and the number and size distribution of crystallites was obtained by means of the Leica QWin software. Up to 15 independent images (depending on the magnification) were recorded about 100  $\mu\text{m}$  away from the edge of the cross-section (i.e. from the surface of the rod) as well as in the centre of the rod. The total area investigated per sample was 115,000–122,000  $\mu\text{m}^2$ .

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