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Fast and direct determination of fragility in metallic glasses using chip calorimetry

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Abstract

We directly determine the thermodynamic fragility index of two metallic glasses ($Mg_{65}Cu_{25}Gd_{10}$ and $Au_{49}Cu_{26.9}Si_{16.3}Ag_{5.5}Pd_{2.3}$) from fictive temperature shifts induced by a variation of the quenching rate using fast differential scanning calorimetry (FDSC). Recent chip calorimeters are able to achieve the cooling rates necessary to perform such an evaluation. For the $Mg_{65}Cu_{25}Gd_{10}$ and $Au_{49}Cu_{26.9}Si_{16.3}Ag_{5.5}Pd_{2.3}$ metallic glasses studied, we find very good agreement of the kinetic fragility index with literature data obtained by conventional calorimetry and rheology. The thermodynamic fragility indices are m=25.5 $\pm$ 1.5 for $Mg_{65}Cu_{25}Gd_{10}$ and m=50.3 $\pm$ 2.3 for $Au_{49}Cu_{26.9}Si_{16.3}Ag_{5.5}Pd_{2.3}$, respectively. The FDSC method discussed here allows for fast and reliable determination of the kinetic fragility of metallic glasses, and is thus competitive with high-frequency methods.

Keywords: Materials science, Thermodynamics, Condensed matter physics

1. Introduction

A useful approach describing the deceleration of the dynamics of a glass forming liquid upon cooling towards the glass transition is the concept of fragility. In his seminal publications Angell [1,2,3] distinguished two main classes of glass-forming liquids, which he defined as strong, when the viscosity η vs. the ratio of the glass transition to temperature, T_g/T, follows an Arrhenius law and as fragile, when η vs. T_g/T can only be described by a Vogel−Fulcher−Tammann (VFT)-type law. This property known as fragility [1] has fundamental implication for the molecular and atomic mobility upon temperature changes in the material and is therefore also highly relevant for the mechanical properties of glassy systems. The fragility is also closely related to the glass-forming ability (GFA) [4], and together with the reduced glass transition temperature ($T_{rg} = T_g/T_l$, with T_l the liquidus temperature) and the critical cooling rate, it may be used to predict and quantify it. Simulations indicate that, if the short-range order (SRO) is considerably affected by temperature changes, the glass-forming liquid is more fragile, while it is stronger if the SRO remains mostly unaffected [5].

The fragility is quantified by the slope of the equilibrium viscosity, η_{eq}, as a function of the reciprocal temperature T and can be determined through flow experiments. The fragility index m_{rheo} is then written as

$$m_{rheo} = \frac{d\ln\eta_{eq}}{d\frac{T_g}{T}}\bigg|_{T_g}, \tag{1}$$

where T_g is the glass transition temperature. The fragility index (Equation 1) is useful to quantitatively asses and compare the underlying physical relaxation processes and the glass transition in the supercooled liquid state [8].

According to the classification proposed by Angell [1,2], a strong liquid has a fragility index close to 20, while fragile ones will reach fragilities up to 200−250. Viscosity measurements are time consuming and need very stable conditions to yield reliable results. For small samples sizes and masses such measurements may not be possible at all.

For good glass-forming systems, which vitrify at cooling rates below ≈ 5 K/s, such as many polymers, a calorimetric method using differential scanning calorimetry (DSC) has been developed by Moynihan et al. [6,7,8,9]. This method requires determination of the limiting fictive temperature T_f' as a measure of the glass transition as a function of the cooling rate β_c preceding the isochronal DSC run. The fictive temperature is defined as the intersection of the extrapolated enthalpies $H(T)$ of the equilibrium liquid and glassy states. The calorimetric fragility index m_{calo} is defined as

$$m_{\text{calo}} = -\frac{\text{dlog}_{10}\beta_c}{\text{d}\frac{T_g}{T'_f}}\Bigg|_{T'_f} . \tag{2}$$

An adapted method [10] has been used for glasses with critical cooling rates exceeding the achievable rates of conventional DSC devices [7,11,12], because up to the introduction of chip calorimeters this method was not deployable for most bulk metallic glass (BMG)-forming systems requiring rather high critical quenching rates and also relatively high glass transition temperatures. This adapted method uses the activation enthalpy ΔH_g^* of the glass transition onset as determined by an Arrhenius evaluation via calorimetric experiments performed at different heating rates β_h [7]:

$$\ln\beta_h = -\frac{\Delta H_g^*}{R\,T_{g,\beta_{\text{ref}}}} + \text{const.} \tag{3}$$

Here, the fragility index m_{act} is given by

$$m_{\text{act}} = \frac{\Delta H_g^*}{R\,T_{g,\beta}}\Bigg|_{T_{g,\beta}} . \tag{4}$$

This method, however, implies some challenges, as the determination of the kinetics of T_g in heating experiments is problematic due to the different kinetics of structural changes [13]. The method is hence both rather inaccurate and time consuming.

The recently developed fast chip calorimetry [14], however, allows to extend the initial method based on the work of Moynihan et al. via applying high cooling rates *in-situ* to directly determine the calorimetric fragility index. Dhotel et al. [9] revealed the feasibility of this procedure for polymeric materials. Chip calorimetry was used to determine the fragility in lanthanum (La) based metallic glasses using the heating rate dependence of T_g [15] and in gold based (Au) metallic glasses [16,17]. In the present work we demonstrate the power of fast chip calorimetry (fast differential scanning calorimetry, FDSC) in determining the calorimetric fragility index of metallic glasses using shifts in the fictive temperature. In general chip calorimetry proves very effective to determine the fragility of metallic glasses where other fast methods, such as for instance dielectric spectroscopy, are not applicable due to the lack of dielectric moments and when available sample masses are very small (i.e. several ng and more).

2. Materials and methods

We use $Mg_{65}Cu_{25}Gd_{10}$ ($T_g = 421 \pm 2$ K, $T_x = 482 \pm 2$ K, $T_l = 693 \pm 2$ K, determined as onset temperatures by conventional DSC at a heating rate of $\beta_h = 1$ K/s) and $Au_{49}Cu_{26.9}Si_{16.3}Ag_{5.5}Pd_{2.3}$ ($T_g = 377 \pm 2$ K, $T_x = 460$ K, $T_l = 609 \pm$

2 K, at $\beta_h = 1$ K/s) as model systems. For the Mg alloy, a Cu−Gd mixture was first pre-alloyed by arc melting the mixture of pure metals in high-purity argon atmosphere. A mixture of pure Mg and the Cu−Gd pre-alloy was then induction-melted under argon atmosphere and injected into a copper mold to form plate-shaped specimens. Samples for the Au-alloy were produced by melt spinning under protective He atmosphere [18]. Calorimetry was performed with a Mettler-Toledo Flash DSC 1 chip calorimeter using MultiSTAR UFS 1 MEMS chip sensors. Counter-cooling was achieved using a Huber TC100 intracooler to cool the samples to 183.15 K and to achieve high cooling rates. An argon flow of 8 ml/min allowed to avoid condensation and oxidation on the chip and the sample. Prior to the measurements, internal stresses in the MEMS chips were removed by applying 5 conditioning runs performed up to a set-point temperature of 723.15 K and thermocouple correction was applied. An indium reference with a mass comparable to that of the sample was also measured in order to correct the absolute temperature.

The specimens were produced by cutting tiny pieces from the as-cast material with the help of a steel scalpel. Samples on the order of 100 ng were placed on the chip in order to achieve satisfying cooling rates for *in-situ* amorphization. Mass calibration was performed by comparing the specific heat of fusion $\Delta h_{f,(1\ K/s)}$ of a bulk sample determined at a heating rate of 60 K/min (1 K/s) on a Mettler-Toledo DSC 3+ (under purged argon gas flow of 50 ml/min) with a measurement of the heat of fusion $\Delta H_{f,(1\ K/s)}$ performed at the same rate on a Flash DSC 1. The sample mass M_{sample} was then determined using the expression $M_{sample} = \Delta H_{f,1\ K/s} / \Delta h_{f,1\ K/s}$.

The heating program consisted of iterative heating segments at 1000 K/s each preceded by a cooling segment with variable cooling rate (see Fig. 1). The manufacturer
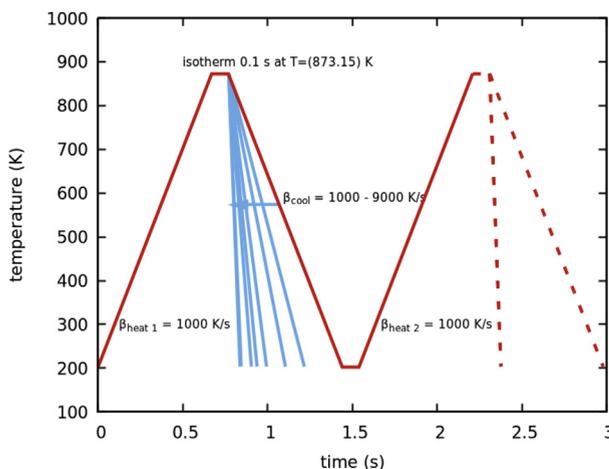

Fig. 1. Schematic representation of the temperature program. After a homogenization heating run at a rate of 1000 K/s the material is quenched at variable rates ($Mg_{65}Cu_{25}Gd_{10}$: 1000−9000 K/s, $Au_{49}Cu_{26.9}Si_{16.3}Ag_{5.5}Pd_{2.3}$: 10−9700 K/s) and subsequently heated at 1000 K/s in order to determine the fictive temperature. Subsequently, the steps are repeated with new cooling rates.

guarantees reliable functioning of the chips up to 723.15 K; however, temperatures up to 873.15 K can be reached for short times (melting of the aluminum contacts occurs at 933.45 K). The service life of the chips is reduced by temperature programs exceeding 723 K but is still sufficient for the current study. Melting of $Mg_{65}Cu_{25}Gd_{10}$ was performed at 873.15 K (set point), while melting of $Au_{49}Cu_{26.9}Si_{16.3}Ag_{5.5}Pd_{2.3}$ was performed at 723.15 K (set point). The collection of data for this analysis was accomplished with a single, multiple-step program that alternately conditions the sample through the glass transition region at successive cooling rates and alternating heating steps at a fixed rate, here 1000 K/s, as illustrated in Fig. 1. The total measurement time for such an experiment is on the order of 10 s, which is one of the most striking benefits of FDSC compared to fragility determination via other methods, such as standard DSC or rheology. Dielectric spectroscopy can reach similar (or even faster) measurement times but is not applicable to materials that have no dielectric moments [19].

3. Results

Examples for FDSC cooling traces of $Mg_{65}Cu_{25}Gd_{10}$ are shown in Fig. 2. Partial crystallization already occurs at a cooling rate below 7000 K/s Fig. 3 shows the related heating curves determined at a rate of 1000 K/s for each cooling rate applied in Fig. 2. Below a quenching rate of 2000 K/s the sample is fully crystalline and no exothermic crystallization peak or glass transition is discernable, while both can be observed for a quenching rate of 3000 K/s.

For $Au_{49}Cu_{26.9}Si_{16.3}Ag_{5.5}Pd_{2.3}$, the critical cooling rates are far lower. The related FDSC cooling traces are depicted in Fig. 4. Partial crystallization occurs below cooling rates of 800 K/s. The related heating curves determined with 1000 K/s for each cooling rate are shown in Fig. 5. The critical quenching rate to completely suppress
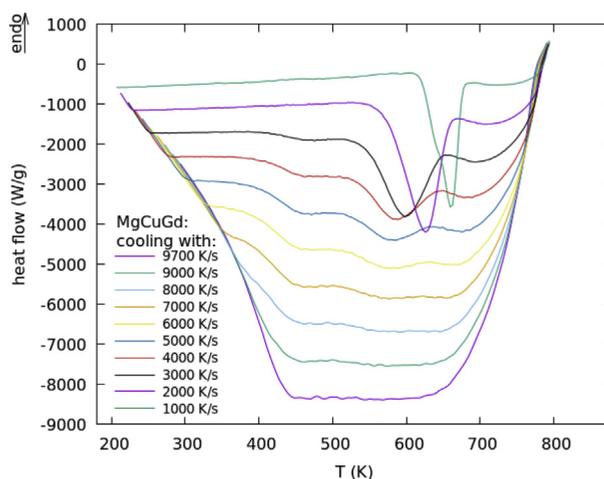

Fig. 2. FDSC cooling curves for $Mg_{65}Cu_{25}Gd_{10}$ measured at rates of 1000 K/s to 9700 K/s.

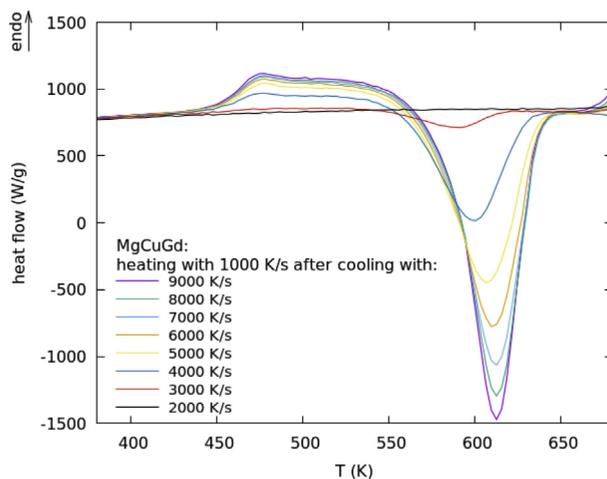**Fig. 3.** FDSC heating curves for $Mg_{65}Cu_{25}Gd_{10}$ at 1000 K/s after cooling at rates of 2000 K/s to 9000 K/s (see Fig. 2).
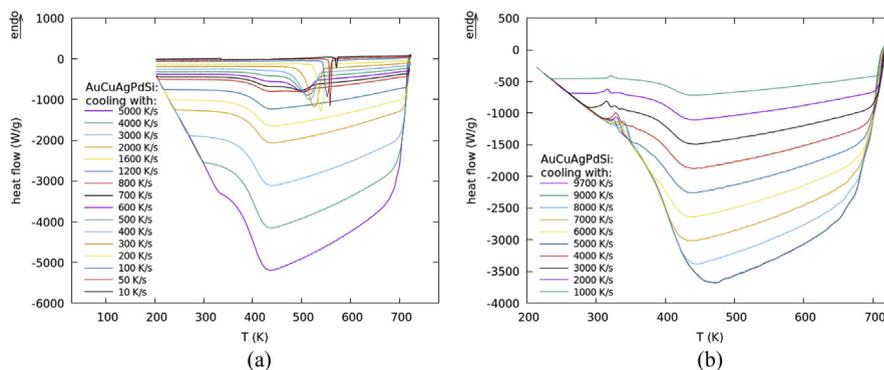

Fig. 4. DSC cooling curves for $Au_{49}Cu_{26.9}Si_{16.3}Ag_{5.5}Pd_{2.3}$. (a) cooling rates from 10 to 5000 K/s, (b) cooling rates from 1000 to 9700 K/s. The small fluctuations between 320 and 380 K are due to crystallization of remaining indium debris from chip calibration.
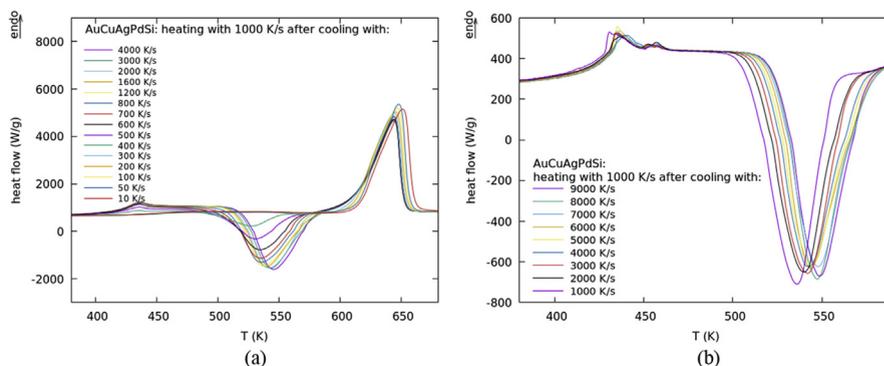

Fig. 5. DSC heating curves for $Au_{49}Cu_{26.9}Si_{16.3}Ag_{5.5}Pd_{2.3}$. (a) cooling rates from 10 to 4000 K/s, (b) cooling rates from 1000 to 9000 K/s. The small endothermic peak at about 429 K (156 °C) is due to melting of remaining indium debris from chip calibration.

crystallization amounts to 200 K/s. For lower rates, no amorphous fraction is present in the sample, as verified by the absence of an exothermic crystallization peak or a glass transition. Both glass transition and crystallization are still discernable for a minimum quenching rate of 300 K/s.

As the glass transition is a time dependent process, the fictive temperature T_f as a useful measure of the glass transition has been introduced by Tool [20]. The term fictive has been chosen to account for the fact that T_f cannot be directly measured because the transition from the glass to the liquid is time-dependent and a non-equilibrium process [8]. The fictive temperature can be determined from DSC experiments by the extrapolated intersection of the pre-transition (glassy) and post-transition (liquid) baselines in enthalpy units. To obtain the enthalpy, the heat capacity curves are integrated with respect to the temperature. The device used in this work operates as a power compensated DSC and as such the heat flow is directly measured in units of power (i.e. in W/g). A reasonable determination of the heat capacity can be achieved by normalizing the heat flow by the heating rate. The absolute
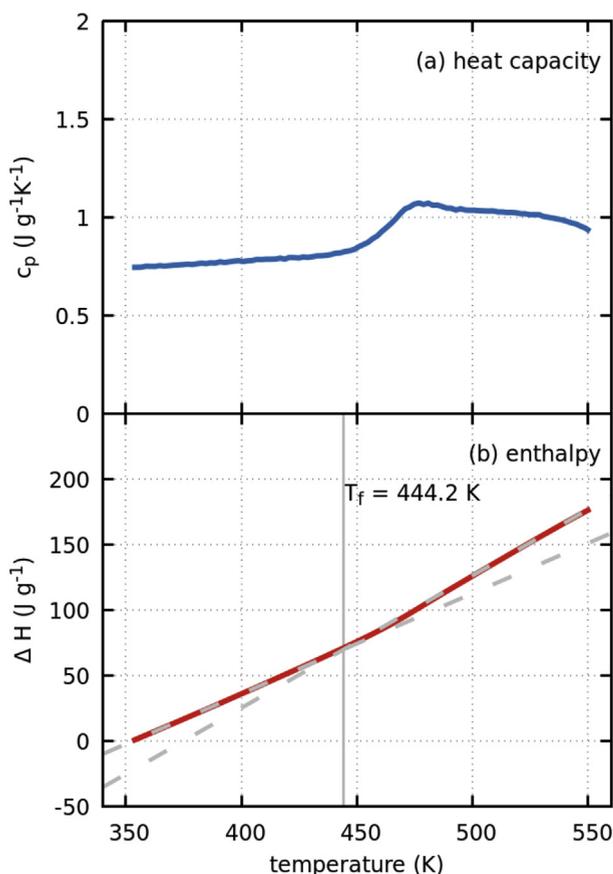

Fig. 6. Representation of the construction for the determination of the calorimetric fictive temperature T_f for $Mg_{65}Cu_{25}Gd_{10}$ cooled at a rate of 5000 K/s. The numerical integration of the temperature dependence of the heat capacity (a) yields the enthalpy (b).

value of the heat capacity is not relevant for the determination of the fictive temperature, as only the change in slope of the enthalpy curve determines the fictive temperature. Another method for determining T_f directly from the heat capacity curve has been developed based on the graphical construction of equi-enthalpic rectangles [8]. Fig. 6 shows T_f on a DSC heat capacity trace and its integral for a representative FDSC trace with a previous cooling at 5000 K/s. The resultant fictive temperature amounts to 444.2 ± 4.0 K.

The big advantage of the fictive temperature is that it is independent of the DSC heating rate used to measure it (see i.e. [21]). Hence, it gives a measure for the glass transition that depends only on the previous cooling rate through the glass transition region, determining the enthalpy state of the material below T_g. The raw data required to reproduce the present findings are available from the corresponding author upon reasonable request as it is matter of further ongoing studies.

4. Discussion

Fig. 7 shows the logarithm of the cooling rate as a function of the normalized reciprocal fictive temperature for both studied alloys. According to Equation (2), a linear fit yields the calorimetric fragility of the material.

The calorimetric fragility value for $Au_{49}Cu_{26.9}Si_{16.3}Ag_{5.5}Pd_{2.3}$ amounts to $m = 50.3 ± 2.3$, which is in good agreement with data reported by Gallino et al. [22,23] based on the combination of FDSC data of Wang et al. [24] (using Equations (3) and (4)) and rheological data [25] finding a value of 46.2 ± 2.7. The same group also published a value of 51.9 ± 2.7 [26,27] and Fiore et al. find a fragility index of 48 ± 3 for the same alloy The best agreement is found with the data of Wang et al. [16] finding a value of 49 ± 1 using FDSC and a similar approach.
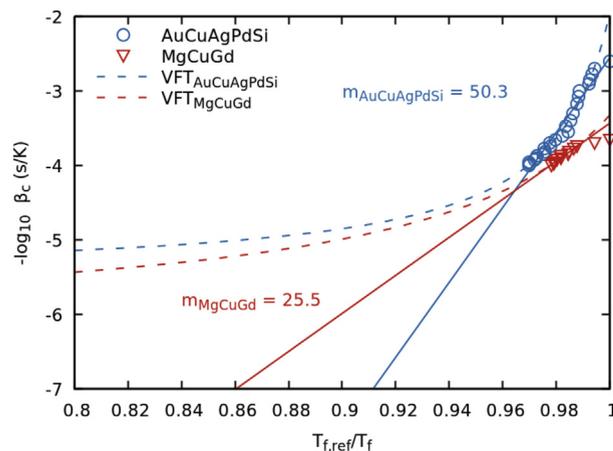

Fig. 7. Logarithm of the cooling rate as a function of the normalized reciprocal fictive temperature. The linear fit yields the calorimetric fragility *m*. VFT fits to the data are shown as dashed lines.

The calorimetric fragility value for $Mg_{65}Cu_{25}Gd_{10}$ determined by direct application of the method of Moynihan et al. [6] with FDSC as described here amounts to $m = 25.5 \pm 1.5$. This is in reasonable agreement with the value of the kinetic fragility D^* $\sim$ 15 from VFT fitting that was found by Chang et al. [28]. D^* can be related to m by the equation [29,30]

$$D^* = \frac{590}{m - 17},$$ (5)

hence yielding a value of $m \sim 22.3$ for the data of Chang et al. D^* (Equation 5), on the one hand, is the kinetic fragility parameter and describes the deviation from the Arrhenius behavior in the VFT Equation

$$\ln \eta = \ln \eta_0 + D^* \frac{T_0}{T - T_0},$$ (6)

with η_0 and T_0 (Vogel-Fulcher Temperature) as empirical material parameters. On the other hand, m is defined as the slope of the logarithmic viscosity as a function of the inverse fictive temperature at the reference fictive temperature as defined in Equation (2).

Through the application of the Frenkel–Kobeko–Reiner (FKR) relationship ($\beta_c \tau = \beta_c/\omega = C$ where τ is the relaxation time, ω the angular frequency and C is a constant [31]) and the VFT Equation (Equation 6) as described for instance by Schawe [32], a combined plot of the FDSC data with rheological data can be produced. As shown in Fig. 8 the FDSC coincides very well with literature data obtained by parallel plate viscosimetry [27,28] conventional calorimetry [33] and isothermal three point bending [22]. Apparently, the presented method extends the cooling rate regimes
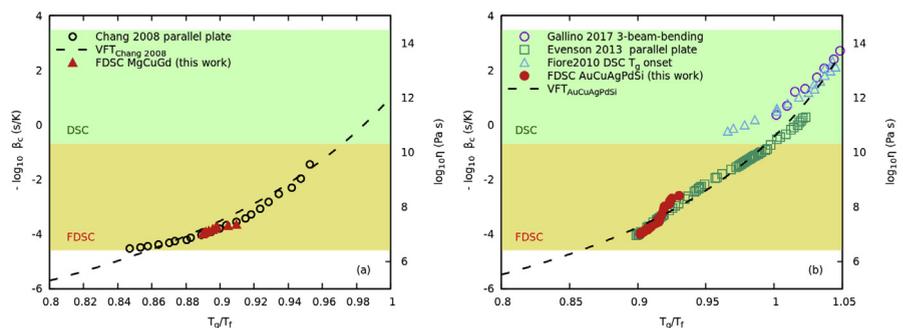

Fig. 8. Logarithm of the cooling rate as a function of the normalized reciprocal (fictive) temperature and comparison with literature data based on rheological and calorimetric methods. The data has been normalized to the glass transition temperatures. The green area reflects the cooling rates accessible via classical DSC and the yellow area the ones accessible via commercially available fast DSC. (a) shows the data for $Mg_{65}Cu_{25}Gd_{10}$ including VFT fits for the FDSC data and literature data by Chang et al. [28] and (b) shows the FDSC data for $Au_{49}Cu_{26.9}Si_{16.3}Ag_{5.5}Pd_{2.3}$ and conventional DSC data of Fiore et al. [33] as well as a VFT fit to the data of Evenson et al. [27] and Gallino et al. [22].

for the determination of the fragility accessible through calorimetric methods for both alloy systems by more than 4 orders of magnitude. As, according to the FKR relation, the cooling rates are on the order of the inverse relaxation times, one can estimate that with state-of-the-art chip calorimeters — reaching cooling rates of 10^5 K s^{-1} and more — structural relaxation times ranging from below 10^{-4} s up to about 10 s (with corresponding frequencies from 0.1-10^4 Hz) can be studied using FDSC.

5. Conclusions

We have applied the method of Moynihan et al. to determine the fictive temperature as a function of the cooling rate using fast calorimetry on two metallic glass systems, namely $Mg_{65}Cu_{25}Gd_{10}$ and $Au_{49}Cu_{26.9}Si_{16.3}Ag_{5.5}Pd_{2.3}$. This allows determining the fragility in a very fast and direct manner with typical measurement times on the order of 10 s. Also very limited sample sizes such as powder particles can be studied. Comparison with data based on conventional calorimetry and rheology published in the literature yields very good agreement for the kinetic fragility indices determined by FDSC. The fast and reliable data acquisition possible with chip calorimetry should allow unveiling new phenomena in the glassy dynamics of metallic glasses as these are not accessible with other fast techniques such as dielectric spectroscopy, while rheological methods are often difficult. For instance, the interesting phenomenon of transitions from fragile to strong behavior previously reported for several glassy systems (i.e. [22,34,35]) can now be studied faster and more systematically.

Declarations

Author contribution statement

Florian Spieckermann: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Innozenz Steffny: Performed the experiments.

Xilei Bian: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

Sergey Ketov, Mihai Stoica, Jürgen Eckert: Contributed reagents, materials, analysis tools or data.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

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