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Size dependent vitrification in metallic glasses

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Two-sentence editor’s summary

Size effects may profoundly impact properties of metallic glasses. Di Lisio et al. reports unprecedented results on the impact of reducing sample size on the glass transition of metallic glasses, showing a reduction in the vitrification temperature for samples with micrometer size.

Abstract

Reducing the sample size can profoundly impact properties of bulk metallic glasses. Here, we systematically reduce the length scale of Au and Pt-based metallic glasses and study their vitrifi-
cation behavior and atomic mobility. For this purpose, we exploit fast scanning calorimetry (FSC) allowing to study glassy dynamics in an exceptionally wide range of cooling rates and frequencies. We show that the main $\alpha$ relaxation process remains size independent and bulk-like. In contrast, we observe pronounced size dependent vitrification kinetics in micrometer-sized glasses, which is more evident for the smallest samples and at low cooling rates, resulting in more than 40 K decrease in fictive temperature, $T_f$, with respect to the bulk. We discuss the deep implications on how this outcome can be used to convey glasses to low energy states.

Introduction

The transformation of a liquid, supercooled below its melting temperature, into a glass, the so-called vitrification or glass transition, remains one of the most intriguing unsolved problems in condensed matter physics\textsuperscript{1,2}. Apart from the underlying fundamental understanding, the way vitrification takes place and the age of the glass\textsuperscript{3–5} can deeply impact the glass properties and their lifetime evolution\textsuperscript{6,7}. Among the variety of glasses, a class of utmost importance from both fundamental and technological viewpoints is that of metallic glasses (MG). They combine different technological relevant properties such as superior mechanical properties and corrosion resistance\textsuperscript{8,9}, which could be deeply affected by how vitrification has previously taken place\textsuperscript{10}. For instance, the fracture toughness of metallic glasses has been directly related to the enthalpic state of the glass\textsuperscript{11,12}, which can be varied by vitrifying at different cooling rates and described by the concept of fictive temperature\textsuperscript{13}, $T_f$. The latter is defined as the temperature at which the glass line drawn from the glass thermodynamic state crosses the supercooled liquid line or, for experiments
conducted on cooling, simply the temperature at which the supercooled liquid falls out of thermo-
dynamic metastable equilibrium.\textsuperscript{14}

Conventional wisdom describes vitrification as triggered exclusively by the main, $\alpha$, relax-
ation exhibiting super-Arrhenius temperature dependence.\textsuperscript{15–20} In this case, the cooling rate de-
dependent $T_f$ exhibits the same behavior as the temperature dependent relaxation time, $\tau$, of the $\alpha$ relaxation. Recently, it has been shown that, for an Au-based MG, the cooling rate dependent vitrification takes place with a weaker temperature dependence than the $\alpha$ relaxation.\textsuperscript{10} As a con-
sequence, vitrification at low cooling rates results in values of $T_f$ lower than those which would be obtained only accounting for the $\alpha$ relaxation. The main consequence of this outcome is that atomic mechanisms different from the $\alpha$ relaxation may be important actors in vitrification kinetics.\textsuperscript{21,22}

Beside the role of different mechanisms in vitrification kinetics, a long-standing problem concerns whether vitrification and atomic/molecular relaxation can be modified by reducing the sample size. Early work on low molecular weight glass formers $o$-terphenyl (OTP) and benzyl alcohol confined in nanopores showed a depression of the glass transition temperature, $T_g$, with re-
spect to the bulk at nanopores sizes below about 70 nm.\textsuperscript{23} Later, Keddie et al.\textsuperscript{24} pioneered studies on the effect of thickness on the $T_g$ of thin polymer films, showing a reduction of $T_g$ for an archetypal polymeric glass former, polystyrene (PS), supported on inorganic substrates for thicknesses smaller than about 50 nm. The intense activity, conducted during the last decades and summarized in several reviews\textsuperscript{25–28}, depicted a scenario where effects on the $\alpha$ relaxation, if any, are present for samples with typical size below 10 nm.\textsuperscript{29–31} Consistently, electron correlation microscopy
with sub-nanometer resolution showed that the dynamics of metallic glasses at the free surface is perturbed at length scales not exceeding a few nanometers\textsuperscript{32,33}. In stark contrast, effects on vitrification kinetics are present for much larger sample sizes and, for polymeric glasses not exposed to adsorbing interfaces\textsuperscript{27}, generally result in significant $T_g$ reduction with respect to the bulk. When the concept of $T_f$ is employed to characterize vitrification kinetics, significant reductions have been found for polymer samples with size exceeding the micrometer length scale\textsuperscript{34,35}. While, in view of the invariant bulk-like $\alpha$ relaxation any explanation invoking any change of dynamics at such large length scale must be discarded, significant effort has been undertaken to explain this finding on the base of a model of equilibration based on diffusion of free volume holes\textsuperscript{26}. A direct visualization of the physical soundness of this model was provided in colloidal glasses\textsuperscript{36}, where the migration and annihilation of free volume holes at the interface was visualized by microscopy.

While deeply investigated in glass forming polymers, whether reducing the sample size in metallic glasses may be of relevance in affecting vitrification kinetics has so far remained completely elusive and largely unexplored. This might have profound implications on the macroscopic properties of the metallic glass. For example, the ordinary temperature previously associated with a ductile-to-brittle transition in metallic glasses was recently proved to play a secondary role\textsuperscript{37}, and the concept of $T_f$-dependent mechanical properties of metallic glasses is emerging\textsuperscript{11,12,37–39}. One of the most intriguing observations is that a gradual change in fracture morphology of a Pt-based metallic glass from vein-pattern to completely smooth fracture surface to necking is observed with decreasing sample size at micrometer length scales and testing temperature\textsuperscript{39}. 
In this work, we investigate size dependent glass transition in two archetypal MG, based on Au and Pt, respectively. For this purpose, we employ fast scanning calorimetry (FSC) permitting a large range of heating/cooling rates from 0.5 K/s up to 5000 K/s. In samples prepared in identical conditions, we investigate both atomic mobility\textsuperscript{40,41}, that is the rate of spontaneous fluctuations taking place in the unperturbed supercooled liquid at equilibrium, and vitrification kinetics\textsuperscript{20} in a wide range of time scales. We find that atomic mobility remains bulk-like for all investigated sample sizes, ranging from bulk to several microns. In contrast, we observe pronounced size dependent vitrification kinetics more evident for the smallest samples and at low cooling rates. As a result, vitrification of metallic glasses takes place at temperatures lower than bulk for samples size below $\sim 10 \ \mu$m. The important implication of this outcome is that mild reductions of the sample size in metallic glasses allow exploring thermodynamic states, in terms of $T_f$, deep down in the energy landscape, thus opening the door to the obtainment of thermodynamically ultra-stable metallic glasses in time scales amenable to the experimental practice.

**Results**

We begin presenting results obtained by using step-response protocols. By applying a linear perturbation, that is, a small temperature change, this methodology conveys information on the time scale of spontaneous fluctuations via the thermal susceptibility. Once Fourier transformation from the time to the frequency domain is carried out, step-response protocols deliver the complex specific heat: $c_p^* = c'_p + i c''_p$. Frequency-dependent reversing specific heat, $c_{p,\text{rev}}$, that is, the modulus of $c_p^*$, which approximately equals the in-phase specific heat, $c'_p$, is presented in Fig. 1. The main
α relaxation is identified as a step in $c_{p,\text{rev}}$. The insets of Fig. 1 show frequency and temperature dependent $c_{p,\text{rev}}$ for both glasses. As customary, increasing the frequency results in a temperature up-shift of the step in $c_{p,\text{rev}}$, implying an acceleration of the α relaxation with increasing temperature. Furthermore, a broad tail in excess with respect to the glassy specific heat, more visible at low frequencies and for Au$_{49}$Cu$_{26.9}$Si$_{16.3}$Ag$_{5.5}$Pd$_{2.3}$ at.%, is detected, which can be ascribed to a secondary relaxation$^{10,42}$.

The main panels of Fig. 1 underline the effect of sample size showing temperature dependent $c_{p,\text{rev}}$, obtained exemplary at 20 Hz, for both alloy compositions with different $l_{eq} = V/A$, where $l_{eq}$ is the equivalent size, and $V$ and $A$ are the sample volume and surface area, respectively; obtained analyzing samples SEM micrographs (see Methods section for details). Irrespectively of the sample size, the step in $c_{p,\text{rev}}$ takes place in the same temperature range, indicating the absence of a size dependence on the metallic glasses atomic mobility. The mid-step of $c_{p,\text{rev}}$ defines a typical relaxation time, $\tau$, of the α relaxation, whose temperature dependence is presented in Fig. 3, panels (a) and (b). The size-independence of the α relaxation observed at 20 Hz (see Fig. 1) generally applies to all frequencies, as indicated by the complete overlap of temperature dependent $\tau$ at different sample sizes. All temperature dependent $\tau$ data can be fitted by the empirical Vogel-Fulcher-Tammann (VFT) equation: $\tau = \tau_0 \exp(D^*T_0/(T - T_0))$, where $\tau_0$, $D$ and $T_0$ are the pre-exponential factor, the fragility index and the Vogel temperature, respectively. The fitting parameters are indicated in the caption of Fig. 3 and are in accordance with previous studies$^{10,43}$.

The characterization of vitrification kinetics is presented in Fig. 2, showing specific heat
Figure 1: Linear response in terms of thermal susceptibility for metallic glasses of different size. Reversing specific heat $c_p$ at 20 Hz for samples with different characteristic lengths $l_{eq}$ (main panels) and for samples with the indicated $l_{eq}$ at different frequencies (insets) as a function of temperature for (a) $\text{Au}_{49}\text{Cu}_{26.9}\text{Si}_{16.3}\text{Ag}_{5.5}\text{Pd}_{2.3}$ at.% and (b) $\text{Pt}_{57.5}\text{Cu}_{14.7}\text{Ni}_{5.3}\text{P}_{22.5}$ at.%.
Figure 2: **Vitrification behavior of metallic glasses of different size.** Specific heat scans for the indicated samples and heating rates \( (q_h) \) after cooling at the indicated rates \( (q_c) \). The grey lines are linear fits of the glass and the melt specific heat.

Scans obtained at the indicated heating rate, \( q_h \), after cooling using a wide range of rates. In Fig. 2, we present the results obtained with two samples of different sizes for each alloy composition, however similar results, reported in the Supplementary Information, were obtained for samples of other sizes. The very general feature observed in all panels of Fig. 2 is the expected development of a pronounced endothermic overshoot, in proximity of the step due to the glass transition. Its intensity grows with decreasing the previously applied cooling rate, signifying the attainment of lower enthalpic states in glasses cooled at lower rates\(^5\). Furthermore, we observe an additional
kinetic phenomenon, that is, a low temperature endothermic excess — governed by an underlying sub-$T_g$ relaxation — whose origin is discussed later. This is mostly visible in the Au-based glass-former.

Panels (a) and (b) of Fig. 3 provide an overview on how different cooling rates convey the supercooled melt to glasses with different thermodynamic states in terms of $T_f$. A complementary representation is reported in Fig. 3, panel (c), that depicts a three-dimensional mapping on the way $T_f$ deviates from the bulk value at different cooling rates when changing sample size. For large cooling rates, vitrification takes place with the same dependence as that of the $\alpha$ relaxation time, independently of the sample size and in a bulk-like fashion. As a result, in this case cooling rate dependent $T_f$ can be fitted by the VFT equation with the same $D^*$ and $T_0$ values as those of the $\alpha$ relaxation. However, decreasing the cooling rate entails marked deviation from the behavior expected if exclusively the $\alpha$ relaxation assisted vitrification (blue and red VFT-lines in Fig. 3 in panels (a) and (b), respectively). The deviation is mild for the largest investigated samples, as previously reported for Au$_{49}$Cu$_{26.9}$Si$_{16.3}$Ag$_{5.5}$Pd$_{2.3}$ at.%$^{10}$. In this case, the vitrification behavior is bulk-like, as no size effects on $T_f$ are detected on further increasing the sample size. In contrast, in this study we observe that reducing the sample size results in increasingly larger decoupling of vitrification kinetics from the $\alpha$ relaxation, indicating increasingly prominent role of fast non-$\alpha$ mechanisms assisting vitrification at low rates. The $T_f$ reduction in the smallest samples with respect to that expected if only the $\alpha$ relaxation assisted vitrification is as large as more than $\sim$ 40 K for both glasses for the lowest cooling rate at which we were able to vitrify the completely
Figure 3: **Overview of temperature dependent vitrification behavior and atomic mobility; and sketch of FVHD model.** (a and b) Temperature dependence of the $\alpha$ relaxation time (left axis) and $T_f$ dependence on the inverse of cooling rate (right axis). The continuous grey; and red and blue lines are VFT fits to $\tau$ and $q_c$ dependent $T_f$, respectively, with: $D^* = 9.8; T_0 = 311 \text{ K}$ for Au$_{49}$Cu$_{26.9}$Si$_{16.3}$Ag$_{5.5}$Pd$_{2.3}$ at.%; and $D^* = 7.4; T_0 = 426 \text{ K}$ for Pt$_{57.5}$Cu$_{14.7}$Ni$_{5.3}$P$_{22.5}$ at.%. The dashed black lines are Arrhenius fits of vitrification kinetics in the low $T_f$ regime. The insets show the inverse of the cooling rate as a function of the equivalent length at the indicated $T_f$. (c) $T_f$ depression with respect to the $T_f$ of bulky samples as a function of $q_c$ and $l_{eq}$ for both investigated glasses. (d) Schematic representation of the FVHD model where, at a given temperature, a system can be, depending on its size, at equilibrium, vitrifying or glassy.
amorphous sample, that is, avoiding crystallization\(^1\). Interestingly, when the distance of \(T_f\) from the bulk value is considered, as shown in panel (c) of Fig. 3, the two investigated metallic glass-formers exhibit the same size and cooling rate dependence.

Both glasses exhibit similar behavior in terms of \(T_f\) reduction. However, it is worth pointing out that a qualitative difference between the calorimetric response of these two glasses exists. In the Au\(_{49}\)Cu\(_{26.9}\)Si\(_{16.3}\)Ag\(_{5.5}\)Pd\(_{2.3}\) at.% metallic glass, the presence of non-\(\alpha\) fast mechanisms of equilibration reflects on the presence of pronounced low temperature excess endotherm, whose intensity increases with decreasing the cooling rate and the sample size (see Fig. 2, upper panels). An analogous phenomenology has been documented in a wide variety of glasses, including metals\(^{44-46}\), plastic crystals\(^{47}\), polymers\(^{48-51}\), glucose\(^{52}\) and phase change materials\(^{53}\), mainly when aged for prolonged times at temperatures way below \(T_g\). Its presence is intimately linked to the fast mechanism of relaxation assisting glass equilibration at low temperatures, where the \(\alpha\) relaxation acquires experimentally unfeasible time scales. In the case of the Pt\(_{57.5}\)Cu\(_{14.7}\)Ni\(_{5.3}\)P\(_{22.5}\) at.% glass-former, the low temperature excess endotherm can also be detected if the specific heat in excess to the high cooling rate reference, \(c_{p,ex}\) is shown (see Supplementary Information). However, its intensity appears to be considerably smaller than in the case of the Au\(_{49}\)Cu\(_{26.9}\)Si\(_{16.3}\)Ag\(_{5.5}\)Pd\(_{2.3}\) at.% glass-former suggesting that this only accounts for a part of the fast mechanism of relaxation and most of the calorimetric signature of non-\(\alpha\) mechanisms is convoluted with the \(\alpha\) relaxation, a behavior analogous to those of glasses aged not too far below \(T_g\)\(^{54,55}\).

\(^1\)At lower rates we observed a decrease of the \(c_p\) step at the glass transition indicating partial crystallization. In this case, the corresponding data were not used in Fig. 3.
Discussion

The glass transition can be seen from the perspective of the characterization of the linear response in terms atomic/molecular motions caused by spontaneous fluctuations or that of unveiling the kinetic pathway transforming the supercooled liquid into a glass. Though related, these two aspects are conceptually different as the former deals with the unperturbed glass at equilibrium, whereas vitrification entails the kinetic transformation resulting from a large non-linear perturbation, in this case a temperature ramp. Exploiting the capabilities of FSC permitted us to attain insights on both aspects in metallic glasses and their dependence on sample size. The sample size independence of atomic mobility associated to the $\alpha$ relaxation is expected considering that the length scale of the $\alpha$ relaxation never exceeds several nanometers. This result is in line with those obtained in polymeric glass formers for sizes of several micrometers. As a result of the limited size of the $\alpha$ relaxation, modifications of dynamics, if any, are observed for sample size of the order of nanometers, which is by orders of magnitude smaller than the here considered sample sizes.

Vitrification kinetics, even for the largest samples, deviates from the behavior of the $\alpha$ relaxation, an aspect already evidenced and discussed in the Au$_{49}$Cu$_{26.9}$Si$_{16.3}$Ag$_{5.5}$Pd$_{2.3}$ at.% bulk glass-former. In this context, the role of equilibration mechanisms beyond the $\alpha$ relaxation has been demonstrated. In the present work, we have shown that fast non-$\alpha$ equilibration mechanisms convey metallic glass-formers to increasingly smaller $T_f$ when the sample size is decreased. Importantly, this takes place at sample length scales in the micrometer range, an unprecedented result in metallic glasses, and is magnified at increasingly lower cooling rates. Furthermore, it
is worth pointing out that, while vitrification at high cooling rates is size-independent and completely coupled to the $\alpha$ relaxation with VFT temperature dependence, size effects appear to be of importance where fast non-$\alpha$ equilibration mechanisms with mild temperature dependence play the major role in assisting vitrification.

For the very same reason that spontaneous fluctuations could be perturbed at length scales way shorter than the ones explored in the present study, the origin of the large $T_f$ depression observed in increasingly smaller samples but always larger than 1 $\mu$m must be sought on physical grounds where an additional size-dependent order parameter is introduced beyond the role of atomic mobility. In a completely general framework, the cooling rate dependent fictive temperature varies as a result of temperature dependent relaxation time — in this case of fast relaxation processes — and geometric factors, included in a function $g(l_{eq})$: $q_c^{-1} = g(l_{eq})\tau$, where $q_c$ is the applied cooling rate and $\tau$ the relaxation time. This is a generalization of the so-called Frenkel-Kobeko-Reiner relation connecting vitrification to dynamics\textsuperscript{2,18}, whose physical ground stands on the Onsager’s regression hypothesis\textsuperscript{58}. The latter states that the macroscopic kinetic transformation of a non-equilibrium system obeys the same laws of atomic dynamics in equilibrium conditions, that is, the spontaneous fluctuations in the system. The connection between the kinetic transformation taking place in glass aging and spontaneous fluctuations has been recently demonstrated\textsuperscript{59}. In the following, we provide strong arguments indicating that the underlying physics behind the function $g(l_{eq})$ can be suitably captured by the free volume holes diffusion (FVHD) model.

The idea that glass equilibration can be assisted by diffusion of free volume holes towards a
free interface and their removal to the outer world was already proposed by Alfrey et al.\textsuperscript{60} and Curro et al.\textsuperscript{61}. While diffusion is of no relevance for bulk glasses, recently, the FVHD model has been revitalized to account for accelerated glass equilibration in polymer films\textsuperscript{62–65} and nanocomposites\textsuperscript{66}. Diffusion of free volume holes was directly visualized in the devitrification of vapor deposited colloidal glasses\textsuperscript{36}. Within the FVHD model, time dependent Fickian diffusion of free volume holes in the glass is described by:

\[
\langle x^2 \rangle = 2Dt
\]  

(1)

where \( \langle x^2 \rangle \) is the mean squared displacement (MSD) and \( D \) the diffusion coefficient. The latter is related to atomic motion in the glass and, therefore, is size-independent being directly related to \( \tau \), via the (fractional) Stokes-Einstein and the Maxwell relations\textsuperscript{67}. Here, it is worth pointing that eq. 1 has been written for the case of one dimensional diffusion, which, strictly speaking, is valid only for films. However, considering that the size of free volume holes is orders of magnitude smaller than the radius of curvature of spheres studied by us, the film approximation can be considered valid for all our samples.

Vitrification takes place on cooling at a given rate, \( q_c \), when the farthest free volume holes from the free interface, located at \( l_{eq}/2 \) from the interface, is only able to displace at such interface without being expelled out of it. This scenario is schematically depicted in panel (d) of Fig. 3, where the vitrifying system is presented in the middle sketch. The same panel shows how, in a
system with smaller size (left sketch in panel (d) of Fig. 3) at the same temperature, the MSD is large enough to maintain equilibrium. The opposite holds for a system with larger size (right sketch in panel (d) of Fig. 3), where, at the same temperature, free volume holes are unable to diffuse out of the free interface, thereby making the system glassy. In the conditions at which the farthest free volume is just able to reach the free interface (middle sketch of panel (d) of Fig. 3), eq. 1 can be re-written as:

\[
\left(\frac{l_{eq}}{2}\right)^2 \sim 2D(T_g)q_c^{-1}
\]

or equivalently:

\[
\log q_c^{-1} \sim 2\log\left(\frac{l_{eq}}{2}\right) - \log 2D(T_g)
\]

To test the validity of the FVHD model via eq. 3, we have considered the cooling rate providing a fixed \( T_f \) at different \( l_{eq} \) in the regime where fast non-\( \alpha \) mechanisms of equilibration dominate. This was \( T_f = 370 \) and 500 K for Au\(_{49}\)Cu\(_{26.5}\)Si\(_{16.3}\)Ag\(_{5.5}\)Pd\(_{2.3}\) at.\% and Pt\(_{57.5}\)Cu\(_{14.7}\)Ni\(_{5.3}\)P\(_{22.5}\) at.\%, respectively. An identical outcome emerges choosing different \( T_f \) values in the fast non-\( \alpha \) mechanism regime. The result of this analysis is presented in the insets of Fig. 3, panels (a) and (b), where the logarithm of the inverse of the cooling rate is plotted as a function of the logarithm of \( l_{eq} \). As can be observed, \( q_c^{-1} \) varies with the square of \( l_{eq} \), which perfectly fulfils the prediction of eq. 3.
3, thereby validating the hypothesis of FVHD driven vitrification. Further corroboration emerges from results of Au$_{49}$Cu$_{26.9}$Si$_{16.3}$Ag$_{5.5}$Pd$_{2.3}$ at.% samples with identical $l_{eq}$ but different geometry. The two samples exhibits identical cooling rate dependent $T_f$ in agreement with the predictions of the FVHD model (see Supplementary Information).

The presence of non-$\alpha$ fast mechanisms of equilibration requires the search for the underlying molecular process. Apart from standard secondary relaxation processes$^{21,68,69}$, recent efforts have stressed on the presence of liquid-like zones deep in the glassy state where the $\alpha$ relaxation is of no relevance$^{70}$. These may be of importance in the vitrification process delaying to lower temperatures the transformation from liquid into a glass with respect to expectations only accounting for the $\alpha$ relaxation. The structural relevance of liquid-like moieties is reflected in the presence of shear transformation zones (STZ)$^{71,72}$, where the presence of low energy barriers allows flow even deep in the glassy state. Very recently, Napolitano and co-workers$^{22}$ have identified a slow Arrhenius process (SAP), bearing potential in the kinetics of equilibration of different phenomena in amorphous materials, including glass equilibration. They identified an intimate relation between SAP activation energy and the material’s $T_g$. Data shown on Fig. 3, panels (a) and (b), allows extracting the activation energy of the fast mechanisms of vitrification via the Arrhenius equation: $\log q_c^{-1} = \log q_{c0}^{-1} \exp(E_a/kT)$, shown as dashed lines. The resulting activation energies are: $E_a = 75 \pm 5$ kJ/mol and $E_a = 180 \pm 10$ kJ/mol for Au$_{49}$Cu$_{26.9}$Si$_{16.3}$Ag$_{5.5}$Pd$_{2.3}$ at.% and Pt$_{57.5}$Cu$_{14.7}$Ni$_{5.3}$P$_{22.5}$ at.%, respectively. These values are compatible with the expected activation energies of the SAP for the two glasses considering $T_g = 372$ K and $T_g = 505$ K for Au$_{49}$Cu$_{26.9}$Si$_{16.3}$Ag$_{5.5}$Pd$_{2.3}$ at.% and Pt$_{57.5}$Cu$_{14.7}$Ni$_{5.3}$P$_{22.5}$ at.%, respectively (see Fig. 3 of Ref.
This outcome makes the SAP a suitable candidate as the atomic mechanism assisting vitrification at low cooling rates. On more theoretical frameworks, the presence of different equilibration mechanisms can be derived on the base of the self-consistent Langevin equation and the random first order transition (RFOT) theory.

The size dependent $T_f$ depression underlines the ability of small samples to maintain and reach equilibrium faster when subjected to a large non-linear stimulus, in this case a temperature ramp. However, this can be extended to other types of stimuli, including mechanical stress. It has been observed that the propensity for shear localization in MGs decreases with decreasing sample size. The structural disorder created by STZ can be effectively equilibrated in smaller samples resulting in more homogeneous-like deformation. Hence, the increasing ductility of metallic glasses when the sample size is reduced to microns is naturally explained by the ability of these small samples to promptly respond to a non-linear mechanical stimulus. Here, it is noteworthy that — despite the low $T_f$ attained, indicating strong thermodynamic stability — the ability to respond promptly to a non-linear external stimulus makes small samples kinetically unstable. Hence, the criterion on glass ductility exclusively based on the $T_f$ value requires refinement to account for the glass size dependent kinetic stability, that is, how this low $T_f$ has been achieved.

As a final important observation, it is worth of remark that the smallest samples of both investigated metallic glasses attain a thermodynamic state with $T_f$ 40 K lower than that of the corresponding bulk material at cooling rate of the order of 1 K/s, corresponding to observation time scales in the order of seconds. This underlines the attainment of remarkably low energies, which,
in bulk glasses, would be reached only after prolonged natural aging\textsuperscript{48,55,81,82}. Hence, one can expect that aging under appropriate conditions, where the observation time scales can be enlarged at wish significantly above a few seconds, can be used to create very low energy glassy states in micron size samples, otherwise hardly attainable in bulk glasses, and bearing potential to convey insights on issues of extraordinary importance, such as the existence of the ideal glass\textsuperscript{50,83–85}.

**Methods**

The gold-based metallic glass, with composition Au\textsubscript{49}Cu\textsubscript{26.9}Si\textsubscript{16.3}Ag\textsubscript{5.5}Pd\textsubscript{2.3} at.% was produced as-spun ribbon of 7 ± 1 \(\mu\)m of thickness, prepared by a procedure described already elsewhere\textsuperscript{43}. Nanoneedles of a Pt-based metallic glass, with composition Pt\textsubscript{57.5}Cu\textsubscript{14.7}Ni\textsubscript{5.3}P\textsubscript{22.5} at.%, were obtained according to the procedure described in refs.\textsuperscript{11,39}. For fast scanning calorimetry (FSC) measurements, five specimens of different size were obtained by manually cutting either a ribbon or a needle under an optical microscope. Cutting from the tip of the nanoneedles facilitated the procedure of obtaining the smaller and smaller samples for the Pt-based glass. The masses of the samples ranged from 3 to 2000 ng.

The morphology of the sample was assessed by scanning electron microscopy (SEM) performed directly on the FSC chips. We used a Hitachi TM3000 Tabletop Microscope for the Au-based samples and a Zeiss Sigma VP (secondary electron mode) for the Pt-based samples. We determined the characteristic lengths of the Flash DSC specimens, in terms of the ratio between sample volume and free surface area. This metric is independent of the sample geometry and is the
relevant parameter for the application of the FVHD model. SEM micrographs of all of the used specimens are shown in Fig. 4. The observed sample geometry was naturally obtained allowing the material to flow repeatedly heating the sample on the chip-sensor prior to the SEM analysis above the melting temperature. The sample geometry highly depends on the composition of the specimen and its wetting behavior with the substrate underneath.

The mass and geometrical parameters of each specimen are listed in Supplementary Table 1 and they are determined as follows. We first estimated the mass of the sample from the heat flow rate step, $\Delta(HF)$, at a defined temperature in proximity of the glass transition, i.e., 420 K and 520 K for Au and Pt based metallic glasses, respectively. From the knowledge of the specific heat, $c_p$, from conventional calorimetry, we determined the samples mass as: $m = \Delta(HF)/(c_pq_H)$, where $q_H$ is the heating rate of the experiment. The volume of the specimen, $V$, was determined from the
ratio of the estimated mass of the specimen and the calculated density of the metallic glass.

The sample free surface, $A$, was estimated in two different ways, depending on the geometry of the sample. For the Au-based specimens molten on ultra fast sensors (UFS) and employed in the Flash DSC 1, a film-like geometry was obtained, revealing a complete wetting behavior of this alloy with the substrate of the active area of this sensor, made of aluminium. The free surface was straightforwardly determined from SEM micrographs. The Pt-based specimens were deposited on high-temperature sensors (HTS), suitable for the Flash DSC 2+ analyses. The active area of these sensors consists of a membrane made of silicon nitride. In this case the wetting of the liquid specimen with the substrate was hindered and a spherical geometry was obtained. In this case, the surface area was estimated by measuring the diameter of the sphere. As said above, the Au$_{49}$Cu$_{26.9}$Si$_{16.3}$Ag$_{5.5}$Pd$_{2.3}$ at.\% composition was mostly characterized using the Flash DSC 1 and UFS sensors, whereas the Pt$_{57.5}$Cu$_{14.7}$Ni$_{5.3}$P$_{22.5}$ at.\% composition using the Flash DSC 2+ using HTS sensors. However, one sample of Au$_{49}$Cu$_{26.9}$Si$_{16.3}$Ag$_{5.5}$Pd$_{2.3}$ at.\% was also characterized in the Flash DSC 2+ using a HTS sensor. This specimen after deposition and melting on the HTS sensor did not show complete wetting behavior and resulted in a sphere-like specimen bearing irregular shape (see Supplementary Information).

Different fast scanning devices and sensors were used for calorimetric experiments. Flash DSC 1, operating between 173 and 723 K was used to characterize the Au$_{49}$Cu$_{26.9}$Si$_{16.3}$Ag$_{5.5}$Pd$_{2.3}$ at.\% glass-former. One sample of this glass-former is also investigated using the Flash DSC 2+ (see Supplementary Information for details). The Pt$_{57.5}$Cu$_{14.7}$Ni$_{5.3}$P$_{22.5}$ at.\% glass-former is analyzed
exclusively with the flash DSC 2+ with maximum operating temperature of 973 K. The samples were inserted manually onto the active area of the sensors using a optical microscope and a single brash hair. Flash DSC 1 was purged with nitrogen, whereas Flash DSC 2+ with both nitrogen and argon gas at a flow rate of 20 ml/min. Temperature calibration was performed with indium standard deposited on the reference area. Prior to experiments, samples were stabilized onto the sensor by means of a standard pre-treatment that included melting at 723 K for \( \text{Au}_{49}\text{Cu}_{26.9}\text{Si}_{16.3}\text{Ag}_{5.5}\text{Pd}_{2.3} \) at.% or 973 K for \( \text{Pt}_{57.5}\text{Cu}_{14.7}\text{Ni}_{5.3}\text{P}_{22.5} \) at.% , that is, above the alloys melting temperatures, i.e., \( T_m^{\text{Au}_{49}} = 673 \) K and \( T_m^{\text{Pt}_{57.5}} = 873 \) K, respectively. After the melting step, it followed a rapid cooling with constant cooling rate \( q_c = 5000 \) K s\(^{-1}\) down to room temperature.

The kinetics of vitrification was assessed at cooling rates between 0.55 and 3000 K s\(^{-1}\) for \( \text{Au}_{49}\text{Cu}_{26.9}\text{Si}_{16.3}\text{Ag}_{5.5}\text{Pd}_{2.3} \) at.% and between 0.2 and 5000 K\(^{-1}\) for \( \text{Pt}_{57.5}\text{Cu}_{14.7}\text{Ni}_{5.3}\text{P}_{22.5} \) at.% . To avoid crystallization, samples were melted above the liquidus temperature and quenched at 5000 K s\(^{-1}\) down to 443 K for \( \text{Au}_{49}\text{Cu}_{26.9}\text{Si}_{16.3}\text{Ag}_{5.5}\text{Pd}_{2.3} \) at.% and 553 K for \( \text{Pt}_{57.5}\text{Cu}_{14.7}\text{Ni}_{5.3}\text{P}_{22.5} \) at.% . Subsequently variable cooling rates were applied down to 183 K. The heating scan was applied with heating rates between 100 and 5000 Ks\(^{-1}\), depending on the sample mass. The optimal heating rate for each sample has been chosen as a compromise between maximizing the signal to noise ratio and minimizing the thermal lag. This procedure required running identical trial tests on a few samples of different size. The fictive temperature, \( T_f \), was calculated via the Moynihan method\(^{86}\) (see Supplementary Information for details).

Step response analyses, consisting of up-jumps followed by isotherms, from glassy to the
liquid state, was used to assess the atomic mobility. Two main step protocols were used, a first consisted of an up-jump of 2 K with a heating rate of 2000 K s$^{-1}$ followed by a 0.05 s isotherm, that is, a base frequency of 20 Hz, and a second with up-jumps of 2 K at 200 K s$^{-1}$ and 1 s isotherms to assess frequency response with a base frequency of 1 Hz. The frequency dependent complex specific heat, $c_p^*(\omega)$, was calculated by Sliding Fast Fourier Transformation (SFFT) of the heat flow rate and instantaneous heating rate:

$$c_p^*(\omega) = \frac{\int_0^{t_p} HF(t)e^{-i\omega t}dt}{\int_0^{t_p} q(t)e^{-i\omega t}dt}$$

which was repeated for each period of oscillation $t_p$. Accessing higher harmonics allows assessing the complex specific heat frequency response from 1 to 150 Hz for Flash DSC 1 or up to 500 Hz in the case of Flash DSC 2+. The temperature dependent relaxation time, $\tau = 2\pi/\omega$ is determined at the inflection point of $c_p'$.

**Data availability** The datasets generated during and/or analysed during the current study are available from the corresponding authors on reasonable request.

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