Pulling Metallic Glasses Ductile

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Abstract:
A major shortcoming of most known bulk metallic glasses (BMGs) is that they lack sufficient ductility, or toughness, when fabricated under conditions resulting in bulk glass formation. To address this, processing techniques to improve ductility that mechanically affect the glass have been developed, however it remains unclear for which BMG formers they work, and by how much. We show here that, instead of manipulating the glass state, an applied strain rate can excite the liquid, and simultaneous cooling results in freezing of the excited liquid into a glass with a higher fictive temperature. Microscopically, straining causes the structure to dilate, hence “pulling” the structure energetically up the potential energy landscape. Upon further cooling, the resulting excited liquid freezes into an excited glass that exhibits enhanced ductility. We use Zr₄₄Ti₁₁Cu₁₀Ni₁₀Be₂₅ to demonstrate how pulling BMGs through this excited liquid cooling methods can lead to a tripling of the bending ductility.
**Introduction:**

When a metallic glass-forming liquid is cooled, its structure continuously reconfigures into new temperature-dependent metastable equilibrium structures. Such reconfiguration, referred to as structural relaxation, proceeds with a characteristic time, $\tau_{\text{rel}}$, that rapidly increases with decreasing temperature. Reconfiguration occurs as long as the required time scale for relaxation exceeds the available time, which is usually set by the cooling rate, $R$; $\tau_{\text{cool}} = 1/R$. However, at a certain temperature, $T_f$, usually referred to as the fictive temperature or glass transition temperature upon cooling, the metastable liquid can no longer find its metastable equilibrium and freezes into a glass. For metallic glasses, it has been generally observed that higher fictive temperatures result in higher ductility of the corresponding amorphous structure.\(^1\)-\(^6\)

Realizing a higher $T_f$, and hence a ductile state in a glass upon cooling, requires either a slower relaxation process or faster cooling. As the relaxation process of a BMG-forming liquid is an alloy-specific and intrinsic property, only the cooling rate can act as a tool to enhance ductility. As a consequence, ductile states can generally only be realized in thin and simple geometries where sufficiently high cooling rates can be achieved;\(^5\) most BMGs in bulk form lack ductility or fracture toughness.\(^7\)-\(^9\)

Recognizing such limitations in realizing a ductile state under BMG forming conditions has led to the development of processing strategies to enhance ductility after the glass has already been formed. Such strategies are based on mechanical means,\(^10\) and include irradiation,\(^11\)-\(^15\) static loading,\(^16\)-\(^20\) cyclic loading,\(^21\) shot peening,\(^22\) rolling,\(^23\) twin roll casting,\(^24\) thermal cycling,\(^25\)-\(^28\) and severe plastic deformation.\(^29\),\(^30\) A summary of previous results can be found in the supplementary material in table 1. Among methods for addressing the glass are some that offer practical techniques to enhance ductility in BMG-forming alloys.\(^25\) However, it is unclear for which BMGs these technique may lead to rejuvenation or relaxation, and hence either a more ductile or brittle behavior, respectively.\(^27\) Beyond cooling rate, other strategies that directly affect the liquid prior to glass formation have been explored, but remain inconclusive.\(^31\)

Here, during cooling, we strain the supercooled liquid BMG former. The resulting excited liquid originates from the evolving competition between structural relaxation and strain rejuvenation.
Upon freezing into a glass, the temperature at which the excited liquid state has been resumed is the representative fictive temperature of the resulting excited glass. The level to which straining enhances the fictive temperature depends on the differences between the time scales set by the strain rate, which increases the potential energy, and the time scale set by structural relaxation, which decreases the potential energy. Excess fictive temperature is reflected in an increase in ductility, which we measure in bending.

**Results:**

Initially amorphous Zr$_{44}$Ti$_{11}$Ni$_{10}$Cu$_{10}$Be$_{25}$ rods of ~1.8 mm in diameter are heated to a temperature above the calorimetric glass transition temperature of ~$T_g + 80$ K. The sample is then air-cooled whilst simultaneously applying a load of 1-1000 N to rapidly strain the sample. By varying the load, the strain rate can be manipulated (Fig. 1). The resulting decreasing cross section of the deforming sample and the strong temperature dependence of the viscosity together control the evolution of temperature, as well as the strain-rate profile (Fig. 1d). As the cross section of the sample continuously decreases, the cooling rate continuously increases (at least for $T > T_g$). Strain rate, under constant applied force, as a function of temperature, is controlled by the temperature or time dependent cross-sectional area, and by the temperature-dependent viscosity. The later can be approximated with a Vogel-Fulcher-Tammann (VFT) temperature dependence, hence exponentially increasing with decreasing temperature. Qualitatively, $\gamma(T)$ exhibits a peak with values of several hundred strain per second before decreasing again.
Figure 1. Experimental realization of excited liquid cooling. a) Induction heating is used to heat a BMG rod to a desired temperature in the supercooled liquid region. b) A constant force, which can vary between 1 and 1000 g is applied to strain the sample. Upon straining, the sample is air cooled with a varying cooling rate ranging ~10-100 K/s. The variation of the cooling rate originates from the decreasing diameter of the sample upon straining from initially ~1.8 mm to a final ~ 0.1 mm. Strain γ is calculated from the sample’s initial length, L₀, and length at time, L(t), by γ(t) = ((L(t) - L₀)/L₀) * 100. c) Snap shots of the deforming BMG in its supercooled liquid state. d) A typical time evolution of temperature and strain. Temperature evolution is estimated assuming convective air cooling and estimated through a lumped-capacitance model, which gives T(t) = Tₐₙ₉ + (T₀ − Tₐₙ₉)e⁻ᵗ/τ, Tₐₙ₉: room temperature, T₀: initial temperature of the sample, τ: time variable of the system, defined by τ = mc/(hA); m: mass of the sample, c: specific heat capacity, h: heat transfer coefficient, A: heat transfer surface area (see supplementary material).
The samples which were processed according to the simultaneous cooling and straining processing protocol (Fig. 1) were subsequently characterized to determine their ductility (Fig. 2). We choose to use a bending characterization to determine the BMG samples’ ductility. BMGs exhibit typically no ductility in tension,\(^8\) and ductility measurements in compression are often overshadowed by misalignment and confinement effects.\(^{32}\) Hardness and modulus trends have been associated with ductility trends and used for experimental convenience; however, they offer at best indirect information. Most reliable quantification of ductile vs. brittle behavior can be achieved through fracture toughness measurements.\(^{33}\) Because those measurements are unachievable due to the samples’ geometry after pulling, we carried out bending experiments. It has been shown that some BMGs, including the Zr\(_{44}\)Ti\(_{11}\)Ni\(_{10}\)Cu\(_{10}\)Be\(_{25}\) alloy considered here, exhibit a well-defined and characteristic bending ductility in geometries where their thickness is below \(\sim 1\) mm.\(^{34-36}\) As the absolute value of the bending ductility is a function of the samples’ thickness,\(^{34}\) only samples with similar thickness should be compared.

A summary of the bending characterization of the variously strained BMG samples is shown in Fig. 2. The bending fracture strain, \(\varepsilon_F^B\), increases with an increased experimental strain rate. For the same thickness of 100 microns, the as-cast Zr\(_{44}\)Ti\(_{11}\)Ni\(_{10}\)Cu\(_{10}\)Be\(_{25}\) exhibits an average \(\varepsilon_F^B = 6\%\). With an increasing strain rate, \(\varepsilon_F^B\) increases from \(\sim 4\%\) for \(\dot{\gamma} \sim 40\) s\(^{-1}\) to a maximum value of \(\varepsilon_F^B = 16\%\) for \(\dot{\gamma} = 890\) s\(^{-1}\). In some cases, even higher plastic bending strains of up to \(\varepsilon_F^B \sim 20\%\) are observed. We contribute the large scatter in the resulting bending fracture strain to the experimental difficulty of our setup in applying strain rate and cooling rate in a controlled synchronized way.

It is a challenge to isolate the effect of the applied strain rate from other effects, such as the cooling rate.\(^{31}\) To do so, we annealed one half of each wire at \(T_g + 60\) K for 180 sec (\(\sim 500\) times the relaxation time\(^{37}\)) and subsequently applied the same air-cooling protocol as was applied to the pulled wires. The history of the straining is thereby erased in the annealed wires while maintaining the same cooling profile as in the as-pulled samples. Subtracting the property values of the annealed samples from those of the as-pulled samples allows us to isolate the effect of strain rate on the ductility.
The samples that have been annealed after the pulling process exhibit a slightly higher but very similar $\varepsilon_F^B \sim 7\%$ compared to the as-cast material of $\sim 6\%$. This suggests that the significant enhancement in $\varepsilon_F^B$ measured in the as-pulled samples is predominantly due to the applied strain rate.

**Figure 2. Characterization of the effect of excited liquid cooling on Zr$_{44}$Ti$_{11}$Ni$_{10}$Cu$_{10}$Be$_{25}$ BMG bending ductility.**

a) Wires are mechanically characterized through bending around cylinders of successively small diameter until fracture.  
b) To separate the effects of excited liquid cooling from the fast cooling rate of the small geometry, wires are separated into two, with one segment characterized as pulled and the other annealed.  
c) As-pulled wires show a positive correlation between maximum strain rate of the pulling process and bending fracture strain. Annealed wires lose the added ductility to approximately the value of the as-cast sample. However, as the final wire thickness decreases slightly with increasing strain rate, a small positive correlation between bending fracture strain and applied strain rate is present in the annealed wires, due to geometric effects in determining bending ductility. $^{34}$
Thermal characterization was also carried out on samples processed through excited liquid cooling (Fig. 3). Specifically, we consider the enthalpy of relaxation, $\Delta H_{\text{rel}}$, which has been used as a thermodynamic measure to quantify the degree of rejuvenation.\textsuperscript{27,38-41} For the strained samples, an increase in $\Delta H_{\text{rel}}$ compared to the annealed sample is present (Fig. 3a). Specifically, $\Delta H_{\text{rel}}$ increases from 0.21 kJ/mol for $\dot{\gamma} = 215$ s$^{-1}$ to 0.81 kJ/mol for the highest $\dot{\gamma} = 830$ s$^{-1}$ (Fig. 3b). The maximum absolute value of $\Delta H_{\text{rel}}$ of 0.81 kJ/mol is comparable to previously reported sub $T_g$ mechanical rejuvenation techniques, including high pressure torsion and notched triaxial strain,\textsuperscript{16,20,42} and is among the highest reported changes in enthalpy of relaxation when compared to the reference sample.

![Thermal Characterization](image)

**Figure 3.** Thermal characterization of Zr$_{44}$Ti$_{11}$Ni$_{10}$Cu$_{10}$Be$_{25}$ BMG processed through excited liquid cooling. a) Thermograms measured with differential scanning calorimetry reveal the thermal signal of the excited liquid cooling. b) The enthalpy of relaxation increases with the increasing strain rate applied during excited liquid cooling.
Discussion:
It has been widely shown that metallic glasses of the same chemistry can have greatly different ductility or fracture toughness. Relative to the BMG’s as-cast structure, ductility or fracture toughness can be reduced or enhanced. This can be achieved through thermal treatments such as the use of different cooling rates, annealing protocols, or mechanical treatments such as quasistatic mechanical loading, plastic deformation, thermal cycling, shot peening, and radiation damage. Whereas thermal treatments enable the liquid BMG former to be affected before it freezes into a glass, within mechanical treatments the glass itself is manipulated. Manipulation of the glass is often inhomogenous, and at the most extreme during treatments that generate shear bands in which the majority of the treatment effects are localized in those shear bands which occupy a very small volume fraction of the sample. The general understanding is that with both thermal and mechanical treatments, the potential energy of the glass can be manipulated. Enhancing the potential energy of a glass structure in the potential energy landscape is equivalent to increasing the fictive temperature of a glass. Further, it has been argued that a high $T_f$ can be generally associated with a larger ductility or fracture toughness. The treatment of excited liquid cooling discussed here directly affects the supercooled liquid.

We argue that the straining of the supercooled liquid is counteracting the relaxation process, preventing the liquid from assuming its metastable equilibrium and hence causing it to assume an excited state (Fig. 4). The kinetic freezing of the (supercooled) liquid BMG former into a glass originates from the competition of the involved time scales. Under cooling conditions without an imposed strain rate, one of the involved time scales is set by the relaxation time, $\tau_{rel}$. This is the temperature dependent time required for the liquid to assume the (meta)stable equilibrium configuration, which continuously changes e.g., with temperature. Widely used to approximate $\tau_{rel}$ is the Vogel-Fulcher-Tammann (VFT) equation: $\tau_{rel} = \tau_0 \exp \left( \frac{D^* T_0}{T - T_0} \right)$ with $T_0$ as the VFT temperature, $D^*$ the VFT fragility parameter, and $\tau_0$ the high temperature limit of the relaxation time. This intrinsic time scale, with its exponential dependence on temperature, has to be compared with the extrinsic time scale set by the processing protocol, $\tau_{cool}$. During a typical
cooling process, $\tau_{\text{cool}}$ is defined by the cooling rate, $R$, and can be described by $\tau_{\text{cool}} = \frac{1}{R}$. At high temperatures, $\tau_{\text{rel}} < \tau_{\text{cool}}$, and the liquid has sufficient time to reconfigure during cooling to its temperature-dependent metastable equilibrium. At lower temperatures $\tau_{\text{rel}} > \tau_{\text{cool}}$, due to the exponential temperature dependence of $\tau_{\text{rel}}$. Hence the liquid can no longer reconfigure into its temperature dependent metastable equilibrium. As a consequence, the liquid falls out of metastable equilibrium at $\tau_{\text{rel}} = \tau_{\text{cool}}$, and freezes into a glass. The temperature, $T_f$, at which this freezing occurs ($\tau_{\text{rel}} = \tau_{\text{cool}}$) is referred to as the fictive temperature or the glass transition temperature upon cooling. As $\tau_{\text{rel}}$ is an intrinsic property of the liquid BMG former, one is left with only $\tau_{\text{cool}}$ as a tool to manipulate $T_f$. A higher cooling rate reduces $\tau_{\text{cool}}$ and hence, results in a glass with a higher fictive temperature (Fig. 4a).

Within the here introduced excited liquid cooling method, a strain is applied during cooling of the liquid BMG former, working against the liquid’s drive to assume a more densely-packed metastable equilibrium with decreasing temperatures. Straining a supercooled liquid BMG former causes it to dilate and loosen its packing, which increases its potential energy in opposition to the relaxation process of decreasing potential energy with decreasing temperature. In order to assign a characteristic time to the straining process, we assume a critical strain of 2%, which results in a characteristic time, $\tau_\dot{\gamma} = \frac{0.02}{\dot{\gamma}}$. Our assumption of 2% strain as a critical value to cause a “significant” structural change is based on previous work where this strain level has been observed to cause shear transformation zones to become unstable, and hence cause a “significant” structural irreversible change. However, it has also been pointed out that “weak” shear transformations occur at a much lower strain levels, however significantly less in number.

When cooling a liquid BMG former under a strain rate, all three characteristic time scales, $\tau_\dot{\gamma}$, $\tau_{\text{rel}}$, and $\tau_{\text{cool}}$ have to be considered (Fig. 4). Following the liquid BMG former upon cooling, it remains in metastable equilibrium down to $T_f^\prime$ (Fig. 4). This is because for $T > T_f^\prime$, the time scales are such that $\tau_{\text{rel}} < \tau_\dot{\gamma} < \tau_{\text{cool}}$. Hence relaxation occurs within the available time. With decreasing temperature, $\tau_{\text{rel}}$ increases and $\tau_{\text{rel}} = \tau_\dot{\gamma}$ at $T = T_f^\prime$. For temperatures below $T_f^\prime$, the liquid can no longer reconfigure to reach its metastable equilibrium before that relaxation
process is disturbed by the strain rate. Hence, the structure of the liquid falls out of metastable equilibrium and resumes an excited structure characterized by $T_f^\gamma$. It is important to emphasize that the BMG is still in a liquid state, meaning that the structure rapidly changes, and these changes take place more rapidly than the available time set by the cooling rate $\tau_{cool}$. This “excited liquid” state which is present between $T_f^\gamma$ and $T_f$ is maintained through a competition between straining, causing the potential energy to increase, and relaxation, which decreases the potential energy. Upon further cooling $\tau_{rel} = \tau_{cool}$ at $T_f$, and the excited liquid is no longer able to reconfigure on the time scale set by the experiments and, as a consequence, freezes into an excited glass. Even though the excited liquid freezes into a glass at $T_f$, its structural state has been established at a higher temperature $T_f^\gamma$, which is the underlying mechanism of the excited liquid cooling method to achieve a ductile glass.

Figure 4. Excited liquid cooling mechanism. a) Illustration of the characteristic time scales involved in the excited liquid cooling mechanisms as a function of temperature. The structural relaxation time, $\tau_{rel}$, increases exponentially with decreasing temperature. A requirement for the excited liquid cooling mechanism is that the time scale set by the strain rate, $\tau_{\gamma} = \frac{0.02}{\gamma}$, is smaller than the available time set by the cooling rate, $\tau_{cool} = \frac{1}{\gamma}$. Upon cooling the liquid BMG former remains in metastable equilibrium for $\tau_{rel} < \tau_{\gamma}$ until $\tau_{rel} = \tau_{\gamma}$. Here, an “excited liquid” state is
maintained through a competition between straining, causing the potential energy to increase, and relaxation, which decreases the potential energy for \( T_f^\dot{\gamma} > T > T_f (\dot{\gamma} = 0) \). When \( \tau_{rel} = \tau_{cool} \), at \( T_f \), the excited liquid can no longer reconfigure on the experimental time scale to maintain its metastable equilibrium and freezes into an excited glass. The structure that freezes into a glass at \( T_f \) is that of the excited liquid with a fictive temperature of \( T_f^\dot{\gamma} \). b,c) The effectiveness of excited liquid cooling is controlled by the relative rates of cooling and straining, inversely related to \( \tau_{cool} \) and \( \tau_{\dot{\gamma}} \). For \( \tau_{cool} - \tau_{\dot{\gamma}} > 0 \), the enhancement of fictive temperature \( T_f^\dot{\gamma} - T_f \) scales with \( \tau_{cool} - \tau_{\dot{\gamma}} \). For \( \tau_{cool} - \tau_{\dot{\gamma}} \leq 0 \), structural rearrangements due to \( \dot{\gamma} \) due not occur sufficiently, and hence do not affect fictive temperature or ductility.

The effect of an applied strain rate in excited liquid cooling on increasing the fictive temperature of the glass (and hence ductility) depends on the relative magnitudes of the characteristic time scales. To increase the fictive temperature through an application of a strain rate, meaning \( T_f^\dot{\gamma} > T_f (\dot{\gamma} = 0) \) requires \( \tau_{\dot{\gamma}} < \tau_{cool} \). If \( \tau_{\dot{\gamma}} > \tau_{cool} \), the time required for structural changes to occur due to straining exceeds the time available during the cooling process and hence, structural changes originating from an applied strain rate do not occur. For example, a strain rate > 2 s\(^{-1}\) is required to enhance the fictive temperature, and thereby also ductility during bulk metallic glass formation at a cooling rate of 100 K/s (\( \tau_{cool} = 10^2 \) s). The effectiveness of \( \dot{\gamma} \) in enhancing fictive temperature scales with \( \tau_{cool} - \tau_{\dot{\gamma}} \) (Fig. 4 b&c). For \( \tau_{cool} - \tau_{\dot{\gamma}} > 0 \), the enhancement of fictive temperature \( T_f^\dot{\gamma} - T_f \) scales with \( \tau_{cool} - \tau_{\dot{\gamma}} \). With a decreasing strain rate (but the same cooling rate) such that \( \tau_{cool} - \tau_{\dot{\gamma}} \leq 0 \), structural rearrangements due to \( \dot{\gamma} \) can no longer significantly happen on the time scale of experiment. Hence, it is only for combinations of strain rates and cooling rates that fulfil \( \tau_{cool} - \tau_{\dot{\gamma}} > 0 \) that excited liquid cooling takes place. The effect on ductility increases with increasing \( \tau_{cool} - \tau_{\dot{\gamma}} \).

We will now discuss the proposed mechanism for excited liquid cooling assumptions. Key to excited liquid cooling is the competition between relaxation and straining. Relaxation is a three-dimensional mechanism where atoms under the action of thermal energy (quantified in
temperature) probe a vast range of structural states. On the other hand, the strain rate applied here is a one-dimensional mechanism. During excited liquid cooling the two effects compete with each other. However, structural relaxation is a more efficient mechanism utilizing all three physical dimensions to decrease potential energy whereas strain rate only accesses one dimension to increase potential energy. This makes a quantitative comparison of both contributions challenging.

Furthermore, in the above discussion on the mechanism of excited liquid cooling, we assumed a constant applied strain rate down to \( T = T_f \). In general, such an assumption is oversimplified. Fundamentally, metallic glasses change their deformation behavior as a function of temperature and strain rate. At high temperatures, they deform in an homogenous fashion, essentially entirely affine, whereas at low temperatures, deformation is highly localized and non-affine. \(^{58}\) To qualitatively represent this dramatic change in behavior as a function of temperature, we assume \( \dot{\gamma} = \text{const} \geq 0 \) as a finite and constant strain rate for \( T > T_f \) and \( \dot{\gamma} = 0 \) for \( T < T_f \). This behavior is however simplified, as the practically realizable changes in \( \dot{\gamma}(T) \) between \( T_i \) and \( T_f \) are less drastic.

It is generally understood that the viscosity in BMG forming liquids for \( T > T_f \) is strain rate-independent. \(^{59,60}\) However, for high strain rates, significant non-Newtonian effects have been observed \(^{61-63}\) which may also take place during excited liquid cooling. In addition, straining of the sample may also generate heat which will affect cooling rate. Considering all this, our model to describe excited liquid cooling under the current assumptions offers an only qualitative description. For a quantitative description, more complicated calculations using more detailed values of evolving process variables would be required.

In order to compare the effectiveness of excited liquid cooling with other BMG rejuvenation methods, we use the enthalpy of relaxation, \( \Delta H_{\text{rel}} \), which has been reported in the majority of publications on rejuvenation techniques (see table 1 in supplementary section). Comparison reveals that excited liquid cooling is among the most effective techniques to enhance the potential energy of the glass, offering a considerable increase in the enthalpy of relaxation through a mechanism directly affecting the liquid. It should be mentioned that comparison by
their effect on mechanical properties is not possible, as the reported studies of the various methods use different properties.

The technological motivation of the various techniques to rejuvenate metallic glasses is to improve mechanical properties. Therefore such methods, including our excited liquid cooling, must be practical in order to be used as a toughening strategy for metallic glass articles. Key to an effective practical usage of the excited liquid cooling method is a sufficiently high strain rate \( \tau_{cool} - \tau_{\gamma} > 0 \) present at temperatures including \( T_f \) and \( T_f' \). The excited liquid must also be able to be frozen into a glass state. It is important to mention that the absolute strain occurring during excited liquid cooling is irrelevant. In the present setup we use such high strains only for experimental convenience. To generate and freeze an excited liquid, only the strain rate over a narrow temperature interval is relevant. This interval is in the vicinity of \( T_f \), where it sets \( T_f' \) and maintains this state until \( T_f \). Such a situation can be realized in several metallic glass fabrication methods (Fig. 5). For example, the pulling used here can be utilized to fabricate ductile metallic glass wires as a final product (Fig. 5a). Similarly, sheets can be produced. For their synthesis, in addition to regular rolling, a subsequent pulling of the escaping sheet is required to establish a simultaneous straining and cooling. If one establishes \( \tau_{cool} - \tau_{\gamma} > 0 \) for temperatures down to \( T_f \), ductile sheets can be fabricated (Fig. 5b). The requirement of \( \tau_{cool} - \tau_{\gamma} > 0 \) for temperatures down to \( T_f \) can also be realized during blow molding, and thereby net-shape complex BMG articles while establishing their ductile state (Fig. 5c). Here, the BMG feedstock is deformed through a gas pressure towards a cold mold. It has been previously determined that once the BMG touches the mold, the strain rate drops essentially instantaneous to zero. If the mold is set to a low temperature, and a temperature gradient between deforming feedstock and mold can established through the separating vacuum, the excited liquid can be rapidly frozen into a glass upon touching the mold, hence BMGs parts can be net-shaped into their ductile state.
Figure 5. BMG processing techniques that can be extended to incorporate excited liquid cooling. a) Wire pulling where the wire ductility is controlled through maximizing $T_f - T_f$. For a given strain rate, $T_f - T_f$ scales with the steepness of the spatial temperature gradient. b) In order to fabricate ductile sheets, excited liquid cooling can be realized through hot-rolling and subsequent pulling of the escaping sheet down a temperature gradient. c) Blow molding against a cold mold results into excited liquid cooling, and hence enables to net-shape BMG articles into their ductile state.

In summary, we show here that an applied strain rate can excite the BMG in its liquid state to a higher potential energy. Microscopically, straining causes the structure to dilate, hence “pulls” the structure energetically up the potential energy landscape. Upon further cooling, the resulting excited liquid freezes into an excited glass that can triple its ductility compared to that of the unstrained material. Based on the requirement for the excited liquid cooling, we identify metallic glass processing techniques that allow us to shape and net-shape metallic glasses into a complex geometry while assuming a ductile state.
**Methods:**

**Sample Preparation:** The amorphous Zr$_{44}$Ti$_{11}$Ni$_{10}$Cu$_{10}$Be$_{25}$ rods of ~1.8 mm in diameter were prepared by copper mold casting. High purity ingots (for all constituent purity higher than 99.99) were arc-melted under argon atmosphere to alloy the constituents. Subsequently, the alloy was reheated to a temperature of ~1000 °C and under an argon gas pressure, forced from the quartz nozzle into a copper mold. Thermal analysis on some of the rods reveal the typical thermogram for a fully amorphous sample which was cooled with a rate ~500 K/sec.

**Thermal Analysis:** Thermal analysis was conducted using a TA Q200 differential scanning calorimeter under argon flow with a heating rate of 20 K min$^{-1}$. All samples were heated through crystallization, subsequently cooled, and then heated again with the same heating rate to establish a baseline to be subtracted from the initial heating run. Measurements for the heat of enthalpy were made by finding the area of the curve with respect to the baseline, shown as a dashed line in Fig. 3a.

**Strain Rate:** A sample rod is held from above inside an RF-coil, affixed hanging weight (100 g) and a second weight that is suspended so as to not exert any force on the sample initially (0-10000 g). The RF-coil is turned on, and once the rod deforms sufficiently to lengthen 5 mm due to the 100 g force, the larger weight is released and rapidly strains the sample rod into a wire. Strain rate is determined from video analysis and varied by changing the mass of the second weight. The first processing step with the 100 g weight warrants control over the initial temperature as the deformation to 5 mm is predominately controlled by viscosity, which is highly temperature sensitive. Strain rate is controlled through the use of different weights.
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