

In situ measurements of surface tension-driven shape recovery in a metallic glass

Corinne E. Packard,^a Jan Schroers^b and Christopher A. Schuh^{a,*}

^aDepartment of Materials Science & Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139-4307, USA

^bDepartment of Mechanical Engineering, Yale University, New Haven, CT, USA

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A new technique, involving nanoindentation and in situ scanning probe microscopy at high temperature under an inert atmosphere, is used to study deformation of a Pt-based metallic glass. As temperature is increased into the supercooled liquid regime, impressions made by nanoindentation flatten due to surface tension-driven viscous flow. In situ measurements of shape recovery at various temperatures and times permit an estimation of the apparent activation energy for Newtonian-viscous flow.

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When a metallic glass is heated to a significant fraction of its glass transition temperature ($\sim 0.75 T_g$ or higher), dramatic decreases in strength are observed as deformation delocalizes and diffuse strain accommodation occurs homogeneously throughout the stressed material [1,2]. Increasing the temperature above T_g results in an orders-of-magnitude drop in the viscosity and, as a result, between T_g and the crystallization temperature, i.e. in the supercooled liquid (SCL) regime, metallic glass can be easily molded, extruded, embossed or otherwise formed [3]. Furthermore, an amorphous structure can be maintained through such forming, as long as the material is cooled below the glass transition temperature again before crystallization occurs [4]. The absence of an intrinsic size limitation and the ability to achieve tight molding tolerances using SCL processing makes metallic glass particularly attractive for micro- and nanofabrication of microelectromechanical system (MEMS) devices [5–10].

A recent article [11] explored the response of micro-scale metallic glass features to a thermal excursion above T_g , such as might be experienced during processing. By first forming pyramidal features into the glass by pressing it against a mold in the SCL and subsequently heating the samples without applied pressure, surface tension-driven flattening of the pyramidal features was

observed and quantified [8]. In this letter, we apply a newly developed capability in high-temperature nanoindentation and force scanning microscopy to first impress surface features into a metallic glass (both in the SCL and at lower temperatures) and then measure the process of surface tension-driven shape recovery in situ at high temperatures. We illustrate how this technique not only permits rapid assessment of the major features of deformation and shape recovery on a small specimen, but can also be used to extract quantitative features of these processes; here we assess the activation energy for viscous shape recovery from our in situ measurements.

The material used in this study was $\text{Pt}_{57.5}\text{Cu}_{14.7}\text{Ni}_{5.3}\text{P}_{22.5}$ bulk metallic glass, processed by water quenching from a melt of high-purity feedstock materials under an inert atmosphere and confirmed amorphous in Ref. [12]. The samples were sectioned and mechanically polished using diamond pastes until a mirror surface was achieved. Following surface preparation, the samples were mounted in a custom-made high-temperature nanoindentation system based on the Ubi1 test platform (Hysitron, Inc.) capable of testing at temperatures up to 500 °C while under vacuum to prevent oxidation of the sample surface. Details of the basic apparatus are provided in Ref. [13], with further details on the atmosphere control in Ref. [14]. The indentation chamber was pumped down and purged with argon before evacuating the chamber to a base pressure of 2×10^{-2} Torr for testing. A diamond Berkovich tip was used in all of the experiments.

* Corresponding author. Tel.: +1 617 452 2659; e-mail: schuh@mit.edu

A series of experiments were performed at each of the following temperatures: 25, 176, 227, 240 and 250 °C, which respectively correspond to 0.6, 0.9, 1, 1.02 and 1.04 T/T_g , with the glass transition $T_g \approx 230$ °C. At each temperature, a series of nine indentations was first performed on a 3×3 grid of 5 μm spacing, using a symmetric loading function with a peak load of 10 mN and loading/unloading rates of 10 mN s^{-1} . Approximately 3 min elapsed between indentations, during which time the machine was re-zeroed, the tip was moved to the next position using the piezo scanner and time was allowed for the scanner to settle. Following the set of nine indentations, the indenter tip was rastered over the entire indented area to produce a contact force microscopy image of the residual impressions. Such imaging scans were performed at the test temperature, with a $2 \mu\text{N}$ set-point load at 1 Hz over a $25 \times 25 \mu\text{m}$ square. These experiments were used to make baseline qualitative observations about the shape recovery kinetics of indentations.

A second set of tests was also performed at each temperature to more accurately capture the fine details of the residual impressions and to track the impression shape as a function of time at temperature. In these experiments, an indentation was first performed by loading at 5 mN s^{-1} to a peak load of 5 or 10 mN, followed by unloading at 5 mN s^{-1} to 20% of the peak load for 10 s before complete unloading. The residual impressions were then imaged at a $2 \mu\text{N}$ setpoint load at 1 Hz over a smaller $5 \times 5 \mu\text{m}$ square. Such imaging was conducted at the test temperature, both immediately after the indentation was complete and also 20, 40 and 60 min after the initial scan.

Although the main purpose of this letter is to explore surface tension-driven flow, it is important to first verify that the deformation response measured during indentation conforms to expectations for metallic glasses (e.g. [15–17]). Figure 1 shows representative load–displacement curves acquired at each test temperature. We observed a loss of flow serration with increasing temperature, which is consistent with expectations over

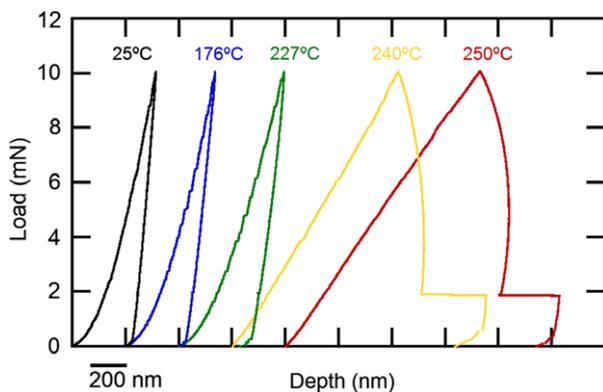


Figure 1. A typical series of load–displacement curves measured on Pt-based metallic glass. Curves are offset for clarity to show the loss of serrated flow as temperature is increased to the glass transition temperature (~ 230 °C), and the sharp decrease upon further temperature increase. As temperatures above T_g are reached, softening of the glass is observed, as well as continued deformation during unloading and creep during the holding segment at 2 mN load.

this range of temperatures [15,16]. We also observed a significant reduction in the pile-up around the impression sites at higher temperatures (not shown). Additionally, the onset of viscous creep flow became evident near and above T_g , as manifested by “noses” in the unloading curves, and displacement accumulation in the 20% unload condition, at which the load was held constant for 10 s. All of these features are consistent with the transition from inhomogeneous flow in discrete shear bands to the delocalized flow characteristic of behavior in the homogeneous deformation regime.

Our in situ imaging of 3×3 grids of identical indentations gave initial qualitative insight on surface tension-driven flow kinetics. At temperatures below T_g , all nine indentations in such a grid appeared identical. However, above T_g a different behavior was observed, as shown in Figure 2 at 250 °C. The arrows in Figure 2 show the sequence in which the indentations were performed, with the first in the upper left corner and the last in the lower right. The last indentations performed in the set of nine are sharper and deeper than the first, which are rounded and shallow; those between show a gradual transition between these extremes. From this image, it is qualitatively clear that the earliest indentations lost their definition by a time-dependent shape recovery process over the time it took for the set of indents to be completed (~ 40 min).

More quantitative data were obtained by imaging individual indentations at a slower scanning rate to track the maximum impression depths. At temperatures below the glass transition, imaging scans revealed negligible changes in the residual impressions even after more than an hour of elapsed time, while at 240 and 250 °C significant recovery was observed on the same timescale.

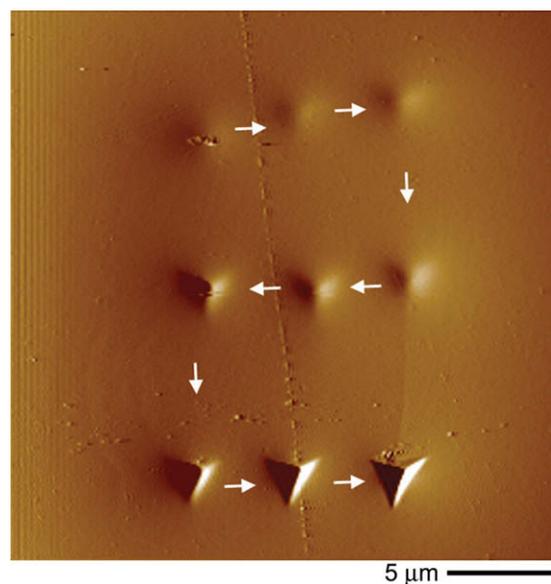


Figure 2. In situ recovery of indentations in a Pt-based glass at 250 °C, as presented in a gradient image of identical indentations performed to a maximum load of 10 mN at ~ 3 min intervals, in the serpentine pattern shown by the white arrows. The final indent in the series (lower right) looks pristine compared to the first indent (upper left), which has almost completely recovered. A linear background subtraction has been applied to the image.

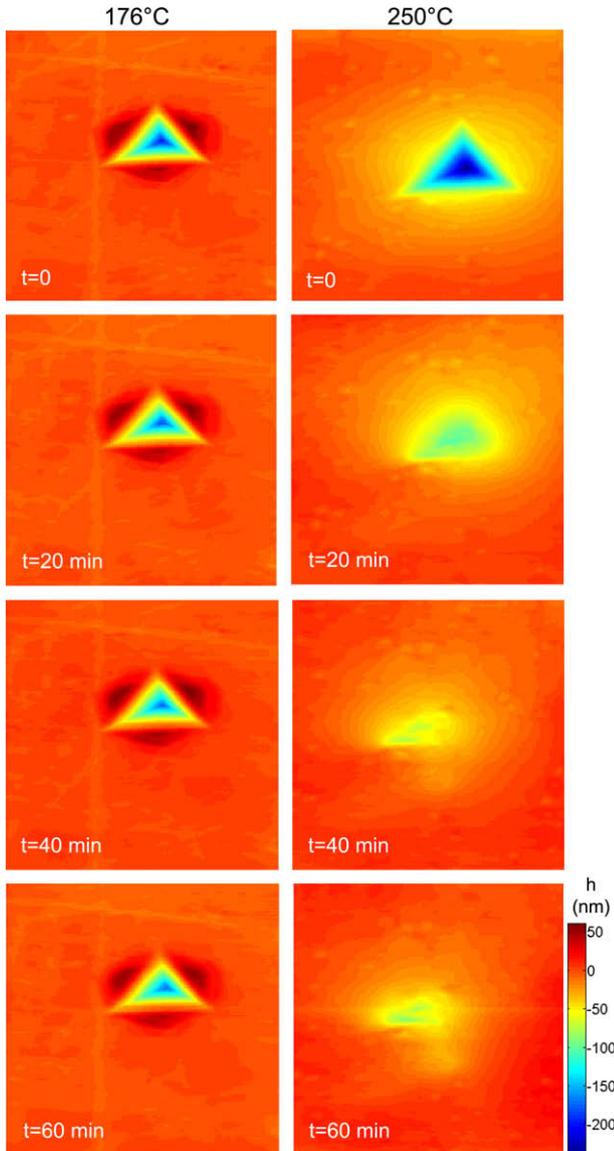


Figure 3. Topographic images of two indentations in the Pt-based metallic glass, imaged at temperature at 20 min intervals. The indentations were performed to a maximum load of 10 mN at 176 and 250 °C, and illustrate relative stability and substantial shape recovery, respectively. Parabolic background subtractions have been applied to each image.

Figure 3 shows a time-series of topographical images of single indentations performed at 176 and 250 °C to illustrate this change in behavior. In addition to shape recovery of the impression, another change was also apparent; though these indents were performed on the same sample, an intrinsic surface roughness of ~ 8 nm is visible in the area around the impression at 176 °C but is no longer present at temperatures above T_g . Such self-smoothing of metallic glass surfaces has been reported previously in Ref. [11].

Figures 4a and b shows the quantitative data from the three temperatures where shape recovery was observed, with impression depths normalized by the height recorded on the first imaging scan (which is assigned $t = 0$). Vertical error bars represent a propagated uncertainty of 10 nm on the initial and instantaneous impression depths, estimated by comparing the residual depth

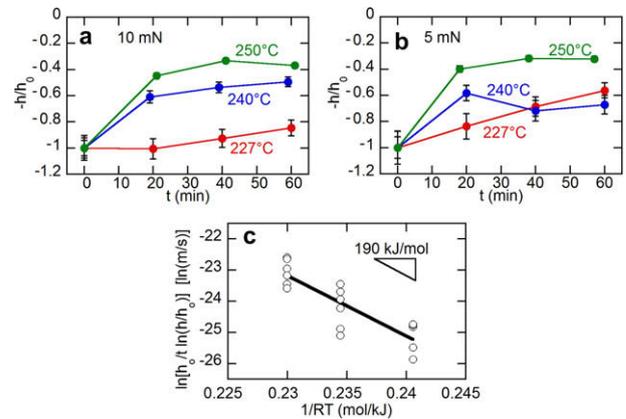


Figure 4. Quantitative data from in situ imaging studies of recovering indentations, showing the change in the maximum impression depth vs. time for peak indentation loads of (a) 5 and (b) 10 mN. In (c) the slope of the curve gives the activation energy for viscous recovery, assuming an Arrhenius form for the viscosity.

from a load–displacement curve to the impression depth obtained by imaging at room temperature, where no shape change occurs in between. Figures 4a and b demonstrate a clear trend of increased flow kinetics with temperature. The data obtained from 5 mN indentations at 250 °C show the greatest recovery, but the trends at lower temperatures are muddled by the increased relative error from using a shallow indentation. A maximum of 60–70% height recovery is observed for the highest temperature after 60 min; in principle, full recovery may be achieved after longer times or at slightly higher temperatures.

At temperatures above 250 °C, we observed crystallization of the specimen after some period of time, as evidenced by (i) loss of creep deformation during indentation and (ii) loss of impression shape recovery afterwards. These results are in line with expectations for this glass [12], which crystallizes in under 2 h when held isothermally at 260 °C. Although we have not shown the data from these tests here, they do permit one important conclusion to be drawn about the results in Figures 2 and 3: it is unlikely that the impression shape recovery we see here is associated with surface diffusion, which would occur at higher temperatures whether or not crystallization had occurred (surface atoms would still retain high mobility despite crystallization). We conclude, therefore, that the shape recovery we see in these experiments is driven by surface tension, and effected by viscous flow facilitated by the drop in viscosity in the SCL regime.

To model Newtonian-viscous shape recovery of metallic glass features, Kumar and Schroers [11] used several approximations to capture the basic scaling features of the process:

$$h = h_0 \exp\left(-\frac{\gamma}{3\eta h_0} t\right) \quad (1)$$

where h is the feature height that begins at a value h_0 , t is time, η is the viscosity and γ is the surface energy. Eq. (1) can be extended further to include temperature dependence through the viscosity, using, for example, an Arrhenius equation for a “strong” glass former [18] or a Vogel–Fulcher–Tammann equation for a “fragile” one [18–21]. Lacking experimental details of the flow

law for the present glass, we take a simple Arrhenius form for the viscosity,

$$\eta = \eta_0 \exp\left(-\frac{Q}{RT}\right) \quad (2)$$

where η_0 is a pre-exponential constant, Q is the apparent activation energy for flow, R is the universal gas constant and T is temperature. By combining Eqs. (1) and (2), a plot taking the form of Figure 4c is suggested as a means of evaluating the apparent activation energy, Q . Though the units on the y -axis are somewhat unconventional, plotting the data in this manner allows extraction of Q from the slope without requiring knowledge of either the constant η_0 or the surface energy, γ . From our data, we estimate an apparent activation energy of $\sim 190 \pm 50 \text{ kJ mol}^{-1}$, which compares well to the range of 80–230 kJ mol^{-1} for the viscous flow of various different metallic glasses as reported by Argon and Kuo [22]. Furthermore, the range of viscosities calculated (10^9 – 10^{10} Pa s) using the fitting constants and an assumed γ of 1 J m^{-2} [11,23] compares well with the results from various glass compositions acquired using more conventional methods [14].

In summary, we have reported a new technique to both deform metallic glass samples and study the kinetics of surface tension-driven shape recovery at elevated temperatures in the SCL regime. Although viscoelastic shape recovery of indentations has been measured at room temperature in other materials [24–26], we believe the present report to be the first in situ contact-mode imaging study to directly observe viscous–plastic shape recovery at high temperatures. The technique is also amenable to quantitative assessment of activation parameters by testing at multiple temperatures; for Newtonian-viscous flow of $\text{Pt}_{57.5}\text{Cu}_{14.7}\text{Ni}_{5.3}\text{P}_{22.5}$ glass, we estimate an activation energy of $\sim 190 \text{ kJ mol}^{-1}$.

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