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SURFACE SELF-HEALING OF METALLIC GLASSES IN THE SUPER-COOLED LIQUID REGION $\Delta T = T_x - T_g$

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Abstract. Many metallic glasses undergo glass transitions at T_g some times up to more than 100K below their crystallisation temperatures T_x. They thus possess a so-called super-cooled liquid region $\Delta T = T_x - T_g$ to which they can be heated in principle without crystallization. This temperature region has been used for shaping and joining metallic glasses or for writing motifs on them. The flow stress σ_{flow} required to achieve such shape changes in the ΔT temperature range depends on the viscosity η which is strongly temperature dependent near T_g.

Here we report microscopic shape changes occurring under no applied stress simply due to surface tension γ. Surfaces of melt-spun metallic glasses carry traces of shape instabilities. These surface defects are usually deep pockets of gas trapped on the cooling substrate (wheel) side and very thin (few microns) elongated "wave-like" defects on the free surface side.

Pd-based melt-spun ribbons were heated in protective atmosphere to 583K which is just above T_g and the free surfaces photographed after different times. Surface defects were found to disappear or "self-heal" in the ΔT temperature range. The results are discussed in terms of the experimental self-deformation rates and viscosity.

1. INTRODUCTION

Metallic glasses often have corrosion and wear resistant surfaces while they are usually of eutectic compositions with low melting temperatures T_m which facilitates fabrication and processing. Many metallic glasses undergo glass transitions at T_g with $T_g/T_m > 0.55$ and T_g a few degrees to more than 100K below their crystallisation temperatures T_x. They thus possess a so-called super-cooled liquid region $\Delta T = T_x - T_g$ at near 0.6 to 0.7 T_m (often between 550 and 800K) to which they can be heated in principle without crystallization.

Thus, in addition to metallic hardness and toughness, BMGs have the formability of polymers in their super-cooled liquid region's temperature window ΔT which is far below the temperatures required for Nabarro-Herring creep of crystalline lattices. This temperature region has therefore been used for shaping and joining metallic glasses or for creating micron or submicron-scale motifs on them.

Die forming was proposed [1,2] for production of amorphous metallic articles such as golf club heads by thermo-mechanical processing at temperatures between T_g and T_x. Thermo-mechanical shaping requires the heating and cooling of the BMG specimen as well as the deformation dies, with the ensemble usually placed in a furnace.

To avoid furnace heating, electromechanical shaping using Joule heating instead of conventional heating methods was introduced for mechanical shaping of BMGs at or above T_g and has been successfully applied [3-6] for shaping, joining to form complex shapes, welding, complex net-shaping,

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shaping into BMG-based composites and electro-mechanical engraving, by taking advantage of the high electrical resistivity ρ of bulk metallic glasses.

Lithographic techniques have been used to create submicron motifs on metallic glass surfaces [7,8]. Micro-replication was also obtained by hot pressing in the super-cooled liquid region on silicon wafers [9] and onto WC or Ni dies [10]. The flow stress σ_{flow} required to achieve such shape changes in the ΔT temperature range depends on the viscosity η which is strongly temperature dependent near T_g.

In the present study we report observations of microscopic shape changes occurring under no applied stress simply due to surface tension γ.

While the surfaces of copper cast bulk metallic glasses can be very smooth microscopically, surfaces of melt-spun metallic glasses carry traces of shape instabilities. These surface defects are usually deep pockets of gas trapped on wheel side and very thin (few microns) elongated "wave-like" defects on the free surface side. We use the traces of this surface roughness to study the kinetics of self-healing. We have heated glassy Pd-based melt-spun ribbons in protective atmosphere to 583K which is just above T_g and photographed the free surfaces after different times. Surface defects were found to disappear or "self-heal" in the ΔT temperature range. The results are discussed in terms of the experimental deformation rates, viscosity and surface tension forces.

2. EXPERIMENTAL

$Pd_{40}Cu_{30}Ni_{10}P_{20}$ glassy ribbons were obtained by melt-spinning under argon gas on a copper wheel as a substrate rotating at 26 and 48 m/s. The evolution of the surface roughness of the freely solidified side of the ribbons was observed during heating on the hot-stage of an optical microscope under protective atmosphere.

3. RESULTS

The optical micrograph of Fig. 1 shows the freely solidified side of a melt-spun glassy Pd-based ribbon once placed in the optical microscope hot-stage and prior to heating (in the as-quenched state).

A highly anisotropic surface roughness with long lines of alternating convex (mountain-like) and concave (valley-like) microstructures with a wavelength (one mountain plus one valley) of width about 4 μm is detected over the entire area of observation

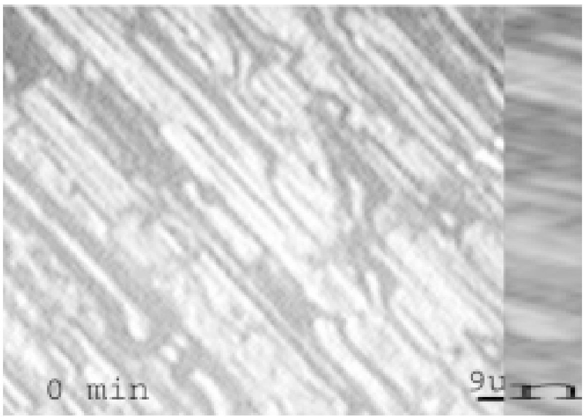

Fig. 1. Optical image of the as-quenched state of the freely solidified side of the Pd-based glassy ribbon.

which is approximately 0.12 mm x 0.12 mm. The specimen was then rapidly heated to 583K under inert gas and held at that temperature. Fig. 2 shows the evolution of the surface roughness with time at 583K.

After 30 seconds the roughness appears to be unchanged at least as observed from above. However, after 60 s at 583K, the initial roughness has nearly totally disappeared but some traces of the disappeared "mountains and valleys" remain visible as for example on the right middle side of the examined area. After 90 seconds at 583 K, no trace of the initial roughness structure is detectable but finer defects of unknown origin (non-elongated) remain. Even these tend to disappear or are significantly reduced in numbers after 120 s at 583K. Crystallisation (not shown) begins after 180 seconds at this temperature.

It is thus found that surface defects on the scale of a few micrometers tend to disappear without crystallisation as the glassy surface undergoes self-healing when heated to the super-cooled liquid region above T_g.

4. DISCUSSION

The as-quench surface roughness on the freely solidified side of the examined glassy ribbon (Fig. 1) shows an elongated (anisotropic) alternating mountain-valley structure that repeats itself with an approximate wavelength of 4 μm. Assuming that the depth (or amplitude) of this roughness relief is of the order of half the width of a mountain or a

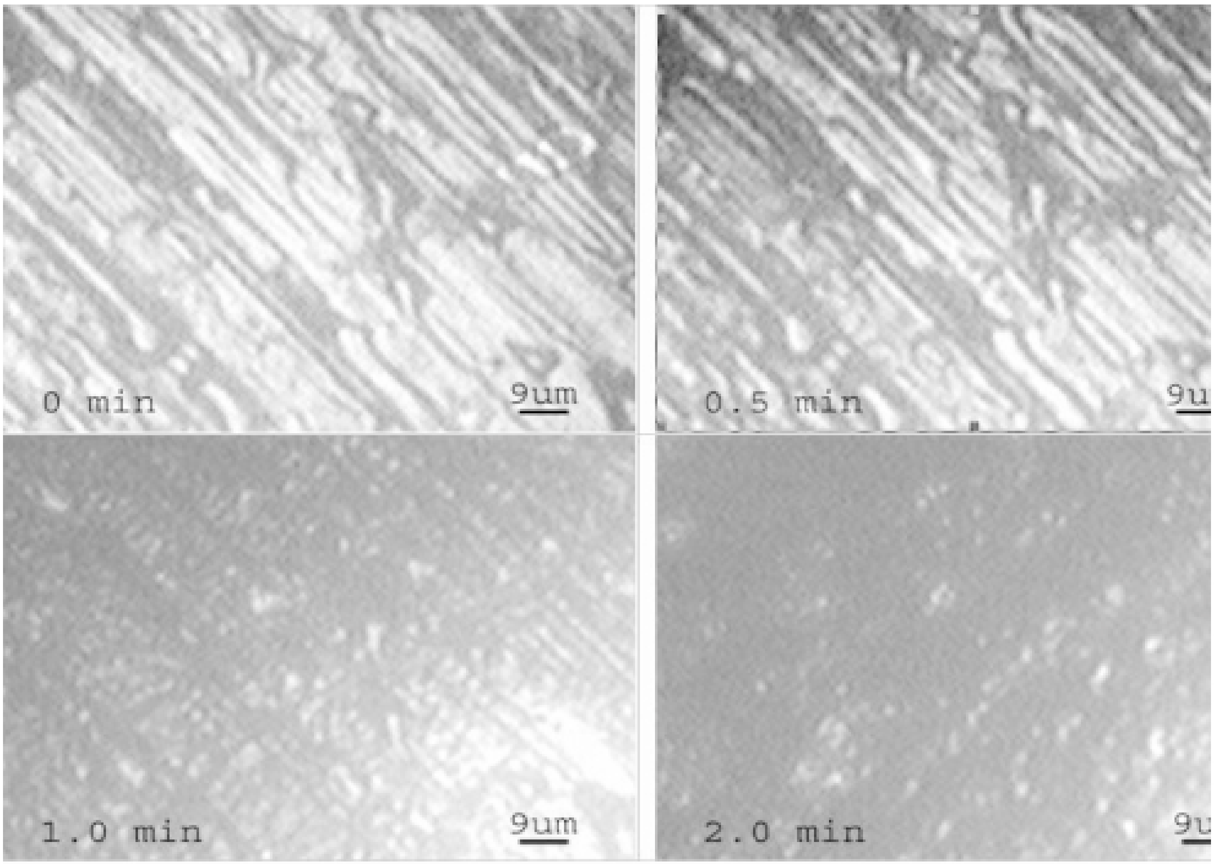

Fig. 2. Optical micrographs of the ribbon surface after various times at 583K; top left: 30 s; top right: 60 s; bottom left: 90 s and bottom right: 120 s.

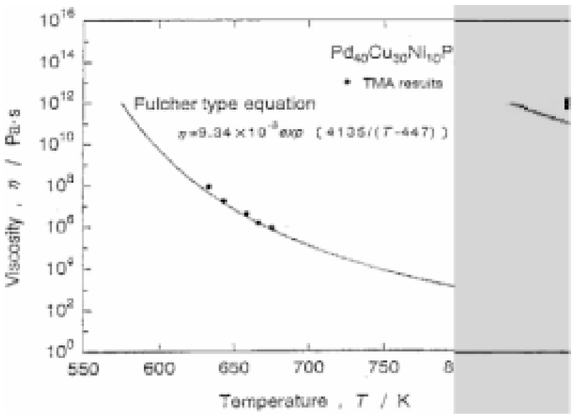

Fig. 3. Pd-based alloy viscosity η versus temperature [12].

valley, it would be of the order of 1 μm. Thus we can idealise the surface relief as a repetition of a surface wave with wavelength 4 μm and amplitude 1 μm. We expect that in conditions of perfect wetting (self-wetting), the surface would tend to reduce energy by reduction of the amplitude of such roughness to zero if kinetically allowed. This would result in a thermodynamic stress of magnitude $\sigma \approx 2\gamma/r$ where the liquid surface energy γ can be taken to be about 10^{-4} J/cm^2 [11] for an order of magnitude calculation. Assuming Newtonian flow in the supercooled liquid region just above T_g, we can write:

$$\sigma_{flow} = 3\eta d\varepsilon / dt \approx 2\gamma / r, \qquad (1)$$

where η is the viscosity, ε the strain and $d\varepsilon/dt$ is the strain rate. Now the observations in Fig. 2 indicate that the surface roughness with wavelength $4r$ and amplitude $r \approx 1$ μm practically disappears after 120 seconds. If we consider the corresponding deformation (filling of the valleys by matter from *the* mountains) to correspond to a deformation $\varepsilon \approx 0.5$, we obtain a deformation rate $d\varepsilon/dt \approx$ (1/240) s^{-1}.

Substituting these values into Eq. (1) and solving for the viscosity $\eta(T)$ at the annealing temperature of 583K, we obtain $\eta \approx 2 \cdot 10^8$ Pa.s. An examination of previously established temperature dependence of the viscosity η(*T*) taken from [12] and reproduced in Fig. 3 indicates that our estimation of η at 583K based of the kinetics of self-healing of the surface roughness is within three orders of magnitude of the expected experimental value for 583K and corresponds to η at ~620K. This discrepancy may be due to the crudeness of the approximations in Eq.(1), to the precision of the surface temperature measurement or both.

In conclusion, it is found that surface defects on metallic glasses tend to self-heal when they are heated to the supercooled liquid region above T_g. The kinetics are such that defects with dimensions of the order of a micron have sufficient time to disappear prior to the onset of crystallization. The observed self-healing is a technologically interesting phenomenon as regards micron or submicron scale engraving, writing or replication on metallic glass surfaces and their restitution.

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