

Amorphous Materials: Phase Transformations and Mechanical Behavior

Frans Spaepen

Division of Engineering and Applied Sciences
Harvard University, Cambridge MA 02138, USA

An amorphous material is one without translational symmetry in its atomic structure. A liquid is amorphous, as is its low temperature, high-viscosity form, the glass. Some amorphous solids can only be prepared by atomic deposition, such as sputtering or electrodeposition, or by ion bombardment.

The ease of glass formation varies greatly: covalent oxides, such as SiO_2 , are classic easy glass formers, and are even difficult to crystallize; metals, on the other hand, can be made into glasses only for certain alloy compositions. The basic measure for the ease of glass formation is the ratio of the glass transition temperature, T_g , and the melting (or liquidus) temperature, T_m . This criterion arises from the analysis of the probability of homogeneous nucleation of a crystal in the melt [1]. If $T_g/T_m > 2/3$, as for SiO_2 , nucleation is negligible, and glasses can be obtained by slow cooling. If $T_g/T_m \sim 0.5$, as for many metal alloys, glasses can only be formed by rapid cooling ($> 10^6$ K/s) of the melt.

The recently discovered bulk metallic glasses, such as $\text{Fe}_{48}\text{Cr}_{15}\text{Mo}_{14}\text{Y}_2\text{C}_{15}\text{B}_6$, [2] are highly engineered multi-component alloys. The presence of many elements aids glass formation in several ways. (i) Thermodynamically: alloying often leads to a pronounced lowering of the liquidus temperature. Since its effect on the fluidity of the

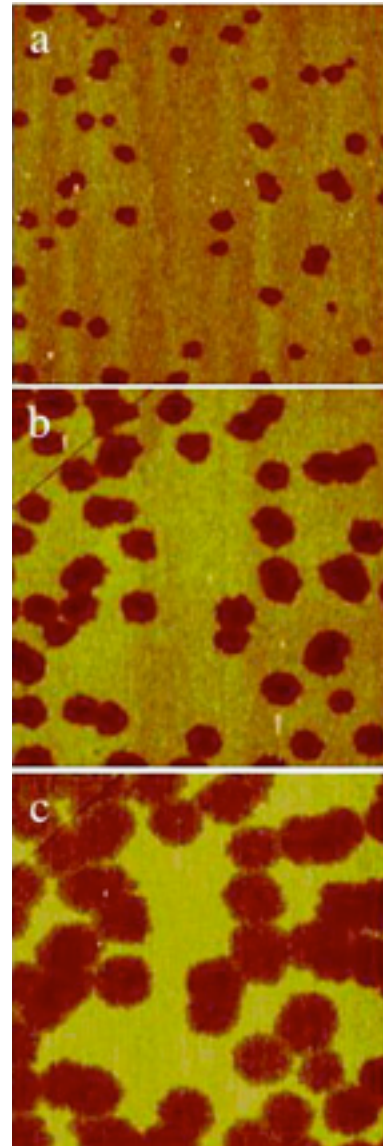


Figure 1: Growth of crystals, measured by AFM from the density change, in an amorphous $\text{Ag}_{0.55}\text{In}_{0.65}\text{Sb}_{59}\text{Te}_{29}$ thin film annealed at 182°C for (a) 5s, (b) 8s and (c) 11s. From [7].

liquid, and hence T_g , is much weaker, alloying often raises T_g/T_m . Early binary

glasses were often found near deep eutectics. (ii) Kinetically: the greater complexity of diffusive sorting of multiple elements upon crystallization slows down the process ("the confusion principle"). (iii) Certain elements may be needed for subtle reasons, such as the preferential gettering of oxygen into less harmful heterogeneous crystal nucleants.

Marginal glass-forming liquids ($T_g/T_m \sim 0.5$) remain amorphous if quenched at high cooling rates, but crystallize if cooled more slowly. This is exploited in thin films of chalcogenide (Te) alloys, where the cooling rate of the liquid is controlled by the length of a laser or current pulse. The difference in optical reflectivity or electrical resistivity of the crystalline and amorphous phases makes it possible to use these chalcogenides for non-volatile optical and electronic data storage. Improvement in the technology requires more detailed understanding of the kinetics of crystal nucleation and growth in these materials. For example, analysis of the undercooling of liquid $\text{Ge}_2\text{Sb}_2\text{Te}_5$ showed that steady state homogeneous nucleation would be impossible to suppress under technological conditions, and the formation of the amorphous phase is made possible by the transient time effects. [3]

The absence of periodicity in the structure of amorphous materials precludes their plastic deformation by the formation and motion of dislocations, as in crystals. As a result, they are very hard: the yield strength of a typical amorphous metal is about one order of magnitude smaller than the shear modulus. Yield in amorphous metals is accompanied by extensive

deformation-softening (see Figure 2) and localization of the shear into a small number of very thin bands. [4] Their eventual use of metallic glasses as structural materials depends on the ability to control the number and distribution of these shear bands.

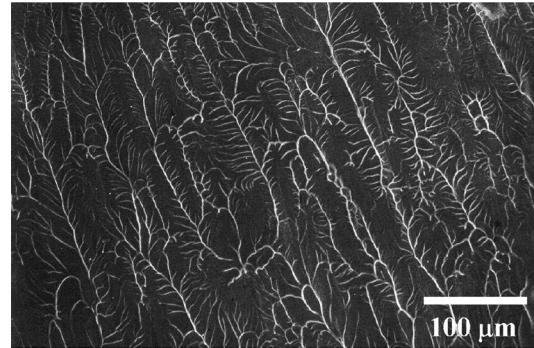


Figure 2: Typical fracture surface of a metallic glass ($\text{Pd}_{41}\text{Ni}_{10}\text{Cu}_{29}\text{P}_{20}$). The river pattern results from a Taylor-Saffman fracture [8] of the fluid layer that forms in the shear band due to shear-induced dilatation [4]. From [9].

The formation of shear bands is the result of the accumulation of defects that form as a result of deformation [5]. The formation of these defects can be studied in "slow motion" at lower stresses, where the deformation remains homogeneous through the volume, but the strain rate at constant stress nevertheless increases with time (see Figure 3). The free volume model provides a unified picture: the defect is a density fluctuation greater than a critical size and the formation of new defect is the result of shear-induced dilatation, a phenomenon well known in soil mechanics for shear of close-packed granular materials. [6]

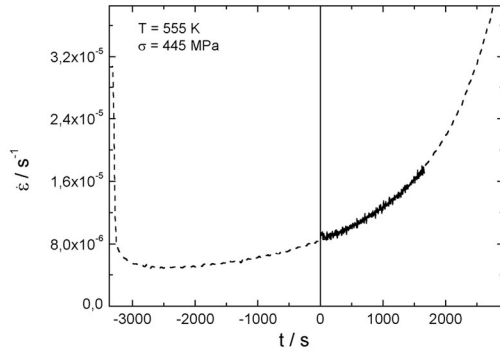


Figure 6: Strain rate as a function of time of a $Pd_{41}Ni_{10}Cu_{29}P_{20}$ glass at 555K. First and third run at 445MPa; increasing strain rate due to creation of defects. Second run (not shown): 58000s at 14MPa; annealing out of defects. The offset time axes show that defect creation is reversible and reproducible.

From [6].

References:

- [1] D. Turnbull, *Contemp. Phys.* 10, 473 (1969).
- [2] V. Ponnambalam, S.J. Poon and G.J. Shiflet, *J. Mat Res.* 19, 1320 (2004).
- [3] J. Kalb, F. Spaepen and M. Wuttig, submitted to *J. Appl. Phys.*
- [4] F. Spaepen, *Acta Metall.* 25, 407 (1977).
- [5] F. Spaepen, in *Physics of Defects, Les Houches Lectures XXXV* Amsterdam: North Holland Press; 1981. p.133.
- [6] M. Heggen, F. Spaepen and M. Feuerbacher, *J. Appl. Phys.* 97, 033506 (2005).
- [7] J. Kalb, F. Spaepen and M. Wuttig, *Appl. Phys. Lett.* 84, 5240 (2004).
- [8] F. Spaepen, *Acta Metall.* 23, 615 (1975).
- [9] M. Heggen, Ph.D. Thesis, RWTH (2004).

