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FINAL REPORT

1) CREEP AND RELAXATION BEHAVIOR OF VAPOR-DEPOSITED AMORPHOUS SELENIUM FILMS: 2) FLOW BEHAVIOR OF GLASSY METALS

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Abstract

It has been shown that a-Se films deposited from the vapor onto low temperature substrates, when annealed at or just below their glass temperature, become indistinguishable, in flow and transformation behavior, from melt-quenched specimens. Photoillumination, in the visible range, of these films (a) sharply increases their rate of approach to configurational equilibrium while not affecting the flow rate of equilibrium, (b) greatly increases the number density of crystals heterogeneously nucleated while not producing...
measurable homogeneous nucleation, (c) generally increases the rates of
growth of crystals within the films.

It has been shown that the plastic deformation behavior of glassy metals
can be represented satisfactorily by a deformation map of the type presented
by Ashby and Frost for various crystalline materials. The available
evidence indicates that the temperature dependence of the isoconfigurational
creep rate below the glass temperature is relatively much smaller for
metallic alloy than for non-metallic glasses.

R.B. Stephens of our laboratory (paper in preparation) developed a high precision technique for measuring the creep rates of thin films. With this technique he investigated the dependence of the creep rates of a-Se films, when relaxing toward configurational equilibrium and when in their fully relaxed states, on time, temperature and photoillumination. The following conclusions emerged from this study.

a) The shear viscosities of the fully relaxed vapor-deposited films are practically identical with those of bulk melt-quenched specimens, measured [by Jenckel, Kolloid Zeit 84, 266 (1933) and by Cukierman and Uhlmann, J. Non-Cryst. Solids 12, 199 (1973)], by quite different methods, over the entire viscosity range, $10^{10}$ to $10^{12}$ poise, of measurement overlap. Stephens' measurements extended beyond the overlap range to the viscosity $3 \times 10^{14}$ poise.

b) From the relaxation studies, the temperature dependence of the isoconfigurational flow of the films in various, partly relaxed states was determined. The activation energy, $E_J$, opposing this flow was about 50 kcal/gm.atom, roughly independent of the degree of relaxation. This value is, roughly, only 40% of the apparent activation energy, $E_\eta \approx 130$ kcal/gm.atom, for flow in the fully relaxed state.

c) Illumination with light in the visible range had no measurable effect on the creep rates of the fully relaxed specimens but it sharply increased the relaxation rates toward configurational equilibrium.
d) The far infrared spectrum of fully relaxed films is virtually indistinguishable from that of melt-quenched specimens.

e) Thus, despite the rather large energy barrier thought to oppose ring-chain interconversion in a-Se, films of a-Se relax quite rapidly in the glass transition range to configurational states which appear to be the same as those of bulk melt-quenched specimens.


Our analysis indicates that, just as for a-Se, the rate constant for homogeneous creep of any glassy metal is composed of an isoconfigurational mobility factor and a configurational excitation factor determined by the actual average configuration (e.g., as characterized by the free volume or configurational entropy). Further the available data on the homogeneous creep rates of glassy metals, at temperatures near to and far below the glass temperature, yield activation energies, $E_J$, for isoconfigurational flow which, in contrast with the results on a-Se, are only a small fraction, $\frac{1}{10}$, of the apparent activation energy for flow in the fully relaxed states. An important consequence of this behavior is that high flow rates can persist in localized regions where high amounts of configurational disorder are retained or imposed by some external force to temperatures far below the glass temperature.

Spaepen showed (ONR Technical Report No. 7, "A Microscopic Mechanism for Steady State Inhomogeneous Flow in Metallic Glasses") that the available deformation data on glassy metals can be satisfactorily represented by a deformation map of the type presented by Ashby and Frost for various crystalline materials. This map depicts creep rates and the prevailing deformation mechanism with variances of the reduced temperatures and flow stresses. The position of the boundary line between the homogeneous and inhomogeneous flow regions on the deformation map was consistent with calculations of it based on the concepts outlined above and the free volume model for flow.
Papers Published or in Press


David Turnbull: Invited Talks 1976


2. Northeastern University Chemistry Department Colloquium, "The Glass Transition in Monatomic Systems", 1/19/76.


Frans Spaepen: Invited Talks 1976


Other Contracts

1. "Study of the Mechanisms for "Fast Diffusion in Metals". 
   National Science Foundation.

2. Share of Materials Research Laboratory, 
   National Science Foundation.

3. Adviser (no student or post-doctoral report) on "Preparation and 
   Characterization of Improved Superconducting Materials". 
   National Science Foundation.