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ANIELASTIC RELAXATION OF METALLIC GLASSES

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1. Introduction
Metallic glasses produced by extremely rapid quenching of the melt exhibit a metastable structure from thermodynamical principles /1/. The frozen-in liquid structure may be considered to contain excess or free volume /2,3,4/ which is believed to play an important role in the mechanisms of deformation of the glassy material /5,6,7/. The free volume also appears to be involved in structural relaxations upon anneal /8,9/ and perhaps in the embrittlement after annealing at temperatures far below crystallization /10,11/.

In this work conventional stress relaxation experiments in tension (similar to /12,13/) have been performed to examine the stability of the glassy structure under load as well as the effect of slight annealing. From measurements of the temperature and stress dependence of anelastic stress relaxation an attempt is made to estimate the shape of the spectrum of activation energies for structural relaxations of the Metglas 2826A.

2. Experimental Details
Metallic glass ribbons of type 2826A (Fe32Ni36Cr14-P12B6, Allied Chemical) with polished edges (width 2.25 mm, thickness 50 μm, free length 30 mm) were clamped into flat grips held in a special jig for mounting (and demounting) for tensile tests in the Instron machine equipped with a load measuring device of increased sensitivity (maximum load 500 N, resolution ±5 mN). The machine could be controlled by a microprocessor system which also provided a first evaluation of the raw data (appropriate averaging of load readings in adapted intervals). Load relaxation P(t) was recorded with electrically suppressed zero load level at high sensitivity after loading with a cross-head speed of 0.01 cm/min to different load levels, after repeated loading/unloading cycles with various waiting times at zero load, as well as at several temperatures between -94 and +61 °C. Samples were used in the asquenched condition as well as after annealing treatments in Ar atmosphere for 20 h at temperatures of 80, 120, 160, and 200 °C.

The measured relaxation curves were evaluated by fitting the relation

\[ P = P_\infty + \sum P_i \exp(-t/\tau_i) \]

which will be justified below as a simplified approach to the continuous spectrum of relaxation times actually present. Combining the graphical method of /14/ with a computer optimization, 4 relaxation times \( \tau_i \) were found to be sufficient to approximate the curves in the interval \( 1 \leq t(s) \leq 10^3 \) within an accuracy of \( \Delta P/P \approx 3\% \). Eventual corrections for machine characteristics, thermoelastic effect and temperature fluctuations were checked. Because of general difficulties to establish a well-defined stress state in the very thin sample of non-uniform cross section only relative trends of results taken from the same sample will be evaluated.

3. Results
3.1. Repeated loading and stress relaxation of as-quenched specimens.
Hysteresis effects observed during loading/unloading cycles indicate during first loading some irreversible deformation and during following loadings anelastic deformations most of which occur in times short enough to be nearly completed during the loading time. Therefore, the apparent Young's modulus \( E^{\text{app}} \) (Fig. 1) calculated from recorded load, elongation and measured cross section, and corrected for relaxations with \( \tau > 2 s \), increases after the first loading and is smaller than values determined by dynamic methods (e.g. /15/).

If the load is kept at its maximum value for some time the width of the hysteresis increases. These additional anelastic processes are examined in more detail on load relaxation curves recorded after stopping the machine cross-head at \( P_0 = 150 \) N for \( t_R = 13 \) min. Repeated load relaxation after unloading, waiting at zero load for \( t_W = 34 \) min and re-
loading to $P_0$ showed less relaxation than before. Results from several cycles of this kind are given in Fig. 2 where the total load relaxation $\Delta P(t_R) = P_0 - P(t_R)$ after a time of $t_R = 13$ min is plotted versus the number of relaxation experiments. Waiting times at zero load for 34 min and 7 d are indicated at the abscissa. Obviously $t_w$, though exceeding $t_R$ considerably, is not long enough to recover the relaxation process completely (this can be estimated to occur only after $t_w \approx 10^9$ s).

Analysis of the load relaxation curves according to eq. (1) shows that the contribution $P_i$ of each relaxation time $\tau_i$ follows a similar course as shown in Fig. 2, the longest time ($\tau_4$) contributing the major part.

3.2 Load relaxation on annealed specimens

A similar procedure of repeated load relaxations was performed on specimens annealed stepwise for 20 h at 80, 120, 160, and 200 °C. Fig. 3 gives some results on two specimens plotted as relative contributions of the processes of the 4 relaxation times $P_i/P_1$ (first loading) versus the number of experiments and annealing treatments. Waiting times at zero load are similar as in 3.1.

After annealing below 160 °C the contributions of $\tau_4$ and later of $\tau_3$ decrease considerably, while $\tau_2$ and $\tau_1$ first increase, later also decrease, i.e. the long relaxation times shift to shorter ones with increasing annealing treatment (relaxation times $< 1$ to 2 s cannot be measured by the load relaxation experiment). Young's modulus remains constant during these treatments (Fig. 1).
A quite different behaviour occurs after annealing for 20 h at 200 °C. The contributions of the longest relaxation time (τ₆) increases considerably. Simultaneously Young's modulus increases distinctly (Fig. 1) and the material becomes brittle: most samples after the 200 °C anneal break during first loading.

3.3. Temperature dependence of load relaxation.

The dependence of load relaxation on temperature was measured in a limited temperature range to avoid structural changes at higher temperatures. Considerable difficulties were encountered because of temperature fluctuations which disturb the highly sensitive load measurements considerably. Therefore, only 3 measurements are shown in Fig. 4 where no temperature drift was observed or where the fluctuations could be corrected satisfactorily. In Fig. 4 the contributions to load relaxation of the τₖ values are given for 3 temperatures. The values for very short and very long times are rather uncertain. With decreasing T the contributions shift to longer relaxation times as expected for a thermally activated mechanism.

4. Discussion

From the trends observed during repeated load relaxation on as-quenched and annealed metallic glass specimens we can obtain some conclusions regarding the stability and structural relaxations of the material on loading and on slight annealing treatments. The observed tendencies of hysteresis loops, apparent Young's modulus, and repeated load relaxations (cf. /12/) on as-quenched samples show a temporal asymmetry of the relaxation processes. This suggests that the atomic positions in the metallic glass according to its random structure are characterized by non-symmetrical potential wells. An imposed external load will disturb the metastable equilibrium and some rearrangements will occur with notable frequency. The kinetics of these processes can be described approximately along lines given early by Becker /16/ and later by Argon /17/ for anelastic aftereffects.

As the total load relaxation effect is small it can be approximated by eq.(1) with

\[ \tau_i = \tau_0 \exp(\Delta G_i/kT) \]

(\( \Delta G_i \) = free enthalpy threshold for thermal activation, \( \tau_0 = 1/2\nu_D \), \( \nu_D = \) Debye frequency /5, 7/) and

\[ P_i = AN v_w^2 P_0^2 f_i \]

where \( f_i \) = number of relaxing regions with free activation enthalpy \( \Delta G_i \) (strictly speaking \( f_i \) also contains an eventual distribution of \( v_w \) values for different \( \Delta G_i \)), \( N \) = total number of relaxing regions, \( v_w \) = their mean volume, \( v_o \) = specimen volume, \( P_0 = \) specimen cross section, \( P_w = \) final value of load after relaxing all regions. \( A \) is a constant of the order of 1 depending on the exact nature of the atomic rearrangement which occurs in each relaxing region and produces some elongation of the specimen /17/ or and some decrease of its load carrying cross section /16/.

The range of relaxation times or activation energies obtained from one load relaxation experiment is limited: 2 \( \leq \tau_i(s) \leq 850 \) or at \( T = 300 \) K \( 0.79 \leq \Delta G_i(eV) \leq 0.95 \) (assuming \( \nu_D = 9.6 \times 10^{12} \) s⁻¹). From Fig. 4 and eqs.(2),(3) we estimate the frequency spectrum \( H = f(\Delta G)/N \) of regions with free activation enthalpy \( \Delta G \) of Fig. 5 for \( T = 300 \) and 334 K, assuming a continuous spectrum which does not change in the small temperature interval, and assuming the same total num-

![Fig. 4 Contributions to load relaxation with 4 relaxation times measured (after several loadings at room temperature) on the same specimen at temperatures of \( T = 179, 300, \) and 334 K.](image)

![Fig. 5 Frequency spectrum of activation enthalpies for relaxation processes derived from measurements at 300 and 334 K (Fig. 4).](image)
number \( N \) of processes (the latter assumption is not valid for the measurement at 179 K, therefore its spectrum cannot be incorporated into Fig. 5). The spectra are qualitatively similar to those determined by Argon and Kuo \(/10/\) from creep tests at higher temperatures for several other metal glasses (AlCuZr, CuZr, PdSi) and indicate that relaxation sites with high \( \delta \), i.e. long \( \tau \) are much more frequent than those with short \( \tau \).

The concept of free volume in metallic glasses suggests that regions with relatively large free volume should permit atomic rearrangements with small activation energy (short \( \tau \)), those with small free volume should correspond to rearrangements with long \( \tau \) values (cf. \(/5/\)).

The change of load relaxation curves with repeated loading (as-quenched specimens) indicates that on first loading some "irreversible" (in the times of measurement) rearrangements have occurred. During further loadings a certain equilibrium between rearrangements and recovery of the different relaxation processes is approached which is determined by the relation between loading and waiting times.

The behaviour after slight annealing treatments (\( \leq 160 ^\circ \text{C} \)) (no change in the apparent modulus, Fig. 1, however, a change in the contributions \( P_1(\tau_1) \), Fig. 3) would mean in the picture above that during this treatment small free volumes segregate to larger ones remaining the same in total. From eq.\((3)\) and the normalizing condition we can estimate the total relaxing volume to be in the order of \( N_{\text{relax}} \approx 10^{-3} \text{ mm}^3 = 0.3 \% \) \( V_0 \) (neglecting the small contribution with \( < 2 \text{ s} \)). Eqs.\((1),(3)\) are valid if \( V_0 \) is smaller or in the order of the mean free volume per atom (\( \approx 0.3 \text{ v}_{\text{atom}} /19/\)).

During annealing at 200 \( ^\circ \text{C} \), on the other hand, the modulus increases definitely (Fig.1) and some free volume disappears (cf. increase of density \( \rho \) by annealing of several other similar glasses \(/20/\)). Further, the increase of the contribution of \( \tau_4 \) could indicate that new small free volumes have been produced, perhaps by decomposition of large ones or by filling them up with some diffusing atom species. Both effects could explain the tendency to embrittlement \(/10, 11/\) which commences after this annealing treatment. A similar destruction of free volume after annealing for \( \leq 2 \text{ h} \) at 250 \( ^\circ \text{C} \) has been observed recently by X-ray diffraction \(/8/\), cf. also \(/4/\).

In summary, from anelastic stress relaxation measurements on Metglas 2828A in the as-quenched and slightly annealed condition we find the following results and conclusions which may be of interest for practical applications of these materials:

1. The metastable structure with asymmetrical potential wells for atomic rearrangements gives rise to an inherent temporal asymmetry of anelastic relaxation processes. Therefore the whole preloading history enters into the results of any experiment. This makes it difficult to obtain reproducible results for mechanical properties.

2. The apparent Young's modulus seems to increase after first loading of the material. Possibly some free volume is removed permanently from the as-quenched structure by this first loading.

3. Slight annealing treatments with temperatures up to 160 \( ^\circ \text{C} \) (20 h) change the structure slightly; in this temperature interval free volume seems to segregate into larger units, but still remains in the sample which keeps its ductility.

4. Annealing for 20 h at 200 \( ^\circ \text{C} \), however, increases Young's modulus and produces a tendency for embrittlement. Probably some free volume disappears and some decomposes into many small free volumes or is filled up by a diffusing atom species.

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