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EMBRITTLEMENT AND DISEMBRITTLEMENT IN AMORPHOUS METGLAS 2826 A

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Introduction

The embrittlement of metallic glasses due to thermal annealing has been studied extensively (1-3). It has been shown that the fracture strain decreases continuously with annealing time and that the decrease is faster for higher annealing temperatures. The embrittlement has been attributed to structural relaxation of these metastable materials. A distinction has been made between topological and chemical short range order processes. The topological relaxation consists of an irreversible annealing-out of free volume. The chemical relaxation involves local rearrangements of the various atoms in these multicomponent glasses. This process is similar to order-disorder processes in crystalline materials. Since the equilibrium value of the short range order parameter describing this process depends on the annealing temperature only, the process should be reversible given sufficient atomic mobility. This reversibility has indeed been observed for a number of local structure dependent properties such as Curie temperature (4), Young's modulus (5), electrical resistivity (6-8) and apparent specific heat (9).

In this paper it will be shown that the fracture strain of Metglas 2826 A is a function of both the free volume concentration and the local chemical order. By a suitable sequence of annealing steps it is possible to recover (partially) the loss of ductility during pre-annealing. Furthermore, it will be shown that, in agreement with a recently proposed model (10), the kinetics of the chemical relaxation processes depend on the amount of free volume present. The results of the fracture strain experiments are supported by measurements of the changes in Young's modulus of specimens which had received identical heat treatments.

Experimental

Specimens of the alloy Metglas 2826 A ($Fe_{32}Ni_{36}Cr_{14}P_{12}B_{6}$) were annealed at 470 K and 520 K in an Argon atmosphere. The width of the specimens was 2.3 mm with an average thickness of 64 μm. The classical bend test (1) was used to determine the fracture strain. At least 10 specimens were used for each annealing condition. A pulse-echo technique similar to the one described in (5) was used to determine changes in Young's modulus by measuring changes in the sound velocity. Measurements of both the fracture strain and Young's modulus were made at room temperature.

Results

The strain at fracture, ε_f, during isothermal annealing at 470 K and 520 K is shown in figure 1. A continuous decrease in ε_f from the as-quenched value of 8% to a value of about 1.5% has been observed which is due to the combined effects of an increase in the local chemical order and a decrease in the amount of free volume. To demonstrate the dependence of ε_f on the local chemical order specimens were pre-annealed at 470 K (for 3.6×10^6 s) or at 520 K (for 4×10^4 and 7×10^5 s) and subsequently annealed at 620 K. The observed fracture strain after annealing at 620 K is shown in figures 2a, 3a and 4a as a function of the annealing time. The arrow in each of the figures indicates the as-annealed value for ε_f. For all three pre-annealing conditions ε_f increases for short annealing periods at 620 K and decreases again for longer annealing times.

Samples with identical preannealing treatments were used to determine changes in Young's modulus

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due to annealing at 620 K. The results of these measurements are plotted in figures 2b, 3b and 4b. The figures show an initial decrease in Young's modulus followed by a continuous increase. It has been shown elsewhere (11) that the initial decrease in Young's modulus is due to chemical disordering and the subsequent increase due to the annealing out of free volume. Comparison of figures 2a with 2b, 3a with 3b and 4a with 4b shows that for identical pre-annealing conditions the times at which the extrema occur in both the fracture strain and Young's modulus curves agree very well. From this it is concluded that the disembrittlement due to annealing at 620 K is caused by reversible chemical effects and that the fracture strain also depends on the free volume concentration.

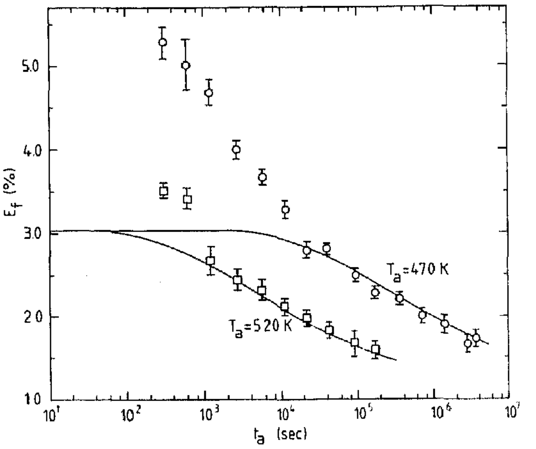

Fig. 1

Isothermal change of the fracture strain at room temperature for two annealing temperatures. For explanation of solid lines see text.

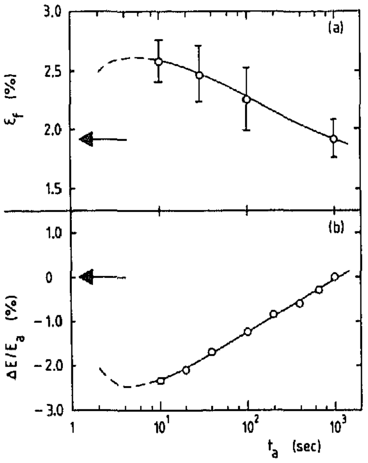

Fig. 2

Isothermal change of the fracture strain (a) and Young's modulus (b) for specimens pre-annealed at 470 K for 3.6 x 10^6 s. T_a = 620 K.

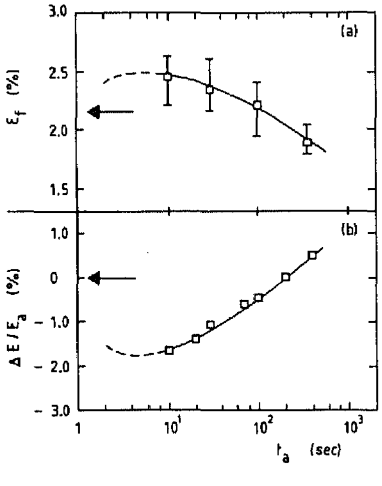

Fig. 3

Idem for specimens pre-annealed at 520 K for 4 x 10^4 s.

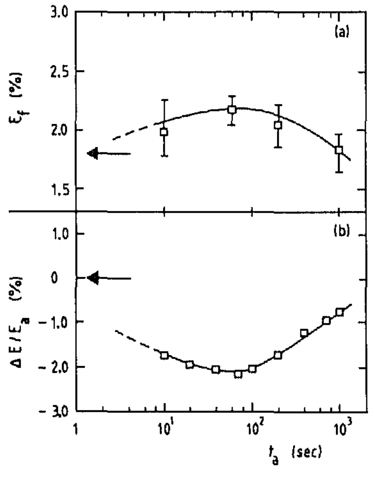

Fig. 4

Idem for specimens pre-annealed at 520 K for 7 x 10^5 s.

Discussion

From the experimental evidence presented here it can be concluded that the embrittlement of Metglas 2826 A during annealing is due to an increase in the degree of local chemical order and a decrease in the free volume concentration. Support for the dependence of the fracture strain of amorphous metals on the free volume concentration comes from recent work by Gerling et al. (12) who observed a strong increase in ductility of $Fe_{40}Ni_{40}B_{20}$ after neutron irradiation. This increase was attributed to the presence of radiation induced free volume.

We will now attempt to describe the embrittlement more quantitatively. In a recent model by Van den Beukel and Radelaar (10) which is based on the work of Spaepen (13), it has been shown that the annealing out of free volume during isothermal annealing can be described as

$$e^{\gamma v^*/v_f} = C' e^{-Q_a/RT} \,.\, t + e^{\gamma v^*/v_{f_o}} \qquad [1]$$

where v_f is the amount of free volume present after an annealing time t, v_{f_o} the initial amount of free volume, Q_a the activation energy for this process, γv^* and C' are constants. For the analysis of the fracture strain experiments the same values for v_{f_o}, Q_a, C' and γv^* as those determined for amorphous $Fe_{40}Ni_{40}B_{20}$ (11) will be used. For a chosen value of $\gamma v^* = 0.1$ it was found that $v_{f_o} = 10.5 \times 10^{-3}$, $Q_a = 170$ kJ.mol^{-1} and $C' = 3.2 \times 10^{18}$ s^{-1}. Using these parameter values the calculated free volume concentration versus the experimental fracture strain is plotted in figure 5 for both the 470 K and 520 K data. For values of $v_f \leq 9.5 \times 10^{-3}$ there is a linear relation between the calculated amount of free volume v_f and the observed fracture strain ε_f. This correlation does not hold for larger amounts of free volume, that is for shorter annealing times. In this time region the decrease of ε_f is not only due to a decrease of v_f but also to a change in the local order parameter from the highly disordered as-quenched condition to the equilibrium state at the annealing temperature. Using the linear relation between ε_f and v_f suggested in figure 5 we have calculated the change in fracture strain due to the free volume component only. This calculated embrittlement is indicated in figure 1 by the two curves. The figure shows that at these low annealing temperatures only a quarter of the total embrittlement is due to free volume effects.

The systematically lower ε_f values for specimens annealed at 470 K in the region $v_f < 9.5 \times 10^{-3}$ might be due to a small difference in the equilibrium local order. However the scatter in the data is such that no firm conclusion can be made.

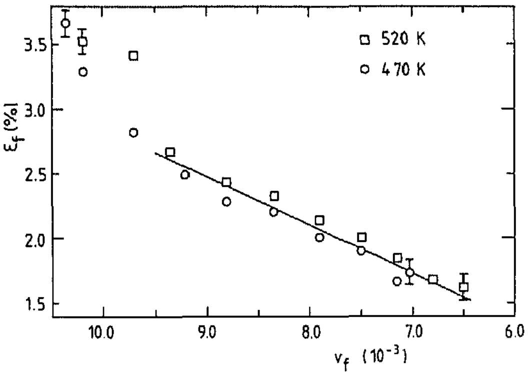

Fig. 5

Plot of calculated free volume concentration versus experimental fracture strain for two annealing temperatures. Data from figure 1.

We will now turn to the disembrittlement experiments. In their model Van den Beukel and Radelaar (10) assumed that the reaction rate of the ordering or disordering process depends on the amount of free volume present:

$$\frac{d\alpha}{dt} = A(T)\, e^{-\gamma v^*/v_f} \qquad [2]$$

where α is the order parameter and A a temperature dependent constant. From [2] it is concluded that at a fixed temperature equal amounts of free volume v_f will yield equal (dis)ordering rates. Based on [1] the pre-annealing conditions for the disembrittlement experiments of figure 2 and figure 3 were chosen to result in the same amount of free volume. Assuming that at the time at which the extrema in the ε_f and Young's modulus curves occur the disordering is completed and taking the position of the extrema as a measure for the disordering rate, the extrema are expected at the same position in figures 2 and 3. Analogously from the pre-annealing conditions used for figure 4 it is expected from [2] that the disordering process in this case will be about 15 times slower than in the former cases. The observed extrema in both ε_f and Young's modulus in figures 2 and 3 and figure 4 do not contradict these predictions.

Finally a few remarks will be made concerning the contribution of local order to the fracture strain. It is supposed that the equilibrium state of order is reached at the time the maximum value of ε_f in the disordering experiments is observed. Since the equilibrium state of order and hence the order component of the fracture strain depends on the annealing temperature, a larger disembrittlement effect $\Delta\varepsilon_f$ is expected for larger differences ΔT_a in annealing temperatures. For specimens pre-annealed at 470 K the maximum increase in ε_f is about 0.70% for ΔT_a = 150 K (figure 2) while for the specimens pre-annealed at 520 K $\Delta\varepsilon_f$ = 0.35% for ΔT_a = 100 K (figures 3 and 4). In both cases the effect of the continuing annealing out of the free volume at 620 K is neglected because its contribution to $\Delta\varepsilon_f$ can be calculated to be of the order of 0.01%. Linear extrapolation of the values of $\Delta\varepsilon_f$ to the as-quenched fracture strain of about 8% yields a fictive temperature between 1500 K and 2000 K, which is higher than the melting point. From this we conclude that either the linear extrapolation used or the supposition regarding the time at which the local order reaches equilibrium is incorrect or that there might be other low temperature processes such as internal stress relief causing embrittlement.

Conclusions

The embrittlement of Metglas 2826 A following thermal annealing is due to an increase in the local chemical order and the annealing out of free volume. Partial disembrittlement of pre-annealed specimens can be obtained by a disordering heat treatment at a higher temperature. The kinetics of this disordering process depend on the amount of free volume.

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