

ON THE KINETICS OF STRUCTURAL RELAXATION IN AMORPHOUS $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$

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1. INTRODUCTION

Low temperature annealing of metallic glasses causes changes in a large number of physical properties¹. This is attributed to atomic rearrangements in the amorphous state and the term structural relaxation is generally used to indicate this process which must be clearly distinguished from crystallization.

Generally the atomic rearrangements are divided into two kinds. In the first kind only the topological atomic positions are considered regardless of the chemical species of the atoms. Changes of these topological positions e.g. the interatomic distances, are thus described in terms of topological short range order (TSRO). As a result of TSRO a.o. the density of the glass will change.

In the second type of rearrangements the chemical species of the atoms is taken into account. Consequently chemical short range order (CSRO) describes changes in the local surroundings of a given atom. It is comparable to order-disorder processes in crystalline materials.

As metallic glasses are produced by rapid quenching from the melt the as-quenched glass will contain a large amount of free volume and the degree of short range order that is frozen in will be low. Structural relaxation during isothermal annealing of an as-quenched glass will result in a decrease of the amount of free volume (TSRO) and an increase of the degree of short range order (CSRO). There is a large amount of experimental evidence¹ that at suitable annealing temperatures the order parameter increases to new temperature dependent equilibrium values and that subsequent annealing at higher temperatures causes a decrease in the state of local order. CSRO is therefore a reversible process. Due to the very nature of its kinetics TSRO cannot reach equilibrium under most experimental conditions before crystallization occurs. Therefore TSRO will be regarded as a non-reversible process.

In a recently proposed model² expressions are given for the decay of free volume and the change of short range order during structural relaxation. In the present paper measurements are presented of the change of Young's modulus of $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$ during structural relaxation which allow a quantitative test of the model.

2. EXPERIMENTAL

Ribbons of the alloy $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$ (Vitrovac 0040) were obtained from Vacuum-schmelze. A pulse-echo technique³ was used to measure the velocity v as Young's modulus E is given by $E = \rho v^2$ where ρ is the density. In this paper changes in E are presented as changes in v^2 .

3. RESULTS

Changes in v^2 resulting from isothermal annealing of as-quenched specimens at various temperatures T_a are shown in Fig. 1 as a function of the annealing time t_a . The value of v^2 of the as-quenched glass is indicated with an arrow. For all temperatures v^2 increases upon structural relaxation in agreement with the results of Scott and Kursumovic⁴. For $T_a = 597$ K and 662 K the rapid increase in v^2 at the long annealing times indicates the onset of crystallization. As v^2 increases continuously until crystallization it is concluded that an increase of the degree of order (CSRO) and a decrease of the amount of free volume (TSRO) both result in an increase of v^2 . Therefore, in Fig. 1 the contributions of CSRO and TSRO to the increase of v^2 cannot be separated.

However, a separation between both contributions can be made by making use of the reversible character of CSRO. If a specimen is annealed long enough for the order parameter to reach the equilibrium value at that temperature subsequent annealing at a higher temperature will cause disordering. This will result in a decrease of v^2 . Fig. 2 shows the results of such an experiment. A specimen was pre-annealed at $T_a = 503$ K for a time $t_a = 1.1 \times 10^6$ s. Subsequent annealing at $T = 578$ K shows an initial decrease of v^2 which is attributed to disordering followed by an increase due to the continued annealing out of free volume.

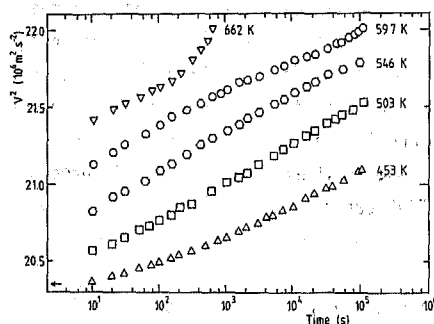


FIGURE 1
Isothermal changes of v^2 for as-quenched specimens

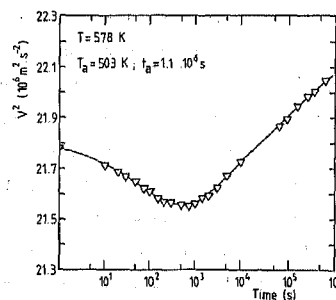


FIGURE 2
Changes of v^2 at 578 K after pre-annealing at 503 K for 1.1×10^6 s

The prediction² that the rate of (dis)ordering decreases with a decreasing amount of free volume present is confirmed by the following series of experiments. A number of specimens was pre-annealed for different times t_a (ranging from 1×10^4 s to 1.1×10^6 s) at a fixed temperature of 503 K. The amount of free volume present at the end of these pre-annealing treatments decreases with increasing annealing time. This series of specimens was subsequently annealed at 578 K. The results are presented in Fig. 3. Taking the time at which the minimum

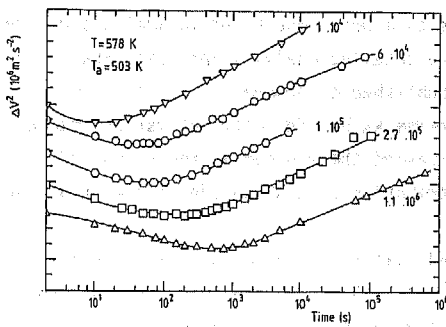


FIGURE 3

As figure 2 but for various pre-annealing times at 503 K.

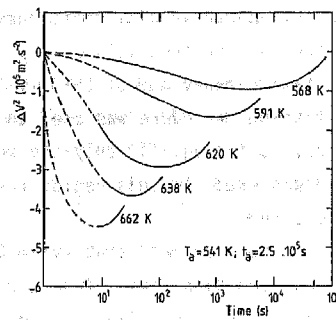


FIGURE 4

Δv^2 for various temperatures for identically pre-annealed specimens

value of v^2 occurs as a measure for the disordering rate, Fig. 3 shows qualitatively that the disordering rate is slower for lower values of v_f .

It is demonstrated in Fig. 4 that the occurrence of a minimum value in v^2 is due to disordering. This figure shows the results for 5 specimens annealed at different temperatures T after an identical pre-annealing treatment ($T_a = 541$ K; $t_a = 2.5 \times 10^5$ s). The maximum decrease in v^2 increases with increasing temperature difference $T - T_a$ and hence with increasing change in the order parameter.

4. DISCUSSION

In the model² the annealing rate of the free volume during isothermal annealing at a temperature T is described by

$$\exp(\gamma v^*/v_f) - \exp(\gamma v^*/v_{f,1}) = C t \exp(-Q_a/kT) = C'(T) \cdot t \quad (1)$$

and the (dis)ordering rate by

$$d\alpha/dt = -(\alpha - \alpha_e) \tau_0^{-1} \exp[-Q_s/kT] \exp[-\gamma v^*/v_f] \quad (2)$$

where v_f is the amount of free volume per atomic volume at the time t , $v_{f,i}$ is the amount of free volume at the start of the anneal, γ is a geometrical factor of the order 1, v^* has the dimension of volume per atomic volume, Q_a is the activation energy for the annealing of free volume, C is a constant, α is the short-range order parameter, α_e is the equilibrium value of α at the temperature T , τ_0 is a pre-exponential factor and Q_s is the activation energy of the ordering process. It is to be noted that equations (1) and (2) are coupled through v_f .

In this paper we will limit ourselves to a brief quantitative analysis of the behaviour of the free volume only. A more detailed analysis including the quantitative behaviour of CSRO will be published elsewhere⁵.

A fitting procedure was used to determine values for $C'(T)$ at various temperatures. To fit eq. (1) only the region beyond the minimum in the curves of Fig. 3 was used. In this region the contribution of CSRO to the change of v^2 can be neglected.

It has been argued² that $\gamma v^* \approx 0.1$ and that the value of $v_{f,i}$ for the as-quenched condition varies from 1.0×10^{-2} to 1.5×10^{-2} depending on the quenching rate. In the "fully relaxed" condition v_f has decreased to a value of about 5×10^{-3} . Therefore the amount of free volume present after an anneal of $t_a = 1.1 \times 10^6$ s at $T_a = 503$ K was taken as $v_f = 7 \times 10^{-3}$. For this set of values for γv^* and $v_{f,i}$ a fit to the data of Fig. 2 yields a value for $C'(578) = 790 \text{ s}^{-1}$. The fit is indicated in Fig. 5 with the dashed line. The change in v^2 was assumed to be proportional to the change in v_f .

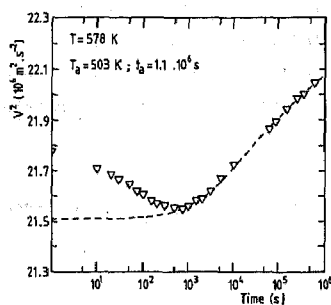


FIGURE 5
Data of figure 2. The dashed line indicates the fit (see text)

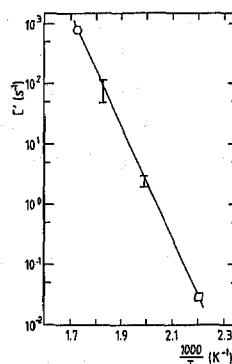


FIGURE 6
Arrhenius-plot of $C'(T)$

The curves for specimens also pre-annealed at 503 K but for different pre-annealing times (Fig. 3) have also been fitted to eq. (1) using the value for $C'(578)$ just obtained. These fits yield values for the amount of free volume as a function of annealing time at 503 K. Using these values in conjunction with eq. (1) both $C'(503)$ and the amount of free volume in the as-quenched condition were calculated, yielding $v_{f0} = 10.5 \times 10^{-3}$ and $C'(503) = 2.5 \text{ s}^{-1}$.

Another set of specimens pre-annealed at 503 K for the same annealing times as those in the 503-578 K series was annealed at 546 K. Using the same amounts of free volume after pre-annealing as obtained from the 503-578 K measurements $C'(546)$ values were determined.

Using similar procedures for specimens pre-annealed at 453 K and subsequently annealed at 578 K or 546 K $C'(453)$ was obtained. The four $C'(T)$ values obtained are plotted in an Arrhenius-plot (Fig. 6) which yields $C'(T) = C \exp(-Q_a/kT)$ with $C = 1.6 \times 10^{19} \text{ s}^{-1}$ and $Q_a = 180 \text{ kJ.mol}^{-1}$. Both values are in good agreement with the results of resistivity measurements by Sonius et al.⁶ on $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$.

It is emphasized that the values of C' and γv^* are coupled. If γv^* is taken equal to 0.1 then either C' or $v_{f,i}$ may be chosen. This choice is rather arbitrary; we chose $v_{f,i} = 7 \times 10^{-3}$ after a pre-annealing treatment $(t_a, T_a) = (1.1 \times 10^6 \text{ s}, 503 \text{ K})$. This results in $C = 1.6 \times 10^{19} \text{ s}^{-1}$. The validity of this choice will be discussed elsewhere⁵. The value of $Q_a = 180 \text{ kJ.mol}^{-1}$ is not affected by the choice.

5. CONCLUSIONS

The increase of Young's modulus upon annealing is due to contributions of both CSRO and TSRO. It has been demonstrated qualitatively that the kinetics of CSRO depend on the amount of free volume present. The kinetics of TSRO are quantitatively in agreement with a recently proposed model².

ACKNOWLEDGEMENTS

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