

# Effect of quench rate on the structural relaxation of a metallic glass

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Measurements of the ferromagnetic Curie temperature,  $T_c$ , have been used to monitor the structural relaxation of the metallic glass  $\text{Fe}_{81.5}\text{B}_{14.5}\text{Si}_4$ . The glass was produced by melt-spinning to various ribbon thicknesses at consequently different quench rates. It is shown that the faster quenched (i.e. thinner) ribbons have lower initial  $T_c$  values, corresponding to less relaxed structures. All the materials, however, tend to the same equilibrium value on annealing. An effect which is particularly marked at low annealing temperatures is that the faster quenched ribbons relax more quickly. The results are interpreted in terms of two relaxation mechanisms.

## 1. Introduction

Annealing metallic glasses causes substantial property changes. It is reasonable to suppose that changes in production conditions would give rise to property variations of similar magnitude. Indeed, some of the discrepancies between results from different workers may indicate such effects. It is important to understand the effects of production variables, not only for optimization of the production, but also in more fundamental studies of metallic glasses. For example, if the property variations arising from the production were similar to those due to composition changes, the interpretation of the effects of composition would be greatly hampered.

Considering their importance, there have been rather few studies of the effects of production variables. This is in large part due to the difficulty of varying the parameters in a controlled way, while still obtaining a glassy product. Metallic glasses can be produced in many ways, but in this paper only those made by melt-spinning [1] will be considered. In melt-spinning there are many parameters which can be adjusted, including the melt superheat and the flow in the molten alloy jet. One of the most controlled experiments, however, is to vary the wheel speed while keeping all other parameters fixed. Experimentally [2, 3] the ribbon thickness,  $D$ , appears to vary with the wheel speed,  $V$  as follows,

$$D \propto V^{-a}, \quad (1)$$

where  $a$  is approximately 0.75.

Thus a higher wheel speed gives a thinner ribbon, but the width is only slightly affected. It is expected that a thinner ribbon will have been quenched at a higher average rate,  $R$ , [4] where

$$R \propto D^{-1} \text{ for Newtonian cooling} \quad (2)$$

and

$$R \propto D^{-2} \text{ for ideal cooling.} \quad (3)$$

It seems that Newtonian cooling is more likely, i.e. that heat transfer across the ribbon-substrate interface is rate-controlling. The quench rate will vary during the cooling from the melt to the final ribbon, but it is desirable to characterize the production by an average quench rate,  $R$ . The ribbon thickness,  $D$ , a readily measured quantity, at least gives the order of values of  $R$  in a series of samples, and may be used to estimate relative values.

The property changes on annealing metallic glasses may be due to (a) the relief of quenched-in internal stresses, which occurs early in the anneal, (b) the structural relaxation of the glassy state, or, (c), in the latter stages of the anneal, the onset of crystallization or of separation into two glassy phases. The effects of quench rate are expected to be analogous, i.e. the property differences between slow-quenched and fast-quenched glasses should be similar to the differences between annealed and unannealed glasses. For example, higher rates

appear to quench-in higher internal stresses [5]. Also, at low rates a partially crystalline product may be obtained. The third effect is on the degree of relaxation of the glassy structure. A metallic glass, in common with other glasses, does not have a unique structural state. A more slowly quenched glass will have a more relaxed structure, akin to what would be obtained on annealing a more quickly quenched glass. In this paper the concern will be with the effect of quench rate on the degree of relaxation of the as-produced glass and on the kinetics of the subsequent relaxation induced by annealing. From the published studies [6–16] of the effect of production variables on the properties of metallic glasses, the work which seems relevant in the present case is summarized below.

For metallic glass ribbons the rate of relaxation of an externally applied stress can be measured readily [17]. The relaxation on annealing is rapid at first, then slower. Williams and Egami [18] have shown that pre-annealing greatly reduces the stress relaxation rate. These observations support the view that an annealed, i.e. more structurally relaxed, glass will have lower atomic mobility. Luborsky and Walter [10] showed that thinner, i.e. faster quenched, ribbons exhibited faster stress relaxation. Their results have been amply confirmed [8, 11, 15] and constitute perhaps the clearest evidence so far of the effect of quench rate on the degree of structural relaxation of metallic glasses.

Allia *et al.* [16] have measured the relative decay of magnetic permeability on annealing. This process also is faster in more rapidly quenched ribbons. The differences in behaviour due to the quench rate are reduced by pre-annealing.

Metallic glasses embrittle on annealing. One would expect that the rate of embrittlement would be greater in faster quenched ribbons. In contrast, however, it is found that faster quenched ribbons embrittle less easily [8, 15], i.e. after longer times or at higher temperatures. This effect can be explained if it is assumed that embrittlement corresponds to a critical degree of structural relaxation. Faster quenched glasses may indeed relax faster, but their starting condition is further from the critical relaxation, and they may therefore take longer to attain it.

The main technological interest in metallic glasses is because of their magnetic properties. These properties are particularly sensitive to

annealing and to quench rate, but are not easily interpreted in terms of structural relaxation. The coercivity, for example, is probably more strongly affected by internal stresses and incipient crystallization than by relaxation. The Curie temperature,  $T_c$ , however, is a useful parameter for studying structural relaxation, being sensitive to the relaxation and convenient to measure [19]. It is unaffected by relief of internal stresses and often unaffected by partial crystallization [20]. The disadvantages of using  $T_c$  are that it cannot be monitored continuously, and that if  $T_c$  is too high, unavoidable relaxation may occur during the determination, thereby obscuring any effects of pre-annealing. The Curie temperature of metallic glasses rises on annealing. It is therefore expected that faster quenched glass will have lower  $T_c$ . Mizoguchi *et al.* [12] have confirmed this. A negative result by Takayama and Oi [9] was due to the relaxation during the  $T_c$  determinations, because of the high  $T_c$  of their alloy.

An important feature of the  $T_c$  studies of relaxation is that at higher annealing temperatures the  $T_c$  eventually levels off after rising rapidly at first. The attainment of a final value of  $T_c$  signifies that an “internal equilibrium” has been reached. This may be true internal equilibrium, when the configuration of the metastable liquid is realised, or it may be a “local equilibrium” constrained by some slow relaxations. It has been suggested [21] that the former case applies to  $\text{Fe}_{80}\text{B}_{20}$  and the latter to more complex glasses. In either case the behaviour is as for true equilibrium, since the final values of  $T_c$  appear to be functions of temperature only and can be approached from higher or lower values. In the light of this, and of the embrittlement results mentioned above, the present aim is to use  $T_c$  measurements to answer two questions:

(a) Given that different degrees of relaxation can be obtained by quenching at different rates, will the various glasses relax to the same “equilibrium” structure on annealing?

(b) If so, will a fast-quenched or a slow-quenched glass attain “equilibrium” sooner?

## 2. Experimental procedure

$\text{Fe}_{81.5}\text{B}_{14.5}\text{Si}_4$  ribbons (composition in at%) were kindly supplied by Drs H. H. Liebermann and F. E. Luborsky of the General Electric Company. The ribbons, in five thicknesses, had been produced as part of a study of the effect of process

variables on the properties of amorphous alloys [15]. They were prepared by melt-spinning on a 25 cm diameter wheel. The wheel speed was varied while all other parameters were held constant. The thickness of the ribbons, which was approximately inversely proportional to the wheel speed, varied from 16.0  $\mu\text{m}$  to 58.2  $\mu\text{m}$ .

The Curie temperatures were determined by differential scanning calorimetry (DSC) using a Perkin Elmer DSC 2. A heating rate of 80  $\text{K min}^{-1}$  was used. General aspects of the technique are described elsewhere [19]. The  $T_c$  values were corrected for the temperature lag in the instrument by measuring them relative to the  $T_c$  of a nickel standard placed in the sample pan for each determination. Only one  $T_c$  determination was carried out on a given DSC sample. It was necessary to run up to six samples to obtain the  $T_c$  value, because there was some scatter.

Annealing was carried out in the differential scanning calorimeter: this has excellent temperature control ( $\pm 0.1$  K) and was calibrated to  $\pm 0.5$  K. The DSC was also used for crystallization studies; in this case the samples were heated at 40  $\text{K min}^{-1}$ . Transmission electron microscopy was performed in a JEM 120 instrument operated at 80 KV. Thin foils were prepared by ion-milling pre-annealed ribbons.

### 3. Results and discussion

#### 3.1. General relaxation behaviour

It was necessary first to verify that the structural relaxation behaviour of  $\text{Fe}_{81.5}\text{B}_{14.5}\text{Si}_4$  glass was similar to that of other iron-based metallic glasses, and that it could be monitored by measuring the Curie temperature. Fig. 1 shows that the measured  $T_c$  of a ribbon of  $\text{Fe}_{81.5}\text{B}_{14.5}\text{Si}_4$  glass varies strongly with the heating rate used to determine  $T_c$ . This is a real variation and does not arise from the temperature lags in the instrument which have been accounted for.  $T_c$  is higher at slower heating rates, because of the greater annealing effect during the determination. Such effects are undesirable (reflecting a rather high  $T_c$  in this case), but can be minimized by using high heating rates (80  $\text{K min}^{-1}$  in the present work). Fortunately the annealing effect during the determinations is not sufficient to obscure the effects of pre-annealing. The data on Fig. 1 indicate that annealing causes the  $T_c$  of  $\text{Fe}_{81.5}\text{B}_{14.5}\text{Si}_4$  glass to rise, in common with other iron-based glasses. In general, annealing these glasses at any temperature causes  $T_c$  to rise

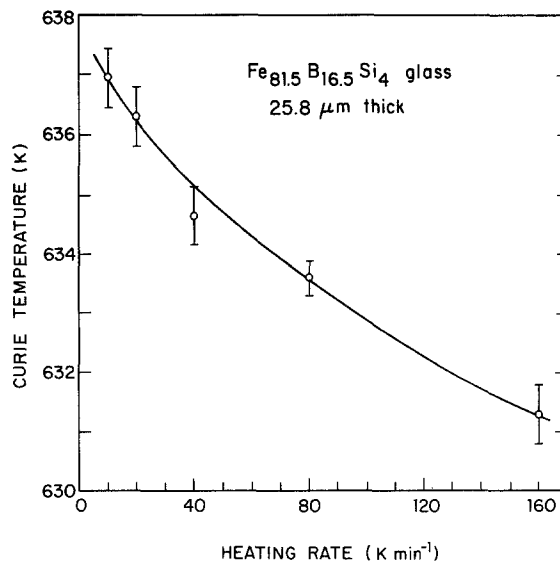


Figure 1 Effect of heating rate on the Curie temperature measured by DSC. Temperature lags in the instrument have been accounted for.

rapidly at first and then level off. The higher the annealing temperature, the more rapid is the  $T_c$  rise, but the lower the final value of  $T_c$  [21]. A common way of observing this behaviour is through a series of isochronal anneals. Fig. 2 shows the results of this experiment on two ribbons of  $\text{Fe}_{81.5}\text{B}_{14.5}\text{Si}_4$  glass. The change in Curie temperature,  $\Delta T_c$ , is plotted against the annealing temperature,  $T_a$ , for 15-minute anneals. The expected result is a peak in  $\Delta T_c$ : at high temperatures, above the peak, the glass gets close to "equilibrium" in the time of the anneal, and the slope of the curve reflects the variation of final  $T_c$  with  $T_a$ ; at lower temperatures, however, the glass is still far from "equilibrium", and the shape of the curve illustrates the faster kinetics as  $T_a$  is raised. It can be seen from Fig. 2 that there is a peak in  $\Delta T_c$  at about 630 K, but this is followed by a sharp rise. It has been suggested that such a rise in other systems could be due to the onset of crystallization [20], and for the present case that will be verified in the next section. The conclusion of this section is that the structural relaxation of  $\text{Fe}_{81.5}\text{B}_{14.5}\text{Si}_4$  glass, as revealed by  $T_c$  changes, is similar to that of iron-based glasses in general. The two curves in Fig. 2 give the first indication of the effect of ribbon thickness, i.e. quench rate, on relaxation behaviour, which is the main concern of this paper.

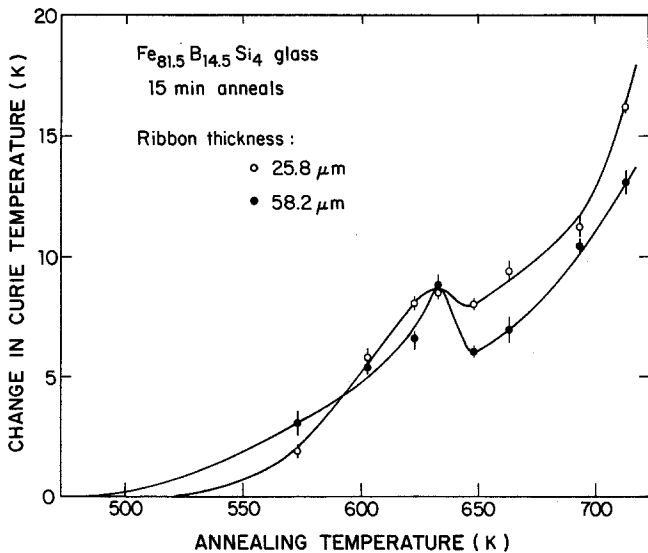


Figure 2 The rise in Curie temperature on 15 min anneals at selected temperatures. Initial values: 633.6 K for the 25.8  $\mu\text{m}$  ribbon; 637.6 K for the 58.2  $\mu\text{m}$  ribbon.

### 3.2. Crystallization

Samples of all the ribbons of the glass were heated at  $40 \text{ K min}^{-1}$  in the differential scanning calorimeter. In all cases two peaks were found on the trace, as illustrated in Fig. 3 for the 21.6  $\mu\text{m}$  thick ribbon. The two peaks indicate two reactions. It was found that pre-annealing could be used to drive the first reaction to completion. For example, an anneal at 718 K for 20 min has this effect (Fig. 3). After this anneal the microstructure was examined by transmission electron microscopy. This shows that the first reaction ("primary crystallization") consists of the precipitation of  $\alpha\text{-Fe}$  in a highly dendritic form (Fig. 4). The den-

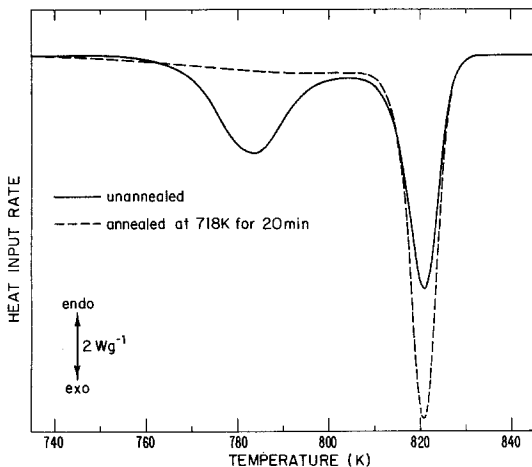
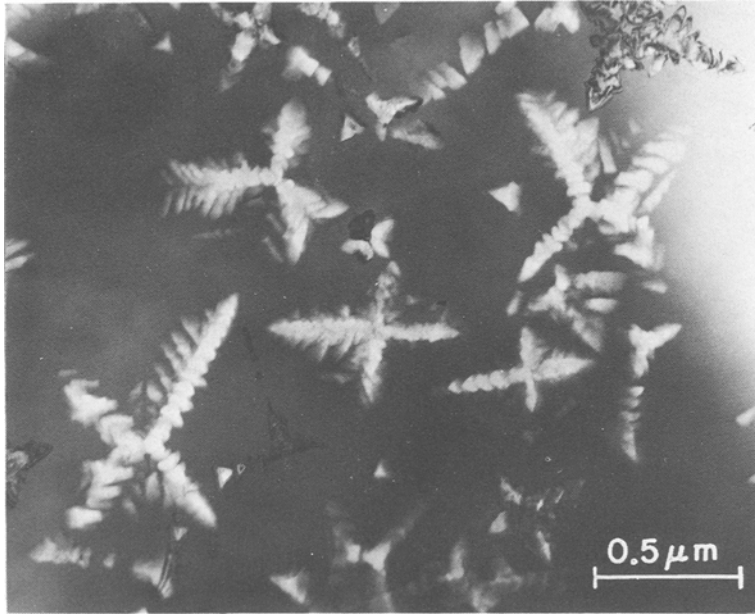


Figure 3 DSC curves obtained on heating samples from a 21.6  $\mu\text{m}$  ribbon of  $\text{Fe}_{81.5}\text{B}_{14.5}\text{Si}_4$  glass at  $40 \text{ K min}^{-1}$ . Pre-annealing can drive the first, exothermic reaction to completion.

drite arms are parallel to  $[100]$   $\alpha\text{-Fe}$ . Some of the crystals appear to be twinned. As far as it is possible to assess, the orientation of the crystals appears to be random. The crystallization morphology is remarkably similar to that found by Swartz *et al.* in an  $\text{Fe}_{81}\text{B}_{13.5}\text{Si}_{3.5}\text{C}_2$  glass [22, 23].

The effect of partial crystallization on the Curie temperature of the remaining amorphous phase was studied on annealing at 718 K. The rise in  $T_c$  is shown in Fig. 5, and at each stage the percentage total primary crystallization is indicated. This percentage was estimated from the relative decrease in the area of the first DSC peak. At this comparatively high annealing temperature it is expected that any rise in  $T_c$  due to structural relaxation will be over quickly ( $\ll 5 \text{ min}$ ), so that the continuing rise at longer times is due to the changing composition of the remaining amorphous phase as the growing  $\alpha\text{-Fe}$  crystals reject B and Si into it. Such a rise is consistent with the results of Durand and Yung [24] who have shown that the  $T_c$  of iron-based glasses rises as the metalloid (particularly B) content is increased. After greater than 15 min at 718 K the  $T_c$  of the amorphous matrix was not detectable by DSC. It is not clear why this is so, but it may be because the magnetic transition is blurred by substantial composition gradients in the matrix. It is concluded that in this alloy primary crystallization of  $\alpha\text{-Fe}$  causes the  $T_c$  of the remaining amorphous phase to rise, and that the rise in  $\Delta T_c$  above 650 K in Fig. 2 can reasonably be attributed to this. By annealing at lower temperatures this effect can be avoided, and the  $T_c$



**Figure 4** Transmission electron micrograph of 21.6  $\mu\text{m}$  ribbon of  $\text{Fe}_{81.5}\text{B}_{14.5}\text{Si}_4$  glass pre-annealed at 718 K for 20 min. Dendritic  $\alpha\text{-Fe}$  crystals in an amorphous matrix.

changes can be attributed to structural relaxation alone.

The DSC curves for the as-received ribbons (e.g. for the 21.6  $\mu\text{m}$  ribbon in Fig. 3) were all identical except for the thickest ribbon (58.2  $\mu\text{m}$ ), for which the first peak occurred about 1 K lower. This would be consistent with a small degree of crystallinity [25]. The magnetic properties determined by Luborsky *et al.* [15] suggest that not only this sample, but also the next thickest (41.7  $\mu\text{m}$ ) could be slightly crystalline.

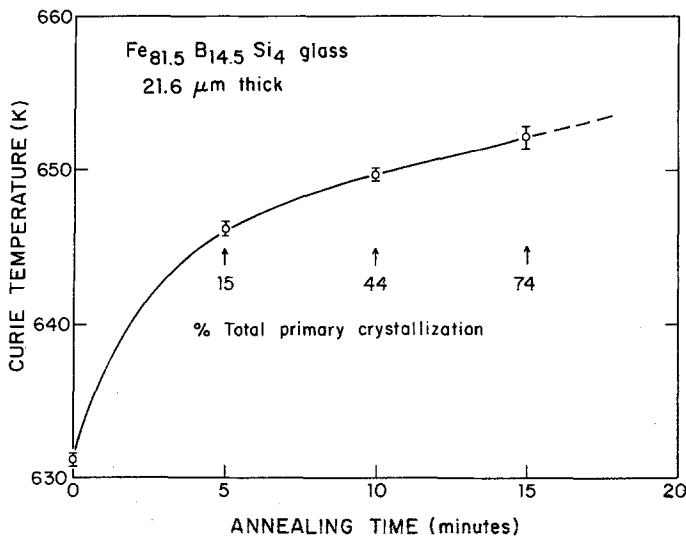
### 3.3. Effect of quench rate

The Curie temperatures of the as-quenched ribbons

are shown as a function of thickness in Fig. 6. Each point represents the average of six determinations and the standard error is shown. As expected,  $T_c$  is lower for the thinner, i.e. faster quenched, ribbons. The thinnest ribbon, however, appears to be anomalous.

It is known that there is an annealing effect during the  $T_c$  determination (Fig. 1). If that effect were greater for the 16.0  $\mu\text{m}$  ribbon it could explain its high value of  $T_c$ . In fact, though, this ribbon exhibited the same variation of  $T_c$  with heating rate as in Fig. 1. Its anomalously high value of  $T_c$  in the as-quenched state is a real effect.

Partial crystallinity of the 41.7  $\mu\text{m}$  and 58.2  $\mu\text{m}$



**Figure 5** The increase in Curie temperature on annealing a 21.6  $\mu\text{m}$  ribbon of  $\text{Fe}_{81.5}\text{B}_{14.5}\text{Si}_4$  glass at 718 K. Primary crystallization occurs during the anneal.

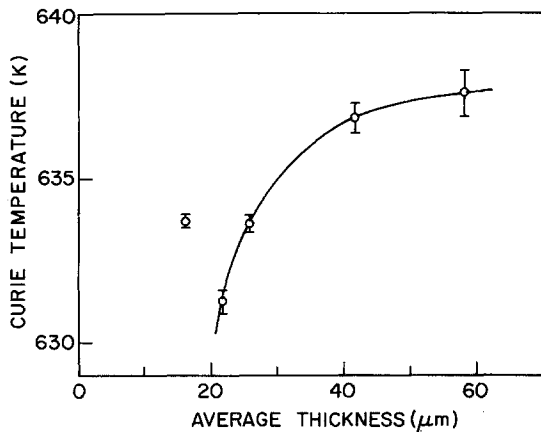


Figure 6 The initial Curie temperatures of five ribbon thicknesses of  $\text{Fe}_{81.5}\text{B}_{14.5}\text{Si}_4$  glass. Each point is the average of six measurements.

ribbons could make a small contribution to their high  $T_c$  values. In any case, measurements on them show a wider scatter than for the other samples.

Fig. 7 shows the effect of annealing the ribbons at 633 K. In all the ribbons  $T_c$  rises rapidly at first and then begins to level off at a final "equilibrium" value. It appears that all the glasses are tending to the same equilibrium: compare the spread in initial  $T_c$  values with the spread after 360 min of anneal. It is also noteworthy that the curves in Fig. 7 do not cross: although at any instant the faster quenched ribbons (with lower initial  $T_c$ ) do relax faster, their  $T_c$  values do not "overtake" those of the more slowly quenched ribbons. Thus to reach "equilibrium", or any given value of  $T_c$  it will take a faster quenched glass longer, despite its greater atomic mobility. This is precisely the effect needed to explain the embrittlement results in the introduction. The 16.0  $\mu\text{m}$  and 25.8  $\mu\text{m}$  ribbons

not only have similar initial  $T_c$  values, but their behaviour on annealing at 633 K is almost identical. This leads to the speculation that these ribbons, despite their different thicknesses, might somehow have been quenched at the same rate.

The relaxation behaviour is very different on annealing at a lower temperature, 573 K. In this case, shown in Fig. 8, the faster quenched glasses relax so much faster that the  $T_c$  curves do cross. At 573 K "equilibrium" is not reached in the time of the anneals used (500 min). Although the curves appear to level off, the  $T_c$  values are likely to continue rising slowly over a period of days (based on experience with other glasses, e.g.  $\text{Fe}_{80}\text{B}_{20}$  [19]). Thus, on low temperature annealing, far from "equilibrium", the kinetics of relaxation seem to be particularly dependent on the quench rate. It is of interest that now the 16.0  $\mu\text{m}$  and 25.8  $\mu\text{m}$  ribbons behave very differently, the thicker ribbon relaxing more slowly as would normally be expected.

That the curves of  $T_c$  against time can cross (as in Fig. 8) is a manifestation of the "memory" effect in metallic glasses [26]. Two ribbons, though they may attain the same value of  $T_c$  during annealing, evidently do not have the same structure, because they do not have identical relaxation behaviour thereafter. The  $T_c$  value is not sufficient to describe the contribution of thermal history to the structure of the glass.

### 3.4. Discussion

The annealing behaviour at 633 K (Fig. 7) indicates that all the glasses tend toward the same "equilibrium". If the saturation of the  $T_c$  changes indicates true internal equilibrium then this result is expected since the glasses came from the same

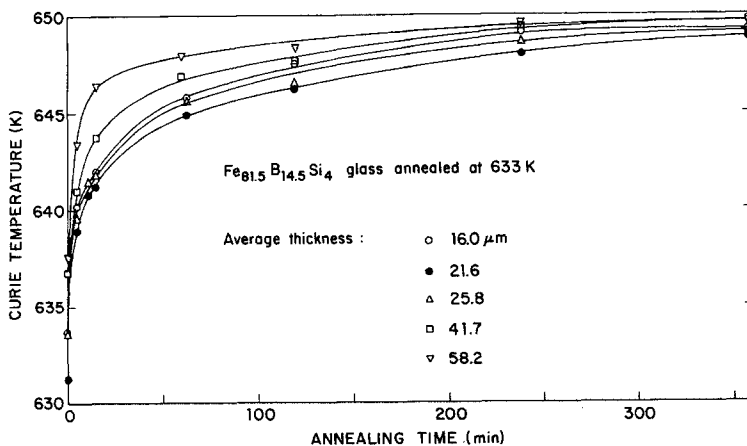


Figure 7 The increase in Curie temperature on annealing ribbons of  $\text{Fe}_{81.5}\text{B}_{14.5}\text{Si}_4$  glass at 633 K. All samples tend to the same equilibrium. (Each point represents the average of at least two measurements.)

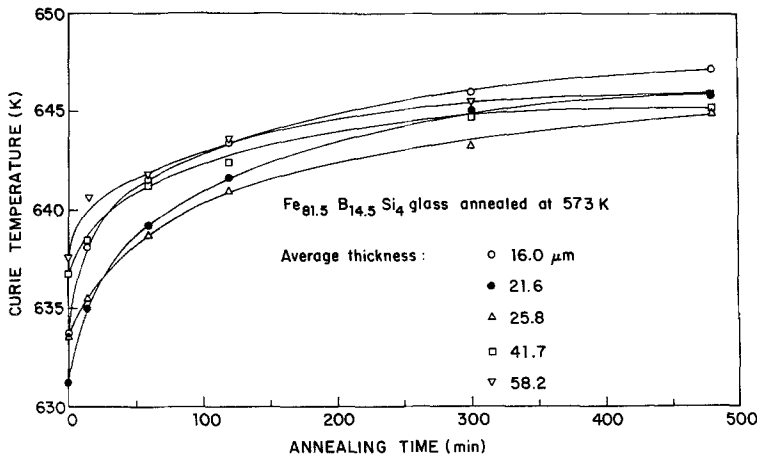


Figure 8 The increase in Curie temperature on annealing ribbons of  $\text{Fe}_{81.5}\text{B}_{14.5}\text{Si}_4$  glass at 573 K. (Each point represents the average of at least two measurements.)

liquid and should attain the equilibrium liquid structure on annealing. Thus, annealing should help to reduce the variability and irreproducibility of properties in as-quenched samples, something which has often been found to be true. In future work it would be interesting to compare melt-quenched glasses with, e.g., sputtered glasses of the same composition. The latter materials might relax to a different internal equilibrium on annealing, since they do not inherit any short-range order from the liquid.

In Section 1 the question “will a fast-quenched glass or a slow-quenched glass be the first to attain a given degree of relaxation on annealing” was posed. The fast-quenched glass will relax faster, but it has further to go. The results presented in Figs 7 and 8 show that either answer is possible. At higher annealing temperatures the slow-quenched glass will attain a given state (or rather a given value of a property, in this case  $T_c$ ) sooner. At lower temperatures, however, the relaxation rate appears to be very sensitive to the quench rate, and a fast-quenched glass may attain a given property value before a slow-quenched one. Since diffusion [27] and viscosity [28] measurements are normally made at low annealing temperatures (to avoid crystallization) and since these atomic transport properties are particularly sensitive to the degree of relaxation, it is clear that the effect of quench rate in these experiments could be significant.

At 573 K the samples are still far from equilibrium, even after 500 min of anneal. The total  $T_c$  change corresponding to the attainment of internal equilibrium may be much larger than the differences in initial  $T_c$  due to quench rate. The relaxation behaviour is dominated by the faster relax-

ation of the faster quenched glasses. At 633 K, however, the differences in initial  $T_c$  are a significant fraction of the total relaxation range, and the initial differences may prevail, giving rise to a different pattern of behaviour.

This argument may be put in more specific terms. Egami [29] was the first to suggest that there are two mechanisms of relaxation in metallic glasses. His suggestion has been taken up by others: for a discussion see [21]. Here the mechanisms will be called “short-range rearrangement” (SRR), taking place at lower temperatures, and “long-range rearrangement” (LRR) at higher temperatures. Both SRR and LRR contribute to the  $T_c$  changes, but the kinetics of the changes are determined primarily by the degree of relaxation or order due to LRR: more LRR gives a more relaxed structure, with slower kinetics. Thus, on low temperature annealing SRR occurs, but no LRR. The relaxation kinetics are controlled by the quenched-in LRR-order. The faster quenched glasses, with less quenched-in LRR-order, relax faster and continue to do so well into the anneal (Fig. 8). At higher annealing temperatures, however, LRR also can take place. During the anneal this acts to diminish the effect of quench rate. The approach to final equilibrium is, then, similar for all the ribbons (Fig. 7).

The idea of two relaxation mechanisms is useful in interpreting the anomalous relaxation of the 16.0  $\mu\text{m}$  ribbon. At 573 K its annealing behaviour suggests that it has the lowest degree of LRR-order, as expected for the thinnest (fastest quenched) ribbon. Its initial value of  $T_c$ , however, is close to that of the 25.8  $\mu\text{m}$  ribbon. This could arise from a higher initial degree of SRR-order, compensating for the LRR-order. On annealing

at 633 K both relaxation mechanisms operate and the overall behaviour of the 16.0  $\mu\text{m}$  and 25.8  $\mu\text{m}$  ribbons can be nearly identical, despite differing contributions from SRR and LRR. That two ribbons can have the same value of a property (in this case  $T_c$ ), and yet have differing degrees of order due to SRR and LRR, is another example of the memory effect, and can be readily explained by their thermal history. During the quench the "freezing" temperature for LRR is higher than for SRR. The behaviour of the 16.0  $\mu\text{m}$  ribbon would seem to indicate, therefore, that its quench rate was normal at the temperature where LRR was frozen out, but that the rate became anomalously low at lower temperatures, quenching in too high a degree of SRR-order. This would be the case, for example, if the ribbon came off the wheel sooner than expected. Obviously, characterizing the quench by a single rate is an oversimplification.

#### 4. Conclusions

Measurements of Curie temperature,  $T_c$ , can be used to monitor structural relaxation in  $\text{Fe}_{81.5}\text{B}_{14.5}\text{Si}_4$  glass. Faster quenching produces less relaxed glasses, affecting not only the properties of the as-produced materials, but also their behaviour on annealing. Structural relaxation is faster in fast-quenched than in slow-quenched glasses, particularly at low annealing temperatures. All the glasses, however, tend to the same equilibrium on annealing. The results can be interpreted in terms of two relaxation mechanisms.

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