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Structural relaxation and embrittlement in Fe–Ni based metallic glasses

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The fracture strain, changes in electrical resistivity and Curie temperature, and the volume change (the amount of annealed-out excess volume) were measured as a function of annealing temperature in some Fe–Ni based metallic glasses ($Fe_{27}Ni_{53}P_{14}B_6$, $Fe_{29}Ni_{49}P_{14}B_6Si_2$, $Fe_{40}Ni_{40}P_{14}B_6$, $Fe_{40}Ni_{38}Si_8B_{14}$ and $Fe_{63}Ni_{15}Si_8B_{14}$), in order to clarify the embrittlement behaviour during structural relaxation. A close relationship between the ductile–brittle transition temperature and the resistivity change was observed in these metallic glasses. Particularly, in $Fe_{27}Ni_{53}P_{14}B_6$ metallic glass, it was found that the ductile–brittle transition temperature is well consistent with the annealing temperature at which the changes in resistivity and Curie temperature are maximum. The results obtained in the present study indicate that the embrittlement behaviour during structural relaxation in these Fe–Ni based metallic glasses is closely related to the formation of more stable short range ordered structure.

1. Introduction

Metallic glasses exhibit excellent mechanical properties such as high strength and plasticity (ductility). However, the mechanical properties of metallic glasses depend strongly on casting conditions and subsequent thermal treatment. Fe-based metallic glasses in particular, often become brittle easily when annealed at temperatures well below the glass transition and/or crystallization temperatures. Although several models [1–8] for embrittlement in metallic glasses have been proposed, the origin of embrittlement is not well clarified at the present time and is still one of the important subjects in metallic glasses.

In general, it is considered that the embrittlement in metallic glasses, which occurs during low-temperature annealing well below the crystallization temperature, is closely related to structural relaxation. As proposed by Egami [9], the most important features in the structural relaxation are short range ordering and the decrease in the quenched-in excess volume. Thus, it is extremely interesting to examine the relationship between the embrittlement behaviour and the short range ordering or the decrease in the quenched-in excess volume during the structural relaxation. A resistometric study is particularly sensitive and informative for the change in short range ordering during structural relaxation in Fe–Ni based metallic glasses [10–12]. The measurement of Curie temperature is also a useful technique for the study of short range ordering in ferromagnetic metallic glasses [9, 13–15]. The decrease in the quenched-in excess volume during the structural relaxation can be estimated from the length changes [16–18].

In the present study, the fracture strain, changes in electrical resistivity and Curie temperature, and the volume change (the amount of annealed-out excess volume) were measured as a function of annealing temperature in some Fe–Ni based metallic glasses ($Fe_{27}Ni_{53}P_{14}B_6$, $Fe_{29}Ni_{49}P_{14}B_6Si_2$, $Fe_{40}Ni_{40}P_{14}B_6$, $Fe_{40}Ni_{38}Si_8B_{14}$ and $Fe_{63}Ni_{15}Si_8B_{14}$), in order to clarify the origin of embrittlement during the structural relaxation in metallic glasses.

2. Experimental procedure

Some Fe-Ni based metallic glasses ($Fe_{27}Ni_{53}P_{14}B_6$,

$Fe_{29}Ni_{49}P_{14}B_6Si_2$, $Fe_{40}Ni_{38}Si_8B_{14}$ and $Fe_{63}Ni_{15}Si_8B_{14}$) were prepared in the form of a ribbon by rapid quenching using a single roller casting apparatus. Since the embrittlement behaviour in metallic glasses depends greatly on the cooling rate [19], casting conditions producing similar cooling rates are desired to clarify the origin of embrittlement. It is well known that the cooling rate is inversely proportional to the sample thickness [20]. Thus, Fe-Ni based metallic glasses with similar thicknesses were prepared in the present study. The sample thickness was around 0.02 mm. Two Metglas 2826 ($Fe_{40}Ni_{40}P_{14}B_6$) with a large thickness produced by Allied Co. were also used; one is ductile with 0.04 mm thickness and the other is already brittle in as-quenched state with 0.05 mm thickness. The amorphous state of the sample was confirmed by X-ray diffraction. The glass transition (T_g) and crystallization (T_x) temperatures were determined by differential scanning calorimetry (DSC) at a heating rate of $10\,K\,min^{-1}$.

The degree of ductility was determined by measuring the radius of curvature at which fracture occurred in a simple bend test between parallel plates [1]. The strain required for fracture, ϵ_f, is expressed as $\epsilon_f = t/(2r - t)$, where $2r$ is the distance between parallel plates at fracture and t is the thickness of the ribbon specimen. Thus, $\epsilon_f = 1$ (when $2r = 2t$) means that the sample is not brittle but ductile. Measurements of electrical resistivity were made using a four point probe method. As-quenched samples were spot-welded carefully by small Cu wires. The resistivity change ($\Delta\rho/\rho$) at various annealing temperatures for as-quenched and pre-annealed samples were measured at liquid nitrogen temperature. The Curie temperatures of as-quenched and annealed samples were measured by DSC or by the temperature dependence of magnetic permeability. Thermal treatment was carried out in an argon or nitrogen gas atmosphere. Volume changes during the structural relaxation and crystallization were estimated using the relation of $3\Delta l/l = \Delta V/V$, where $\Delta l/l$ is the length change and $\Delta V/V$ is the volume change. The length changes ($\Delta l/l$) were measured using a Rigaku Denki TMA unit with an infrared furnace. The isochronal annealing method was used to measure the length changes at various annealing temperatures. In this method, the total length change at an annealing temperature is estimated as a sum of the length change at the annealing temperature and length changes at the lower annealing temperatures. A high heating rate of $100\,K\,min^{-1}$ was used to minimize the possible length change during the heating process from one annealing temperature to the next. The annealing time at each annealing temperature was 30 min. A very small load (~ 2 g) was applied to set up the sample straightly and to minimize possibly creep at high temperatures.

3. Results

In as-quenched $Fe_{27}Ni_{53}P_{14}B_6$ metallic glass, the relationships between the fracture strain (ϵ_f) and the resistivity change ($\Delta\rho/\rho$), the fracture strain and the change in Curie temperature (ΔT_c), and the fracture strain and the volume change ($\Delta V/V$) are shown in Figs. 1, 2 and 3 as a function of annealing temperature, respectively. It is obvious that in as-quenched $Fe_{27}Ni_{53}P_{14}B_6$ metallic glass, embrittlement occurs at low temperature annealing well below the glass transition ($T_g = 375°$ C) or the crystallization ($T_x = 414°$ C) temperatures. The ductile–brittle transition temperature at which the ductility is lost rapidly is around 250° C. Furthermore, it is seen that the ductile–brittle transition temperature is well consistent with the annealing temperature at which the changes in both resistivity and Curie

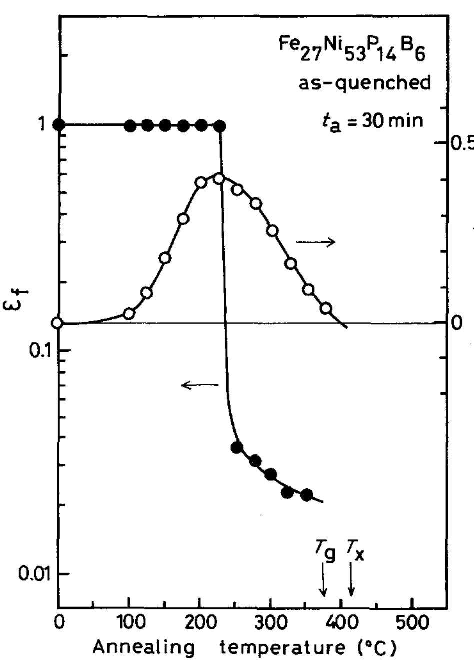

Figure 1 Fracture strain (ϵ_f) and resistivity change ($\Delta\rho/\rho$) as a function of annealing temperature in as-quenched $Fe_{27}Ni_{53}P_{14}B_6$ metallic glass.

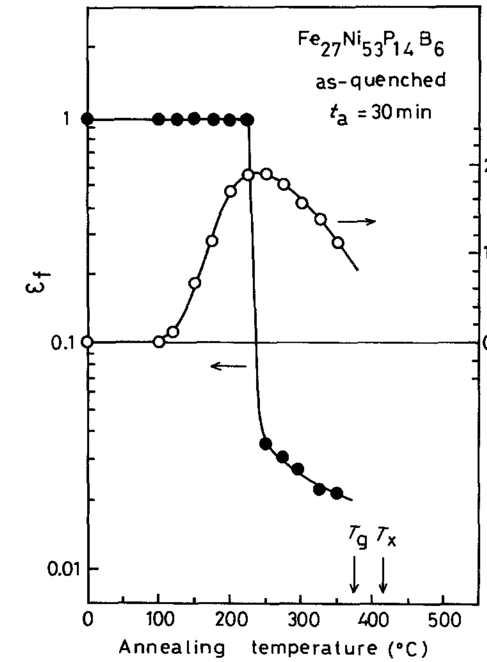

Figure 2 Fracture strain (ϵ_f) and change in Curie temperature (ΔT_c) as a function of annealing temperature in as-quenched $Fe_{27}Ni_{53}P_{14}B_6$ metallic glass.

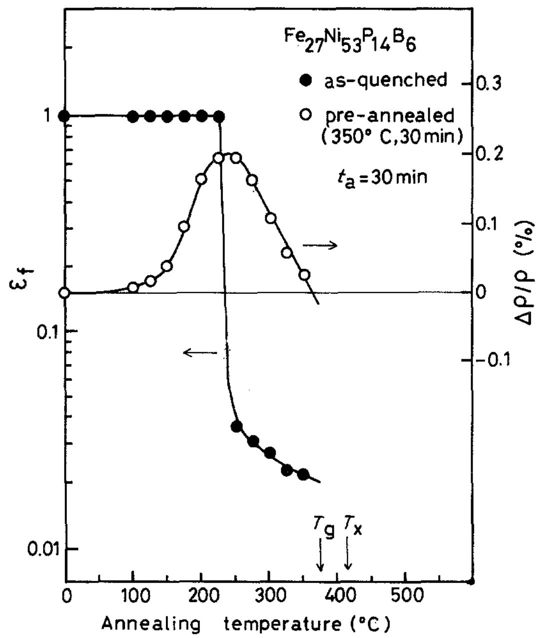

Figure 4 Fracture strain (ϵ_s) in as-quenched sample and resistivity change ($\Delta\rho/\rho$) in pre-annealed sample as a function of annealing temperature in $Fe_{27}Ni_{53}P_{14}B_6$ metallic glass.

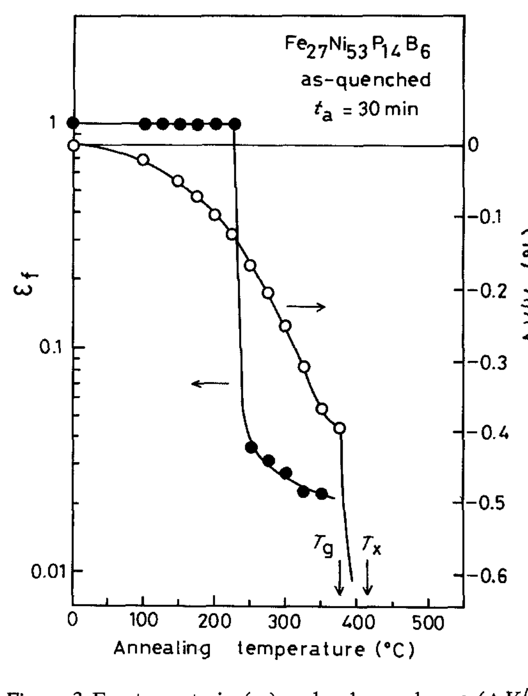

Figure 3 Fracture strain (ϵ_f) and volume change ($\Delta V/V$) as a function of annealing temperature in $Fe_{27}Ni_{53}P_{14}B_6$ metallic glass.

temperature are maximum. As can be seen in Fig. 3, the quenched-in excess volume in as-quenched $Fe_{27}Ni_{53}P_{14}B_6$ metallic glass decreased gradually with increasing the annealing temperature, but any drastic change in volume was not observed around the ductile–brittle transition temperature.

The as-quenched $Fe_{27}Ni_{53}P_{14}B_6$ metallic glass was pre-annealed at 350° C for 30 min, and then the changes in resistivity and Curie temperature which occur during the subsequent annealing below the pre-annealing temperature were measured as a function of annealing temperature and compared with the fracture strain in as-quenched $Fe_{27}Ni_{53}P_{14}B_6$ metallic glass. The results are shown in Figs. 4 and 5. In the pre-annealed sample, the annealing temperature causing the maximum changes in resistivity and Curie temperature during the structural relaxation is determined more clearly. Furthermore, it is obvious that the ductile–brittle transition temperature in the as-quenched sample is well consistent with the annealing temperature at which the changes in resistivity and Curie temperature in the pre-

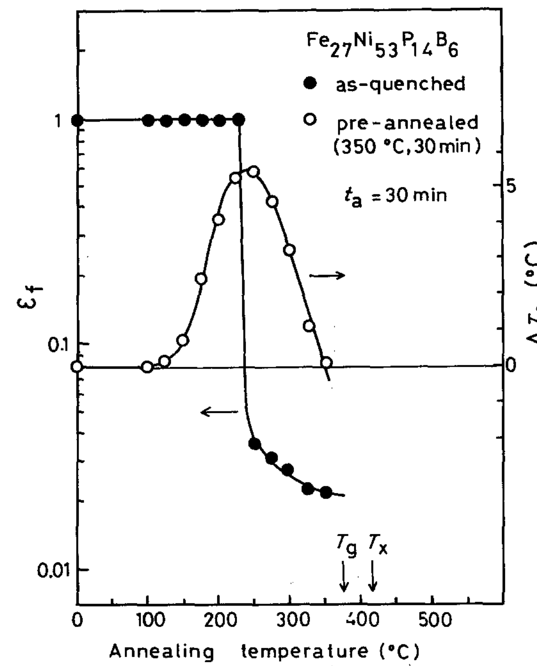

Figure 5 Fracture strain (ϵ_f) in as-quenched sample and change in Curie temperature (ΔT_c) in pre-annealed sample as a function of annealing temperature in $Fe_{27}Ni_{53}P_{14}B_6$ metallic glass.

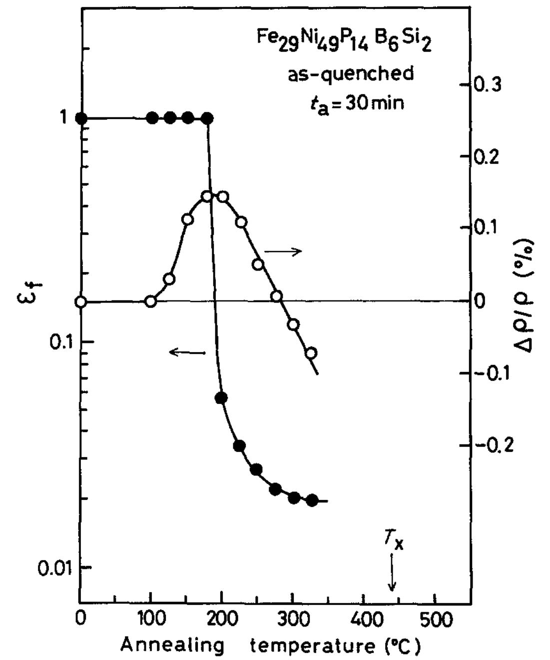

Figure 6 Fracture strain (ϵ_f) and resistivity change ($\Delta\rho/\rho$) as a function of annealing temperature in as-quenched $Fe_{29}Ni_{49}P_{14}B_6Si_2$ metallic glass.

annealed sample are maximum, similar to the case in the as-quenched sample.

The fracture strain and the resistivity change in as-quenched $Fe_{29}Ni_{49}P_{14}B_6Si_2$ metallic glass is shown in Fig. 6 as a function of annealing temperature. The results are similar to those in as-quenched $Fe_{27}Ni_{53}P_{14}B_6$ metallic glass. That is, the ductile–brittle transition temperature ($\approx$ 200° C) is well consistent with the annealing temperature at which the resitivity change is maximum.

In as-quenched $Fe_{40}Ni_{40}P_{14}B_6$ metallic glass with a large thickness (0.04 mm) produced by Applied Co., the fracture strain and the resistivity change are shown in Fig. 7 as a function of annealing temperature. It is clear that $Fe_{40}Ni_{40}P_{14}B_6$ metallic glass becomes brittle at extremely low temperature annealing around 175° C. Furthermore, the ductile–brittle transition temperature ($\approx$ 175° C) is not consistent with the annealing temperature ($\approx$ 200° C) at which the resitivity change is maximum, but is close. The volume changes during the structural relaxation and crystallization in both ductile and brittle $Fe_{40}Ni_{40}P_{14}B_6$ metallic glasses were measured, and the results are shown in Fig. 8. As can be seen from Fig. 8, it is clear that the volume changes during structural relaxation and crystallization in the ductile sample are considerably larger than those in the brittle sample. Particularly, in the brittle sample, the volume change does not

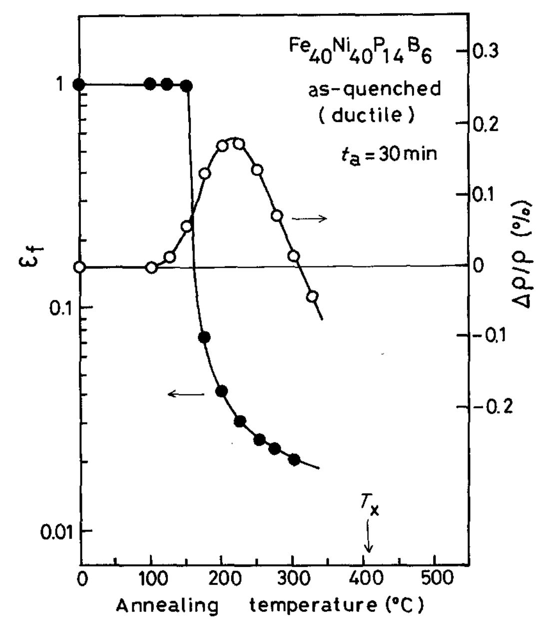

Figure 7 Fracture strain (ϵ_f) and resistivity change ($\Delta\rho/\rho$) as a function of annealing temperature in as-quenched (ductile) $Fe_{40}Ni_{40}P_{14}B_6$ metallic glass.

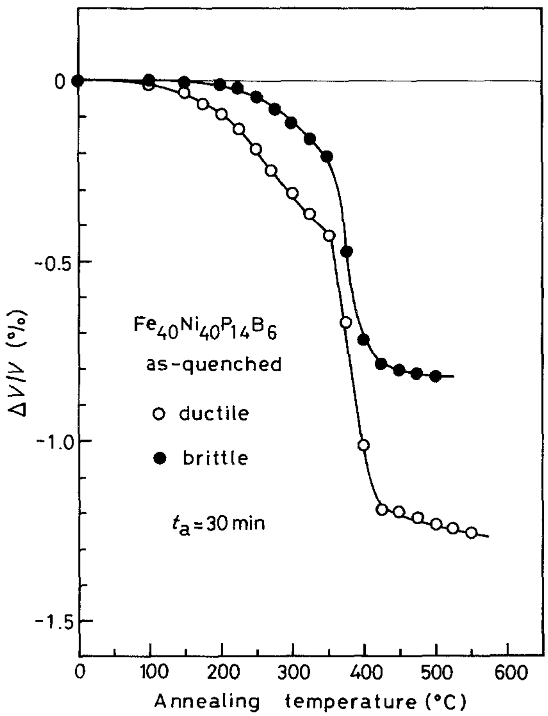

Figure 8 Volume changes ($\Delta V/V$) as a function of annealing temperature in ductile and brittle $Fe_{40}Ni_{40}P_{14}B_6$ metallic glass.

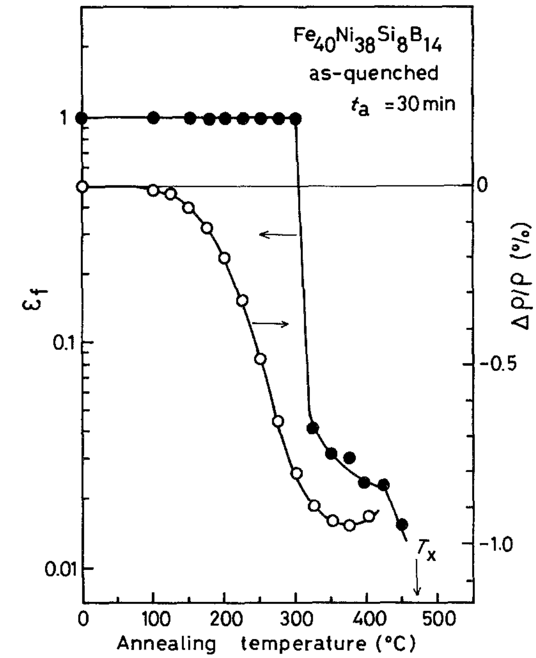

Figure 9 Fracture strain (ϵ_f) and resistivity change ($\Delta\rho/\rho$) as a function of annealing temperature in as-quenched $Fe_{40}Ni_{38}Si_8B_{14}$ metallic glass.

almost occur up to the annealing temperature of around 200° C. Curie temperatures in as-quenched ductile and brittle $Fe_{40}Ni_{40}P_{14}B_6$ metallic glasses were measured by DSC at a heating rate of 30 K min^{-1}, and the values of T_c = 277° C for the ductile sample and T_c = 286° C for the brittle sample were obtained. Thus, the Curie temperature in the brittle sample is larger than that in the ductile sample.

In as-quenched $Fe_{40}Ni_{38}Si_8B_{14}$ metallic glass, the relationships between the fracture strain and the resistivity change, and the fracture strain and the volume change are shown in Figs. 9 and 10, respectively. It is obvious that $Fe_{40}Ni_{38}Si_8B_{14}$ metallic glass becomes brittle at annealing temperatures below the crystallization temperature (T_x = 470° C). The ductile–brittle transition temperature in as-quenched $Fe_{40}Ni_{38}Si_8B_{14}$ metallic glass is around 325° C, and a large decrease in the resistivity was observed in the sample annealed at around 325° C. The Curie temperature in as-quenched $Fe_{40}Ni_{38}Si_8B_{14}$ metallic glass was 350° C, while in the sample annealed at 325° C for 30 min, its value was 357° C. The fracture strain in the as-quenched sample and the resistivity change in the pre-annealed sample (375° C, 1 hour) are shown in Fig. 11 as a function of annealing temperature. It is to be noted that the ductile–brittle transition temperature in the as-quenched sample is almost consistent with the annealing temperature at which the resistivity change in the pre-annealed sample is minimum. Similar behaviour was observed in $Fe_{63}Ni_{15}Si_8B_{14}$ metallic glass, and the results are shown in Fig. 12.

4. Discussion

It is well known that as-quenched metallic glasses have a large anelasticity [21]. A large anelasticity in as-quenched metallic glasses can be explained by considering that some unstable atoms in disordered structure move or change their positions under an applied stress. That is, an applied stress is relaxed easily due to the atomic movements in as-quenched metallic glasses. It is considered that the ductility in as-quenched metallic glasses is closely related to the atomic movements under a shear stress, similar to anelasticity. On the other hand, if a stable short range ordered structure is formed and the quenched-in excess volume decreases during the structural relaxation, it is expected that the atomic movements would become more difficult. In fact, it is well known that various properties such as anelasticity, diffusion and internal friction

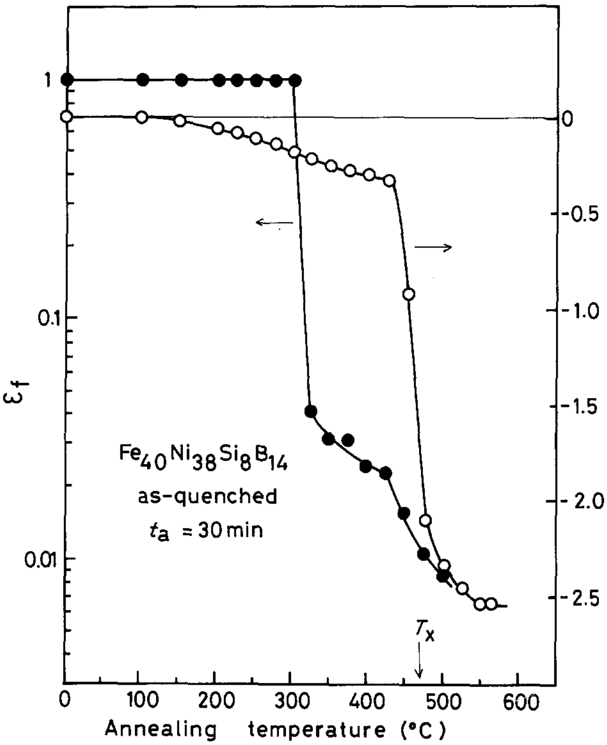

Figure 10 Fracture strain (ϵ_f) and volume change ($\Delta V/V$) as a function of annealing temperature in $Fe_{40}Ni_{38}Si_8B_{14}$ metallic glass.

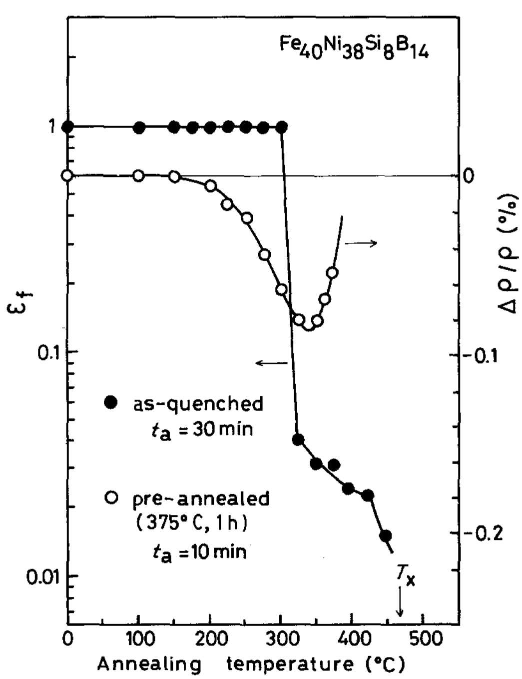

Figure 11 Fracture strain (ϵ_f) in as-quenched sample and resistivity change ($\Delta\rho/\rho$) in pre-annealed sample as a function of annealing temperature in $Fe_{40}Ni_{38}Si_8B_{14}$ metallic glass.

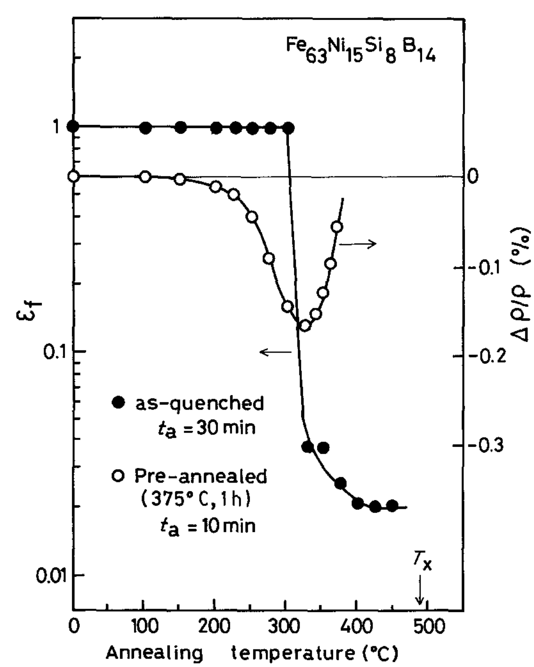

Figure 12 Fracture strain (ϵ_f) in as-quenched sample and resistivity change ($\Delta\rho/\rho$) in pre-annealed sample as a function of annealing temperature in $Fe_{63}Ni_{15}Si_8B_{14}$ metallic glass.

related to the atomic movements are significantly reduced due to the structural relaxation [22–26].

Changes in Curie temperature by annealing is one of the most characteristic phenomena in the structural relaxation of ferromagnetic metallic glasses. Egami [9] has proposed that the increase and reversible changes in Curie temperature in $Fe_{27}Ni_{53}P_{14}B_6$ metallic glass are caused primarily by the short range ordering (SRO) between Fe and Ni atoms. Other authors [13–15] have also discussed the SRO during the structural relaxation in Fe–Ni based metallic glasses by measuring the changes (increase) in Curie temperature. On the other hand, Balanzat [10] and Balanzat *et al.* [11] have shown the formation of SRO during the structural relaxation in $Fe_{40}Ni_{40}P_{14}B_6$ metallic glass by measuring the resistivity change. Recently, Komatsu *et al.* [12] have discussed the SRO during the structural relaxation in $(Fe_xNi_{1-x})_{78}Si_8B_{14}$ metallic glasses from the resistivity change. At the present time, it would be reasonable to assume that the changes in resistivity and Curie temperature during the structural relaxation in Fe-Ni based metallic glasses are due to the formation of SRO. Furthermore, the maximum (or minimum) changes in resistivity and Curie temperature during the structural relaxation in as-quenched or pre-annealed samples may correspond to the formation of more stable short range ordered structure.

In $Fe_{27}Ni_{53}P_{14}B_6$ metallic glass, the ductile–brittle transition temperature is well consistent with the annealing temperature at which the maximum changes in resistivity and Curie temperature are observed. Furthermore, in $Fe_{29}Ni_{49}P_{14}B_6Si_2$, $Fe_{40}Ni_{38}Si_8B_{14}$ and $Fe_{63}Ni_{15}Si_8B_{14}$ metallic glasses, the embrittlement occurs at the annealing temperature which causes the maximum or minimum change in resistivity. These results may indicate that, in as-quenched $Fe_{27}Ni_{53}P_{14}B_6$, $Fe_{29}Ni_{49}P_{14}B_6Si_2$, $Fe_{40}Ni_{38}Si_8B_{14}$ and $Fe_{63}Ni_{15}Si_8B_{14}$ metallic glasses, the embrittlement occurs due to the formation of a more stable short range ordered structure. That is, it is considered that the ductility in these metallic glasses is lost as a consequence of the decrease in atomic mobilities due to the formation of more stable short range ordered structure during the structural relaxation. Recently, Morito and Egami [27] measured the changes in Curie temperature and internal friction during the structural relaxation in $Fe_{32}Ni_{36}Cr_{14}P_{12}B_6$ metallic glass and have reported that an identical atomic rearrangement process produces these changes.

As can be seen from Fig. 8, the amount of annealed-out excess volume in the ductile $Fe_{40}Ni_{40}P_{14}B_6$ metallic glass is large compared with that in the brittle $Fe_{40}Ni_{40}P_{14}B_6$ metallic glass. Furthermore, the Curie temperature in the brittle sample ($T_c = 286^\circ$ C) is larger than that in the ductile sample ($T_c = 277^\circ$ C). These results may indicate that the brittle $Fe_{40}Ni_{40}P_{14}B_6$ metallic glass has already a more stable short range ordered structure in the as-quenched state. In other Fe-Ni based metallic glasses prepared in the present study, it is apparent that a part of quenched-in excess volume anneals out during the structural relaxation. Since the amount of quenched-in excess volume is closely related to the structure of metallic glasses and mobility of constituent atoms, it would be reasonable to consider that the decrease in the quenched-in excess volume during the structural relaxation affects more or less the embrittlement behaviour in Fe-Ni based metallic glasses, although the drastic change in volume was not observed at the ductile–brittle transition temperature.

Recently, Zielinski and Ast [8] have examined the structural relaxation and embrittlement of $Fe_{40}Ni_{40}Si_8B_{12}$ metallic glass by a combination of calorimetric and bending tests, and have reported that the homogeneous deformation mode decreased as a result of free volume annnihilation and embrittlement resulted from the development of chemical short range ordering. The results obtained in the present study indicate more clearly that the embrittlement behaviour during structural relaxation in some Fe-Ni based metallic glasses is closely related to the formation of a more stable short range ordered structure.

5. Summary

Fracture strain, changes in electrical resistivity and Curie temperature, and the volume change (the amount of annealed-out excess volume) were measured as a function of annealing temperature in some Fe-Ni based metallic glasses ($Fe_{27}Ni_{53}P_{14}B_6$, $Fe_{29}Ni_{49}P_{14}B_6Si_2$, $Fe_{40}Ni_{40}P_{14}B_6$, $Fe_{40}Ni_{38}Si_8B_{14}$ and $Fe_{63}Ni_{15}Si_8B_{14}$), in order to clarify the embrittlement behaviour during the structural relaxation. A close relationship between the ductile–brittle transition temperature and the resistivity change was observed in these metallic glasses which become brittle during the structural relaxation. Particularly in $Fe_{27}Ni_{53}P_{14}B_6$ metallic glass it was found that the ductile–brittle transition temperature is well consistent with the

annealing temperature at which the changes in resistivity and Curie temperature are maximum. The results obtained in the present study indicate that the embrittlement behaviour during the structural relaxation in some Fe–Ni based metallic glasses is closely related to the formation of a more stable short range ordered structure.

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