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Correlation between changes in Curie temperature and electrical resistivity during structural relaxation in $Fe_{27}Ni_{53}P_{14}B_6$ metallic glass

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Changes in Curie temperature (ΔT_c), electrical resistivity ($\Delta\varrho/\varrho$) and volume ($\Delta V/V$) caused by isochronal annealing in as-quenched and pre-annealed $Fe_{27}Ni_{53}P_{14}B_6$ metallic glasses were compared. It was found that the ΔT_c against annealing temperature (T_a) curves in as-quenched and pre-annealed samples are very similar to the $\Delta\varrho/\varrho$ against T_a curves. Particularly, almost a linear relationship was observed between ΔT_c and $\Delta\varrho/\varrho$ in the pre-annealed sample. The results strongly suggest that the origins of both ΔT_c and $\Delta\varrho/\varrho$ during structural relaxation in the pre-annealed sample are attributed to identical, reversible, short-range ordering.

1. Introduction

Structural relaxation in Fe–Ni based ferromagnetic metallic glasses has been extensively studied by various measurements such as those of Curie temperature [1–7], electrical resistivity [8–10], induced magnetic anisotropy [11], elastic modulus [12] and specific heat [13], and the change in short-range ordering during structural relaxation has been discussed. However, until now, there have been few experiments directly comparing the changes in these properties in Fe–Ni based metallic glasses. Recently, Flanders *et al.* [14] have found that a linear relationship exists between the changes in Curie temperature and field-induced magnetic anisotropy during structural relaxation in $Fe_{40}Ni_{40}P_{14}B_6$ metallic glass. Yokota *et al.* [15] have reported that the change in Curie temperature during structural relaxation in zero-magnetostrictive Co–Ni–Fe–Si–B metallic glass is closely related to the resistivity change.

Since the Curie temperature and electrical resistivity are the most basic and structure-sensitive properties in metallic glasses, it is very interesting to compare these changes during structural relaxation. In the present study, changes in Curie temperature, resistivity and volume caused by isochronal annealing in as-quenched and pre-annealed $Fe_{27}Ni_{53}P_{14}B_6$ metallic glasses were measured, and correlations among these changes were examined in order to obtain more detailed information about short-range ordering during structural relaxation.

2. Experimental procedure

An $Fe_{27}Ni_{53}P_{14}B_6$ metallic glass was prepared in the form of a ribbon, 20 μm thick and 1.35 mm wide, by rapid quenching using a single roller casting apparatus. 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 Curie temperatures (T_c) of as-quenched and annealed samples were measured by the temperature dependence of magnetic permeability. The measurements of electrical resistivity were made using a four-point probe method. As-quenched samples were spot-welded carefully by small copper wires. The resistivity changes ($\Delta\varrho/\varrho$) by isochronal annealings were measured at liquid-

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nitrogen temperature (77 K). The volume changes ($\Delta V/V$) were estimated using the relation $3\Delta l/l = \Delta V/V$, where $\Delta l/l$ is the length change. The length changes ($\Delta l/l$) due to isochronal annealing were meaured using a Rigaku Denki TMA unit with an infrared furnace. The initial length of samples was 20 mm and the resolution of length change was 2×10^{-4} mm.

To examine correlations among changes in Curie temperature (ΔT_c), resistivity ($\Delta \varrho/\varrho$) and volume ($\Delta V/V$) that occur during structural relaxation, the same annealing method was used for the measurements of these changes. That is, the as-quenched $Fe_{27}Ni_{53}P_{14}B_6$ metallic glass was first annealed isochronally from 100 to 350° C with a temperature interval of 25° C (first run), and then the sample annealed at 350° C was again annealed isochronally from 100 to 325° C (second run). Furthermore, the sample annealed at 325° C was annealed isochronally (decreasing temperatures) from 325 down to 100° C (third run), and finally annealed isochronally (increasing temperatures) from 100 up to 325° C (fourth run). An annealing time (t_a) at each annealing temperature was 30 min.

3. Results and discussion

The glass transition (T_g) and crystallization (T_x) temperatures of $Fe_{27}Ni_{53}P_{14}B_6$ metallic glass prepared in the present study were 375 and 414° C, respectively. The Curie temperature (T_c) of as-quenched $Fe_{27}Ni_{53}P_{14}B_6$ metallic glass was 54.3° C. The changes in Curie temperature (ΔT_c), resistivity ($\Delta \varrho/\varrho$) and volume ($\Delta V/V$) caused by isochronal annealing (first, second, third and fourth runs) are shown in Figs. 1 and 2 for ΔT_c, Figs. 3 and 4 for $\Delta \varrho/\varrho$ and Fig. 5 for $\Delta V/V$. The relationship between ΔT_c and $\Delta \varrho/\varrho$ in the as-quenched (first run) and pre-annealed (second, third and fourth runs) samples are shown in Figs. 6 and 7, respectively.

3.1. Change in Curie temperature (ΔT_c)

As can be seen in Figs. 1 and 2, the value of ΔT_c is not a monotonic function of annealing temperature, and the maximum ΔT_c was observed at the annealing temperature of around 250° C in both as-quenched (first run) and pre-annealed (second run) samples. Furthermore, it is seen that the values of ΔT_c in decreasing and increasing annealing cycles (third and fourth runs) lie on the same straight line above 250° C, and this line intercepts the annealing temperature axis at 350° C, which is a pre-annealing temperature. These results are clearly evidence of a reversible change in the Curie temperature and indicate that, in the high-temperature region above 250° C, a "pseudo-equilibrium state" for the Curie temperature is achieved rapidly by annealing for 30 min.

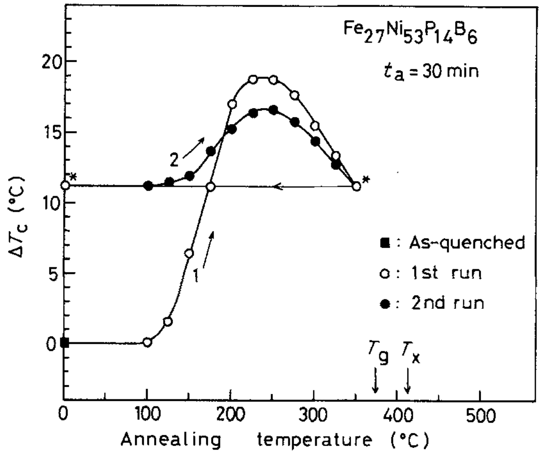

Figure 1 Changes in the Curie temperature (ΔT_c) in as-quenched (first run) and pre-annealed (second run) $Fe_{27}Ni_{53}P_{14}B_6$ metallic glass as a function of isochronal annealing temperature.

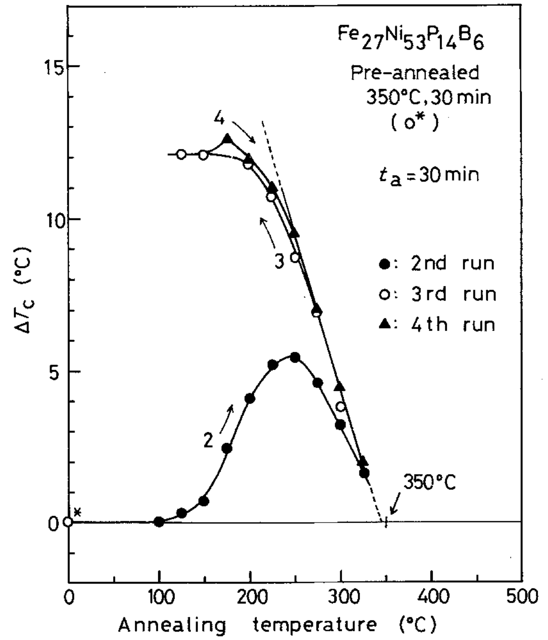

Figure 2 Changes in the Curie temperature (ΔT_c) in pre-annealed $Fe_{27}Ni_{53}P_{14}B_6$ metallic glass as a function of isochronal annealing temperature.

In the structural relaxation of as-quenched metallic glasses, both irreversible and reversible changes in local atomic rearrangements are generally involved, while in metallic glasses annealed at or near the glass transition temperature, a reversible change occurs mainly by the subsequent annealing below the pre-annealing temperature. Since the first proposal by Egami [1], irreversible and reversible local atomic rearrangements are generally called "topological short-range ordering" (TSRO) and "compositional short-range ordering" (CSRO), respectively.

It is well known that the Curie temperature is very sensitive to the formation of short-range ordering (SRO) during structural relaxation. Several authors [1–7] have reported the increase of or reversible changes in the Curie temperature during structural relaxation in Fe–Ni based metallic glasses and have discussed SRO between Fe and Ni atoms. The present results obtained in $Fe_{27}Ni_{53}P_{14}B_6$ metallic glass show the features of changes in the Curie temperature during structural relaxation in Fe–Ni based metallic glasses more clearly than the previous published data [1–7], and the reversibility in ΔT_c (Fig. 2) can be well explained by considering the formation of reversible SRO (CSRO).

3.2. Change in electrical resistivity ($\Delta\varrho/\varrho$)

As can be seen in Figs. 3 and 4, the value of $\Delta\varrho/\varrho$ is not a monotonic function of annealing temperature as in the case of ΔT_c. That is, the maximum $\Delta\varrho/\varrho$ was observed at annealing temperature of around 250° C (first and second runs), and reversibility in $\Delta\varrho/\varrho$ was also clearly observed in the pre-annealed sample (third and fourth runs).

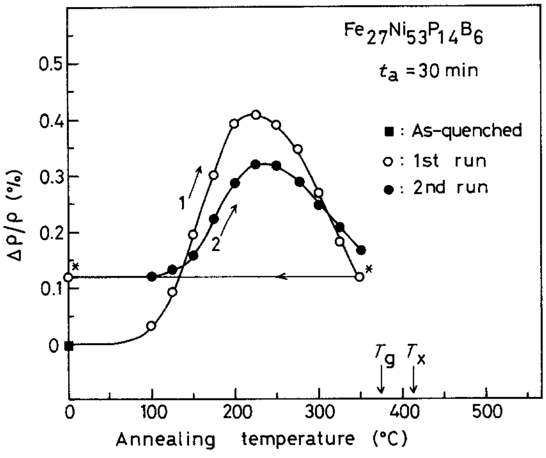

Figure 3 Resistivity changes ($\Delta\varrho/\varrho$) in as-quenched (first run) and pre-annealed (second run) $Fe_{27}Ni_{53}P_{14}B_6$ metallic glass as a function of isochronal annealing temperature.

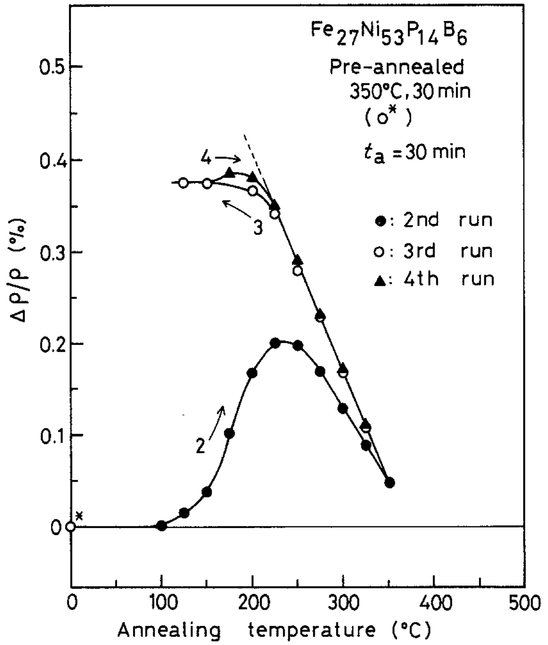

Figure 4 Resistivity changes ($\Delta\varrho/\varrho$) in pre-annealed $Fe_{27}Ni_{53}P_{14}B_6$ metallic glass as a function of isochronal annealing temperature.

The Ziman theory [16] for simple liquid metals and the modified Ziman theory for transition liquid metals extended by Evans *et al.* [17] are very informative about the electron transport phenomena in the metallic glasses. Particularly, the Ziman theory is very useful for describing the temperature coefficient of resistivity and the resistivity change during structural relaxation [18–21]. According to the Ziman theory, the resistivity change during structural relaxation can be interpreted in terms of a sharpening of the structure factor and the relative positions of $2k_F$ and K_p, where k_F is the Fermi wavevector and K_p denotes the position of the main peak of the structure factor. Furthermore, since any reversible change in the structure factor by annealing has not been reported, it is expected from the Ziman theory that the resistivity decreases or increases monotonically and irreversibly with increasing annealing temperature. However, the resistivity change by isochronal annealing in $Fe_{27}Ni_{53}P_{14}B_6$ metallic glass is not monotonic, as a maximum and reversibility in the resistivity change has been observed. That is, the present results indicate that the Ziman theory cannot be applied directly for the interpretation of the resistivity change during structural relaxation in $Fe_{27}Ni_{53}P_{14}B_6$ metallic glass, particularly for the reversible resistivity change in the pre-annealed sample. The Ziman theory should be applied for the resistivity change due to the irreversible SRO in the as-quenched non-magnetic metallic glass.

It is to be noted that the $\Delta\varrho/\varrho$ against annealing temperature (T_a) curves (Figs. 3 and 4) in as-quenched and pre-annealed $Fe_{27}Ni_{53}P_{14}B_6$ metallic glasses are very similar to the ΔT_c against T_a curves (Figs. 1 and 2). Furthermore, almost a linear relationship was observed between the $\Delta\varrho/\varrho$ and ΔT_c in the pre-annealed sample (Fig. 7). These results strongly suggest that the origins of $\Delta\varrho/\varrho$ and ΔT_c during structural relaxation in $Fe_{27}Ni_{53}P_{14}B_6$ metallic glass are attributed to similar local atomic rearrangements and that the reversible resistivity change in the pre-annealed sample is due to the formation of reversible SRO. Balanzat [8] and Balanzat *et al.* [9] have reported that a reversible resistivity change during structural relaxation in $Fe_{40}Ni_{40}P_{14}B_6$ metallic glass is due to reversible SRO (CSRO) between iron and nickel atoms. Recently, Komatsu *et al.* [10] have discussed SRO during structural relaxation in $(Fe_xNi_{1-x})_{78}Si_8B_{14}$ metallic glasses from the resistivity change.

3.3. Change in volume ($\Delta V/V$)

As can be seen in Fig. 5, the volume of the as-quenched sample decreased monotonically with increasing annealing temperature (first run) and no measurable volume change was observed in the pre-annealed sample, except a very slight volume change by annealing of around 350° C (second run). These results indicate that the volume relaxation by annealing is different from the relaxation phenomena in the Curie temperature and electical resistivity. Furthermore, it is concluded that the volume change during structural relaxation is irreversible and no measurable volume change occurs in reversible SRO, at least in $Fe_{27}Ni_{53}P_{14}B_6$ metallic glass.

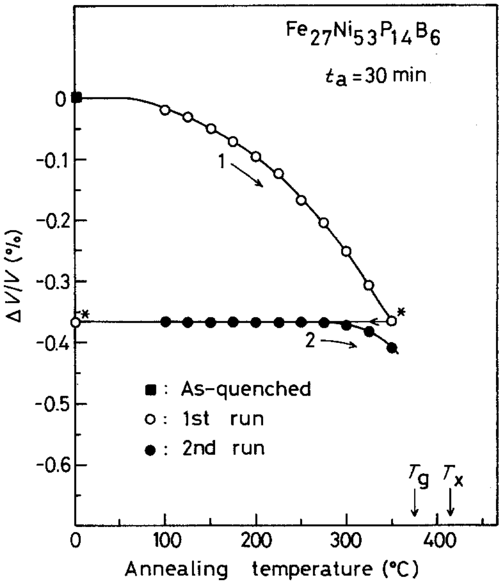

Figure 5 Volume changes ($\Delta V/V$) in as-quenched (first run) and pre-annealed (second run) $Fe_{27}Ni_{53}P_{14}B_6$ metallic glass as a function of isochronal annealing temperature.

3.4. Correlation between ΔT_c and $\Delta\varrho/\varrho$

The most striking point obtained in the present study is that almost a linear relationship was observed between the ΔT_c and $\Delta\varrho/\varrho$ in the pre-annealed $Fe_{27}Ni_{53}P_{14}B_6$ metallic glass. This result indicates that reversible SRO during structural relaxation not only induces the change in Curie temperature but also acts as a scattering centre for conduction electrons. Furthermore, since the pseudo-equilibrium state (above 250° C) for reversible SRO is achieved rapidly by annealing for 30 min and no measurable volume change occurs in reversible SRO, it is considered that reversible SRO during structural relaxation in $Fe_{27}Ni_{53}P_{14}B_6$ metallic glass is a local atomic rearrangement (not a collective phenomenon) and occurs through a very short-range diffusion of iron and nickel atoms.

The Curie temperature in ferromagnetic metallic glasses has generally been analysed by considering only nearest-neighbour interactions between magnetic atoms [22–24]. Recently, Egami [25] reported that the range of Fe–Fe ferromagnetic interaction in $(Fe_xNi_{1-x})_{80}P_{14}B_6$ metallic glasses is about 0.4 nm, covering the first nearest neighbour and a part of the second nearest neighbour. On the other hand, it is generally deduced from the large specific resistivity at room temperatures that the mean free path of conduction electrons in metallic glasses is very small and maybe corresponds to a distance of a few atoms [26]. From the above, it is expected that the ferromagnetic correlation length and mean free path of conduction elec-

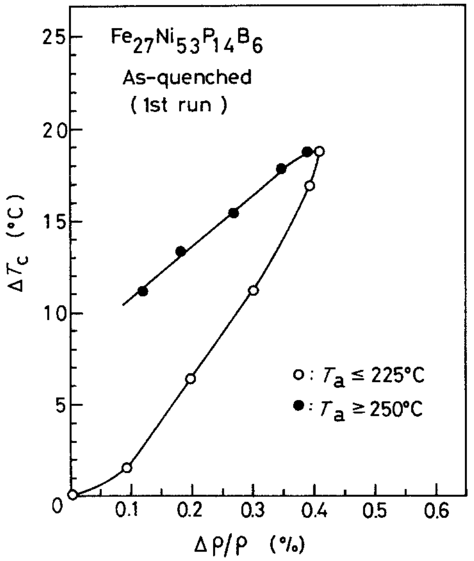

Figure 6 Correlation between changes in the Curie temperature (ΔT_c) and resistivity ($\Delta\varrho/\varrho$) during structural relaxation in as-quenched $Fe_{27}Ni_{53}P_{14}B_6$ metallic glass.

trons in $Fe_{27}Ni_{53}P_{14}B_6$ metallic glass are almost similar, and this would be the reason for the linear relationship between the ΔT_c and $\Delta\varrho/\varrho$ observed in the present study.

Although a linear relationship was observed between ΔT_c and $\Delta\varrho/\varrho$ in the pre-annealed sample (Fig. 7), such a close correlation was not observed in the as-quenched sample (Fig. 6).

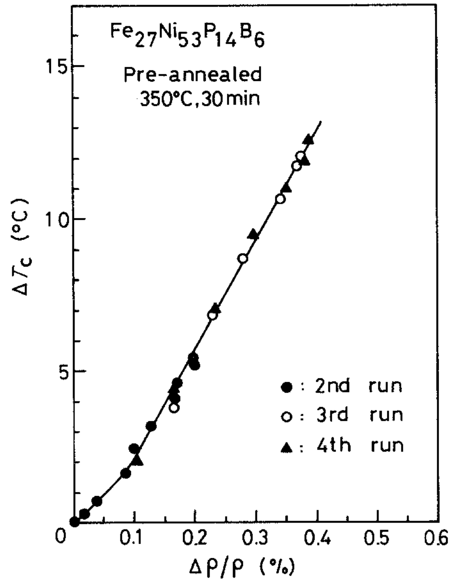

Figure 7 Correlation between changes in the Curie temperature (ΔT_c) and resistivity ($\Delta\varrho/\varrho$) during structural relaxation in pre-annealed $Fe_{27}Ni_{53}P_{14}B_6$ metallic glass.

These results indicate that the amount of contribution of irreversible SRO (TSRO) to the Curie temperature differs from that to the electical resistivity.

4. Summary

Changes in the Curie temperature (ΔT_c), resistivity ($\Delta\varrho/\varrho$) and volume ($\Delta V/V$) were measured as functions of annealing temperature in the as-quenched and pre-annealed $Fe_{27}Ni_{53}P_{14}B_6$ metallic glasses and compared. A very similar relaxation phenomenon was observed in the Curie temperature and resistivity. Particularly, almost a linear relationship was observed between ΔT_c and $\Delta\varrho/\varrho$ in the pre-annealed sample. The results suggest that the origins of ΔT_c and $\Delta\varrho/\varrho$ during structural relaxation in the pre-annealed sample are attributed to identical, reversible, short-range ordering. The volume change during structural relaxation is irreversible.

Acknowledgements

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