Correlation between thermal stability of soft magnetic properties and structural relaxation in $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass

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Effects of isochronal and isothermal annealings on permeability, coercive field, field-induced anisotropy and electrical resistivity in $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass pre-annealed at 743 K for 60 min were examined to clarify the correlation between thermal stability of soft magnetic properties and structural relaxation. It was found that both soft magnetic properties and electrical resistivity changed reversibly, depending on annealing temperature, and the values of activation energy for the changes in these properties were very close, lying in the range 1.8 and 2.0 eV. However, although the deterioration of soft magnetic properties was observed in the specimens annealed below the Curie temperature (T_C), the resistivity changes occurred significantly even in the specimens above T_C. The results strongly suggest that the changes in soft magnetic properties are attributed to an anisotropic chemical short-range ordering (CSRO) among the cobalt, iron and nickel atoms, and the resistivity changes (structural relaxation) are mainly due to an isotropic CSRO.

1. Introduction

Cobalt-based ferromagnetic metallic glasses have been studied extensively because of their soft magnetic properties. In soft ferromagnetic metallic glasses, it is a very attractive and important subject to improve their magnetic properties and thermal stability. To clearly determine the mechanism for the deterioration of the soft magnetic properties on annealing at low temperatures, the mechanism of local atomic rearrangements due to thermal annealing, i.e. structural relaxation, must be elucidated in detail. Flanders *et al.* [1] have examined the relationship between changes in field-induced anisotropy, K_u, and Curie temperature in $Fe_{40}Ni_{40}P_{14}B_6$ metallic glass and have suggested that the microscopic processes which produce these changes are identical. Yokota *et al.* [2] have discussed the relationship between changes in K_u and chemical short-range ordering (CSRO) in $Co_{58.3}Fe_{4.7}Ni_{10}Si_{11}B_{16}$ metallic glass. Fujimori [3] has also proposed that the directional order of atom pairs for K_u in soft ferromagnetic metallic glasses may arise in association with CSRO. At the present time, however, there are insufficient data to draw any conclusive answer about the correlation between the thermal stability of soft magnetic properties and structural relaxation in soft ferromagnetic metallic glasses. More extensive studies on the correlation between them, in particular the comparison of kinetics, are strongly desirable.

In this paper, the effect of thermal annealing on various magnetic properties such as permeability, coercive field and K_u in $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass was examined and correlations between the magnetic properties were clarified. The local atomic rearrangements during structural relaxation in this metallic glass were examined by measuring changes in electrical resistivity. The kinetic parameters such as activation energy for changes in magnetic properties and electrical resistivity were compared, in order to obtain information about correlation between thermal stability of magnetic properties and structural relaxation in this metallic glass. $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass possesses excellent soft magnetic properties because its magnetostriction is almost zero [4]. The method combined with measurements of resistivity changes and quench-experiments has been widely used for the study of structural relaxation in ferromagnetic metallic glasses [5–8].

2. Experimental procedure

$Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass was prepared in the form of ribbon, about 20 μm thick and 1.5 mm wide, by rapid quenching using a single-roller casting apparatus. The amorphous state 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 30 K min^{-1}. The Curie temperature T_C was determined by an a.c. induction method. The d.c. magnetization curve was measured using a conventional integrating fluxmeter using a toroidal sample, and the coercive field, H_c, and field-induced anisotropy, K_u, were estimated from the magnetization curves. The effective magnetic permeability, μ_{eff} (1 kHz, 10 mOe), was measured using a Maxwell bridge. The thermal annealing of toroidal samples was carried out under

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an external magnetic field of 3000 G. The external magnetic field was applied perpendicular to the ribbon length (transverse annealing) and argon gas was passed to prevent an oxidation of samples during magnetic annealing. After each predetermined time interval, the annealing was interrupted and toroidal samples were quenched to room temperature by blowing cold air. All magnetic measurements were carried out at room temperature. The direction of external magnetic field (10 mOe to 20 Oe) for the magnetic measurements of permeability and magnetization curves was parallel to the ribbon length (longitudinal measurements). 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 samples were annealed with and without (3000 G, transverse annealing) an external magnetic field. After annealing, the samples were immersed in liquid nitrogen (77 K) to measure the electrical resistivity.

3. Results and discussion

3.1. Pre-annealing of as-quenched samples

A DSC curve for as-quenched $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass is shown in Fig. 1. An apparent exothermic peak due to the structural relaxation appears at temperatures above 473 K. The values of T_g and T_x were 755 K and 800 K, respectively. The value of T_C in as-quenched samples was 564 K. The soft magnetic properties, such as permeability and coercive field, in as-quenched cobalt-based ferromagnetic metallic glasses are not always excellent because of the existence of quenched-in internal stress and, therefore, the metallic glasses must be first annealed at a certain temperature around T_g, in order to release the internal stress and to obtain excellent soft magnetic properties. This annealing is called "pre-annealing" and is necessary for the study of thermal stability of soft magnetic properties. The values of μ_{eff} and H_c in as-quenched $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass (not pre-annealing glass) are 5000 and 20 mOe, respectively.

We selected 743 K as a pre-annealing temperature. This temperature is very close to T_g and is about 50 K below T_x. In order to determine a pre-annealing time, the changes in μ_{eff} and H_c caused by isothermal annealing at 743 K for the as-quenched sample were measured and the results are shown in Figs 2 and 3 as a function of annealing time, t_a. It is found that the value of μ_{eff} increases with annealing up to around t_a = 100 min and then decreases on further annealing. The value of H_c decreases rapidly by short-term annealing and then increases on annealing for longer than about t_a = 140 min. These results indicate that the quenched-in internal stress is almost released by short-term annealing within 100 min. It is well known that the soft magnetic properties such as high permeability and very low coercive field disappear due to the occurrence of crystallization. The decrease of μ_{eff} in Fig. 2 and the increase of H_c in Fig. 3 caused by long-term annealing may be due to the appearance of crystals. From the dependence of annealing time on the values of μ_{eff} and H_c, the following pre-annealing conditions were determined: the pre-annealing temperature and time were 743 K and 60 min. The values of μ_{eff} and H_c in the sample pre-annealed at 743 K and for 60 min are 50 000 and 6 mOe, respectively, and it is clear that the pre-annealed $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass has excellent soft magnetic properties. It is confirmed from X-ray diffraction that the pre-annealed sample is amorphous. The value of T_C in the pre-annealed sample is 566 K.

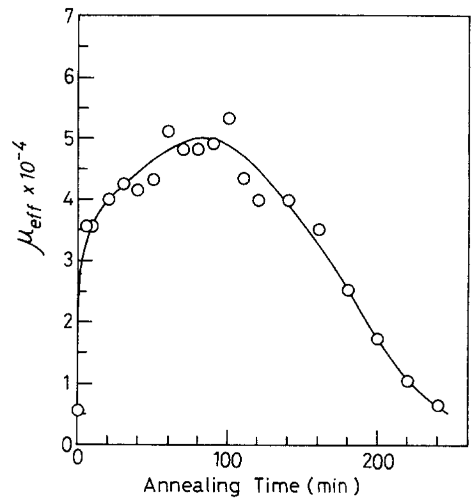

Figure 2 Changes in the effective permeability, μ_{eff}, caused by isothermal annealing at 743 K in the as-quenched $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass.

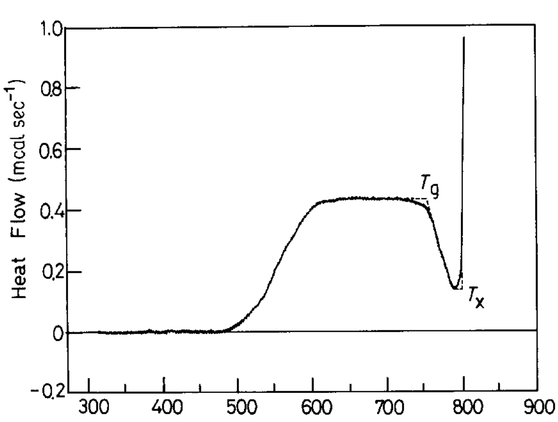

Figure 1 DSC curve of as-quenched $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass. Heating rate $30\,K\,min^{-1}$, sample weight 44.3 mg. Values of glass transition, T_g, and crystallization, T_x, temperatures were 755 and 800 K, respectively.

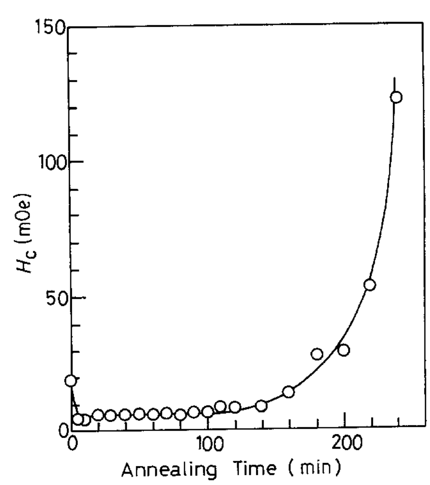

Figure 3 Changes in the coercive field, H_c, caused by isothermal annealing at 743 K in the as-quenched $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass.

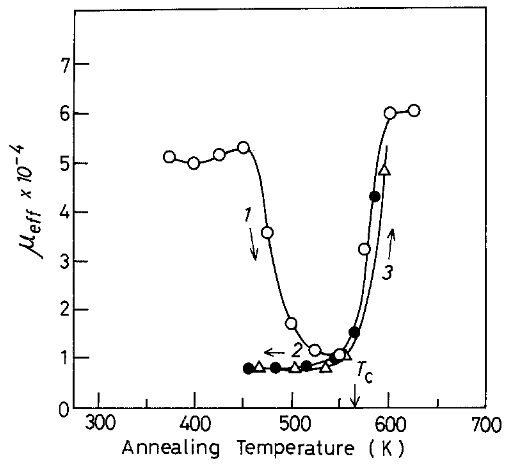

Figure 4 Changes in the effective permeability, μ_{eff}, caused by isochronal annealing cycles (heating and cooling) in $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass pre-annealed at 743 K for 60 min. Annealing time at each annealing temperature was 30 min. (○) first run, (●) second run, (△) third run.

3.2. Effect of annealing on magnetic properties

It is well known that in pre-annealed ferromagnetic metallic glasses which contain two or more kinds of transition metal atoms, various properties such as electrical resistivity [8], permeability [9], field induced anisotropy [10] change reversibly, depending on the annealing temperature. In order to confirm the reversible changes in μ_{eff}, H_c and K_u and to clarify the effect of annealing on them in pre-annealed $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass, these soft magnetic properties were measured as a function of annealing temperature, where isochronal annealings were repeated in the temperature range 373 and 613 K. The results are shown in Fig. 4 for μ_{eff}, Fig. 5 for H_c and Fig. 6 for K_u. Because the value of field-induced anisotropy determined from the magnetization curves of toroidal samples inevitably involves error compared with the value determined from the torque curve [11], only the changes in K_u caused by annealing, $\Delta K_u = K_u(T_a, t_a) - K_u(743\,K, 60\,min)$, were estimated and used throughout this paper.

As can be seen in Fig. 4, the value of μ_{eff} decreases first with increasing annealing temperature up to around $T_C (= 566\,K)$ and then increases rapidly by annealing at temperatures higher than T_C. From the annealing temperature dependence of μ_{eff} observed in the second and third annealing runs, it is clear that the value of μ_{eff} changes reversibly, depending on the annealing temperature. The values of H_c and ΔK_u also change reversibly, depending on the annealing temperature. These values increase on annealing at temperatures lower than T_C and become very small in samples annealed at temperatures above T_C. The annealing temperature dependence of H_c and ΔK_u are thus inverse compared with that of μ_{eff}. These results indicate that the excellent soft magnetic properties in pre-annealed $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass deteriorate largely by further annealing at low temperatures below T_C.

3.3. Correlation between magnetic properties

In soft ferromagnetic crystalline materials, it is well known that correlation between permeability, coercive field and field-induced anisotropy is very important when considering the magnetization mechanism and magnetic domain structure. To date, the study of correlations between these magnetic properties in soft ferromagnetic metallic glasses are very small. The values of μ_{eff}, H_c and ΔK_u in pre-annealed $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass shown in Figs 4 to 6 were compared to obtain information about the magnetization mechanism. As can be seen in Figs 7 and 8, the value of μ_{eff} increases with decreasing H_c and a good linear relationship is observed between the inverse of permeability μ_{eff}^{-1} and H_c. The correlation between H_c and ΔK_u is shown in Fig. 9 and it can be seen that the value of H_c increases linearly with increasing value of ΔK_u. The value of μ_{eff} decreases with increasing ΔK_u and a linear relationship is observed between μ_{eff}^{-1} and ΔK_u except for a slight deviation in the region of small values of ΔK_u, as shown in Fig. 10.

It would be of value to review briefly the magnetic domain structure and magnetization mechanism in cobalt-based soft ferromagnetic metallic glasses. In metallic glass ribbons, the direction of the external

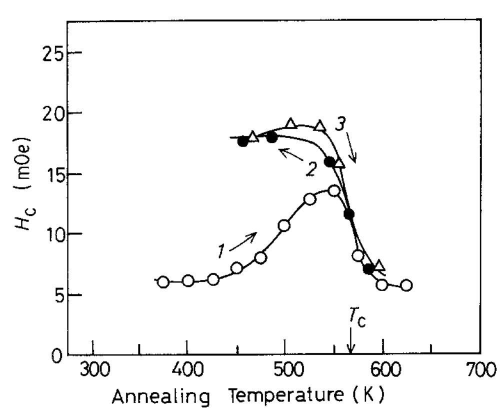

Figure 5 Changes in the coercive field, H_c, caused by isochronal annealing cycles (heating and cooling) in $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass pre-annealed at 743 K for 60 min. Annealing time at each annealing temperature was 30 min. (○) first run, (●) second run, (△) third run.

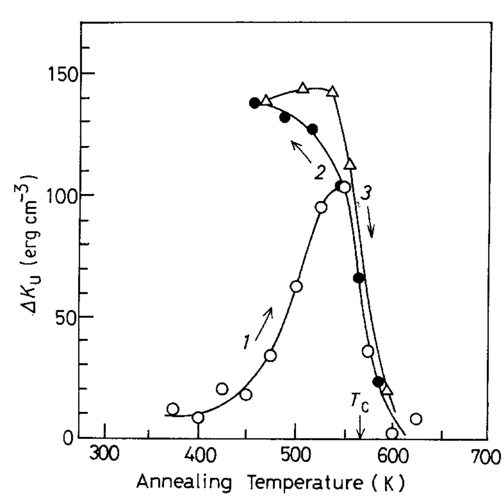

Figure 6 Changes in the field induced anisotropy, ΔK_u, caused by isochronal annealing cycles (heating and cooling) in $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass pre-annealed at 743 K for 60 min. Annealing time at each annealing temperature was 30 min. (○) first run, (●) second run, (△) third run.

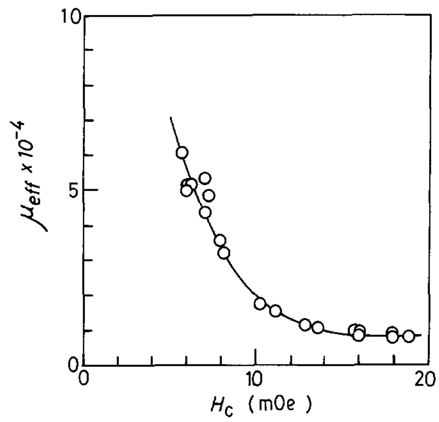

Figure 7 Correlation between the permeability, μ_{eff}, and coercive field, H_c, in pre-annealed $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass.

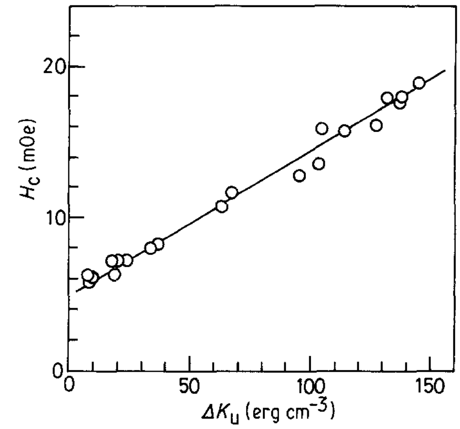

Figure 9 Correlation between the coercive field, H_c, and field-induced anisotropy, ΔK_u, in pre-annealed $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass.

magnetic field during annealing affects largely the magnetic domain structure and the magnetization mechanism [12–15]. Livingston *et al.* [13] and Wit and Brouha [14] have examined extensively the domain structure and magnetization mechanism in zero-magnetostrictive $Co_{70.3}Fe_{4.7}Si_{15}B_{10}$ metallic glass using a scanning electron microscopy technique or the Kerr effect, and have reported the following important results. The external magnetic field annealing perpendicular to the ribbon axis (transverse annealing) produces an uniaxial transverse anisotropy and the magnetization in the direction parallel to the ribbon axis in the ribbons with the transverse anisotropy occurs primarily by rotation of domains. On the other hand, in ribbons with the longitudinal anisotropy, which was produced by field annealing parallel to the ribbon axis (longitudinal annealing), the domain wall motion is dominant as the magnetization mechanism. Domain widths in transverse anisotropy ribbons are much finer than in longitudinal anisotropy ribbons. Jagielinski [15] has shown that there is a linear relationship between μ_{eff}^{-1} and anisotropy K_u induced by transverse annealing in zero-magnetostrictive $Co_{70.3}Fe_{4.7}Si_{15}B_{10}$ metallic glass and the observed dependence can be explained by taking into account the mechanism of reversible rotation of domains. Jagielinski has also proposed that the following relationship holds

$$\mu_{eff}^{-1} = \frac{K_u}{2\pi M_s^2} + \frac{N}{4\pi} \tag{1}$$

where M_s is the saturation magnetization and N is the demagnetization factor of the sample.

The linear relationship between μ_{eff}^{-1} and ΔK_u in pre-annealed $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass shown in Fig. 10 was analysed using Equation 1 and a value of saturation magnetization $B_s(=4\pi M_s)$ of 5500 G was obtained. This value is the same as B_s = 5500 G reported by Hilzinger and Kunz [4]. It is well known that in magnetic materials the coercive field is proportional to the magnetic anisotropy, if the magnetization occurs by rotation of domains. As can be seen in Fig. 9, a good linear relationship was observed between H_c and ΔK_u in pre-annealed $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass. Although we have not measured the domain structure of pre-annealed $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass, the correlations between μ_{eff}^{-1}, H_c and ΔK_u obtained in the present study may indicate that the magnetization in the direction parallel to the ribbon axis in pre-annealed $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass with the transverse anisotropy occurs primarily by rotation, and the contribution of the domain wall motion is small.

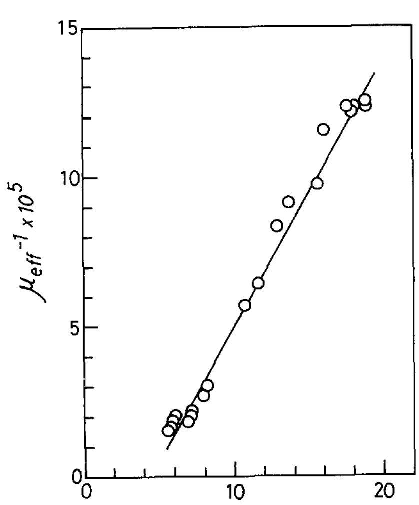

Figure 8 Correlation between the inverse of permeability, μ_{eff}^{-1}, and coercive field, H_c, in pre-annealed $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass.

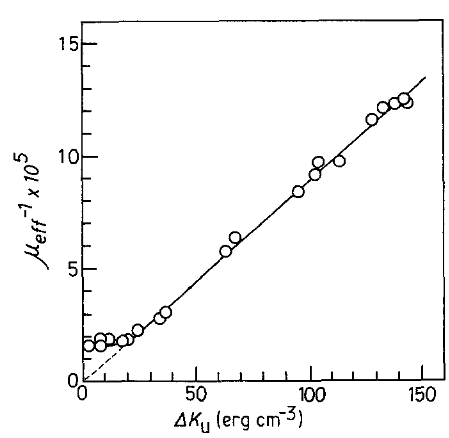

Figure 10 Correlation between the inverse of permeability, μ_{eff}^{-1}, and field-induced anisotropy, ΔK_u, in pre-annealed $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass.

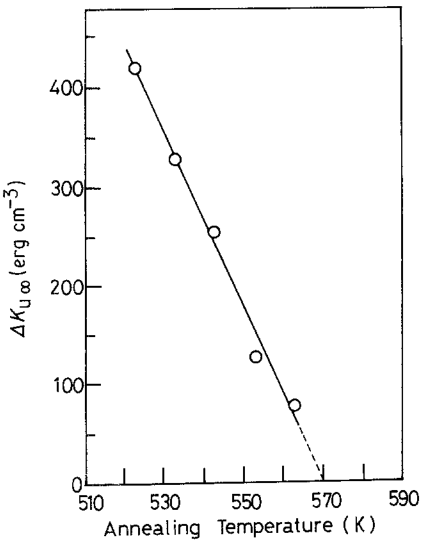

Figure 11 Equilibrium changes in the field-induced anisotropy, $\Delta K_{u,\infty}$, as a function of annealing temperature in pre-annealed $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass.

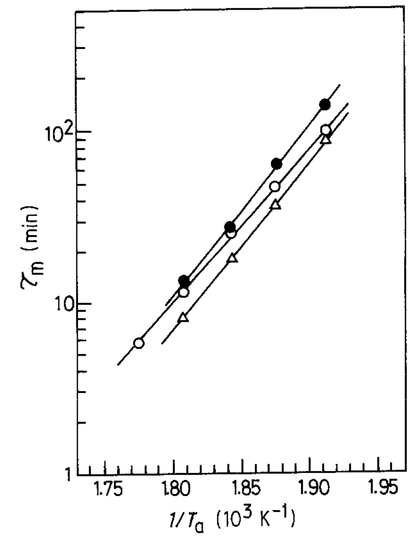

Figure 13 Dependence of the mean relaxation time, τ_m, on the annealing temperature, T_a, for the changes in magnetic properties in pre-annealed $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass. (○) μ_{eff}^{-1}, (●) H_c, (△) ΔK_u.

3.4. Kinetics of changes in magnetic properties

The changes in μ_{eff}, H_c and ΔK_u caused by isothermal annealing in pre-annealed $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass were measured at some temperatures ranging from 523 to 563 K, in order to obtain kinetic parameters for the deterioration of soft magnetic properties due to the thermal annealing at temperatures below T_c. The equilibrium values of μ_{eff}, H_c and ΔK_u at each annealing temperature were obtained, and the results for ΔK_u are shown in Fig. 11. It is seen that the equilibrium values lie on the straight line and this line intercepts the annealing temperature axis at 570 K. This temperature is very close to the Curie temperature $T_C = 566$ K. Because the values of inverse of permeability μ_{eff}^{-1} are proportional to the values of H_c and ΔK_u as shown in Figs 8 and 10, the kinetics of changes in μ_{eff}^{-1} was examined. The normalized changes in μ_{eff}^{-1}, $(\mu_0^{-1} - \mu^{-1})/(\mu_0^{-1} - \mu_\infty^{-1})$, are shown in Fig. 12 as a function of annealing time, where μ_0^{-1} is the value of inverse permeability after pre-annealing treatment and μ_∞^{-1} is the inverse equilibrium permeability after a long-term annealing. The values of mean relaxation time, τ_m, which is equal to the time at $(\mu_0^{-1} - \mu^{-1})/(\mu_0^{-1} - \mu_\infty^{-1}) = 1/e$, are plotted in Fig. 13 and the values of activation energy, E_a, and pre-exponential factor, τ_0, were estimated using the following Arrhenius relation

$$\tau_m = \tau_0 \exp(E_a/k_B T) \qquad (2)$$

where k_B is the Boltzmann constant. The values of 1.80 eV for E_a and 2.9×10^{14} sec for τ_0 were obtained. The kinetics of the changes in H_c and ΔK_u were also examined using a similar analysis to the case of μ_{eff}^{-1}. The temperature dependence of τ_m for the changes in H_c and ΔK_u is shown in Fig. 13. The estimated values of E_a and τ_0 in μ_{eff}^{-1}, H_c and ΔK_u are summarized in Table I. It was found that the values of activation energy for the changes in μ_{eff}^{-1}, H_c and ΔK_u are very close and lie in the range 1.8 and 2.0 eV.

Several authors [10, 15–19] have examined the kinetics for changes in magnetic properties in pre-annealed zero-magnetostrictive cobalt-based metallic glasses. The reported kinetic parameters are summarized in Table II. Chambron and Chamberod [10] have reported that the value of activation energy for the changes in the field-induced anisotropy in $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass pre-annealed at 753 K for 20 min is 1.85 eV. Guo *et al.* [16] have reported that the kinetics for the field-induced anisotropy in $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass pre-annealed at 623 K for 2 h are characterized by a spectrum of activation energies ranging from 1.8 to 2.3 eV. These reported values are almost the same as those obtained in the present study.

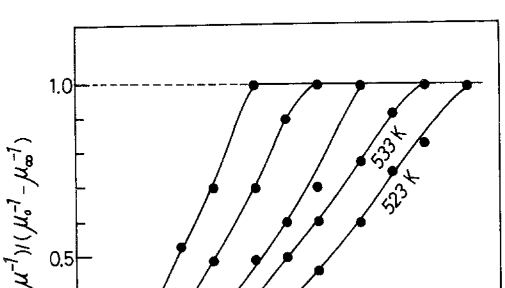

Figure 12 Normalized changes in the inverse permeability $(\mu_0^{-1} - \mu^{-1})/(\mu_0^{-1} - \mu_\infty^{-1})$ caused by isothermal annealing in pre-annealed $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass.

TABLE I The values of mean activation energy E_a and mean pre-exponential factor τ_0 in the kinetics of changes in the inverse of permeability μ_{eff}^{-1}, coercive field H_c, field-induced anisotropy, ΔK_u, and electrical resistivity $(\Delta\varrho/\varrho_0)$ in pre-annealed $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass.

	E_a (eV)	τ_0 (sec)
μ_{eff}^{-1}	1.80	2.9×10^{-14}
H_c	2.02	3.0×10^{-16}
ΔK_u	1.97	5.4×10^{-16}
$\Delta\varrho/\varrho_0$	1.84	2.9×10^{-13}

TABLE II The values of mean activation energy E_a and mean pre-exponential factor τ_0 in the kinetics of changes in magnetic properties in pre-annealed zero-magnetostrictive cobalt-based metallic glasses

Composition	E_a (eV)	τ_0 (sec)	Method*	Reference
$Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$	1.85	5×10^{-16}	a	[10]
	1.8–2.3	6×10^{-16}	a	[16]
$Co_{70}Fe_5Si_{15}B_{10}$	1.9	3.1×10^{-14}	a	[17]
$Co_{70.3}Fe_{4.7}Si_{15}B_{10}$	2.05	4.7×10^{-15}	b	[15]
$(Co_{0.937}Fe_{0.063})_{75}Si_{15}B_{10}$	2.0	7.8×10^{-17}	a	[18]
$Co_{72.1}Fe_{5.9}Si_5B_{15}Mo_2$	2.0		a	[19]

*a, field-induced anisotropy; b, inverse permeability.

It is seen from Table II that the mean activation energy for the changes in magnetic properties in zero-magnetostrictive Co–Fe-based metallic glasses which do not contain nickel atoms are also around 2.0 eV.

3.5. Effect of annealing on electrical resistivity

The resistivity changes due to thermal annealing in pre-annealed $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass were measured to obtain information about atomic rearrangements during structural relaxation. Two different annealing methods were used. One was the magnetic field annealing (transverse annealing at 3000 G), and the other was a normal annealing in which no external magnetic field was applied. The resistivity changes, $\Delta\varrho/\varrho_0$, caused by isochronal annealing are shown in Fig. 14 as a function of annealing temperature T_a. The values of ΔK_u are also shown in Fig. 14 for comparison. It is seen that the resistivity increases gradually with increasing annealing temperature up to around $T_a = 623$ K and then decreases on further annealing at high temperatures. The resistivity changes caused by magnetic field annealing are almost the same as those caused by normal annealing. No anomalous resistivity change was observed on annealing around T_C. Although the field-induced anisotropy was observed only in the specimens annealed below T_C, the resistivity changes occurred significantly even in specimens annealed above T_C. In a previous paper [20], we reported that the resistivity changes in pre-annealed $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass were reversible, depending on annealing temperature, and the value of mean activation energy for the resistivity changes was 1.84 eV. As can be seen in Table I, this value is close to the activation energies for the changes in soft magnetic properties.

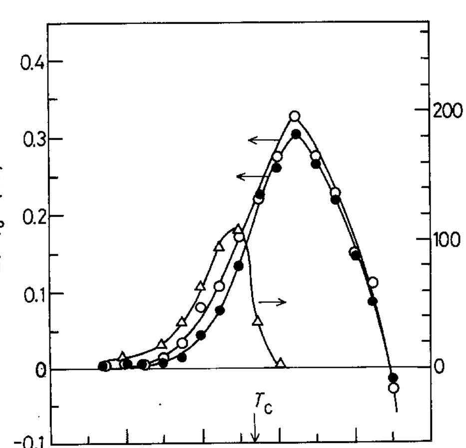

Figure 14 Changes in electrical resistivity ($\Delta\varrho/\varrho_0$), (○) (●), and field-induced anisotropy, ΔK_u, caused by isochronal annealing in pre-annealed $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass. Annealing time at each annealing temperature was 30 min. (○) Normal annealing without magnetic field, (●) magnetic field annealing (transverse annealing at 3000 G).

3.6. Correlation between thermal stability of soft magnetic properties and structural relaxation

It would be of value to describe briefly the origin of field-induced anisotropy and resistivity changes in ferromagnetic metallic glasses which have been proposed in other papers. Fujimori *et al.* [9] have proposed that the induced magnetic anisotropy in Co–Fe–Si–B metallic glasses arises from the directional arrangement of Co–Fe pairs. Miyazaki and Takahashi [11] have also reported that the compositional dependence of uniaxial magnetic anisotropy induced by magnetic annealing in $(Co_xFe_{1-x})_{77}Si_{10}B_{13}$ metallic glasses can be explained by the directional pair model. Dong *et al.* [21] have discussed the mechanism of the deterioration of soft magnetic properties in $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glasses by assuming that an induced anisotropy is caused by directional rearrangements of atom pairs.

On the other hand, Yokota *et al.* [2] suggested that the resistivity changes in pre-annealed $Co_{58.3}Fe_{4.7}Ni_{10}Si_{11}B_{16}$ metallic glass were due to the chemical short-range ordering (CSRO) among transition metal atoms. Recently, Komatsu *et al.* [8] have shown that the resistivity changes during structural relaxation in pre-annealed $(Co_{1-x}Fe_x)_{75}Si_{10}B_{15}$ metallic glasses are largely affected by the Co/Fe ratio and are attributed to reversible changes in the degree of short range ordering between cobalt and iron atoms. The reversible changes in other physical properties such as Curie temperature [22] and elastic modulus [23] during structural relaxation in pre-annealed transition metal (Co, Fe, Ni)–metalloid (Si, B, P) metallic glasses are also attributed to CSRO between transition metal atoms. CSRO in metallic glasses is an order–disorder phenomenon relating to the arrangement of constituent atoms similar to that of short-range ordering in crystalline alloys and corresponds to the increase in the number of atom pairs between different transition metal atoms such as Co–Fe and Fe–Ni pairs. Using this concept, we can explain the experimental facts that the electrical resistivity in pre-annealed metallic glasses changes reversibly, depending on annealing temperature and the reversible resistivity changes are significantly observed in metallic glasses which contain two or more kinds of transition metal atoms.

Egami [24] has introduced the idea of an isotropic and anisotropic CSRO as reversible local atomic rearrangements during structural relaxation in ferromagnetic metallic glasses. The term anisotropic CSRO means an anisotropic arrangement of atom pairs such as Co–Fe and Fe–Ni pairs in the direction parallel to the external magnetic field or local internal magnetic field, and could occur in specimens annealed at temperatures below T_C. The directional rearrangement of atom pairs, which is considered to be a mechanism for field-induced anisotropy, would be regarded as anisotropic CSRO. On the other hand, it is considered that the resistivity changes are due to both anisotropic and isotropic CSRO.

In the pre-annealed $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass, it was found that the values of the activation energy of changes in soft magnetic properties and electrical resistivity are almost the same. This result indicates that atomic rearrangements contributing to the changes in soft magnetic properties are closely related to those contributing to the changes in electrical resistivity. In other words, this result may indicate that the values of activation energy of anisotropic and isotropic CSRO in pre-annealed $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass are almost the same. Furthermore, the fact that the difference between the resistivity changes caused by magnetic field annealing and those caused by normal annealing without magnetic field is very small, may indicate that the amount of anisotropic CSRO is not so large compared with the amount of isotropic CSRO. As a conclusion, it is considered that atomic rearrangements of atom pairs such as Co–Fe, Co–Ni and Fe–Ni pairs, occur during structural relaxation in the pre-annealed $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass, and some parts of atomic rearrangements are structurally anisotropic in the specimens annealed at temperatures below T_C, which leads to the deterioration of soft magnetic properties.

4. Conclusions

Effects of isochronal and isothermal annealings on permeability μ_{eff}, coercive field H_c, field-induced anisotropy ΔK_u, and electrical resistivity in pre-annealed $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass were examined to clarify the correlation between thermal stability of soft magnetic properties and structural relaxation. The results are summarized as follows.

1. μ_{eff}, H_c and ΔK_u change reversibly, depending on annealing temperature.

2. There are linear relationships between H_c and ΔK_u and between the inverse permeability μ_{eff}^{-1} and ΔK_u. These results indicate that the magnetization in the direction parallel to the ribbon axis in pre-annealed $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass with transverse anisotropy occurs primarily by rotation and the contribution of magnetic wall motion is small.

3. The values of activation energy for the changes in μ_{eff}^{-1}, H_c, ΔK_u and electrical resistivity are very close, lying in the range 1.8 and 2.0 eV.

4. The present results strongly suggest that the deterioration of soft magnetic properties in the specimens annealed below the Curie temperature is due to an anisotropic rearrangement of atom pairs such as Co–Fe, Co–Ni and Fe–Ni pairs.

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