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Analysis of reversible resistivity changes during structural relaxation in $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass using different kinetic forms

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Resistivity changes during structural relaxation in pre-annealed $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass were measured as functions of annealing temperature (280 to 400° C) and time and their kinetics were analysed using two different kinetic forms. In the case of the non-linear kinetic form which is expressed as $\psi = \exp[-(t/\tau_m)^n]$, the values of mean activation energy, E_a, and mean pre-exponential factor, τ_0, are 1.84 eV and 2.88×10^{-13} sec, respectively, and it was found that the quality of data fitting to the calculated curve with a constant value of $n = 0.35$ was excellent. In the case of the log normal kinetic form which was developed by Nowick and Berry, the values of E_a and τ_0 are 1.75 eV and 2.4×10^{-12} sec, respectively, and the quality of data fitting to the calculated curve with a constant value of $\beta = 4.5$ was good, except for the slight deviation in the large value of $\log(t/\tau_m)$, where β is the width of the distribution of relaxation times. The kinetic parameters obtained in the present study were compared with various reported values.

1. Introduction

The relaxation of various properties in metallic glasses is generally not described by a single relaxation time and it is often convenient to describe the relaxation process of metallic glasses in terms of the distribution of relaxation time [1]. Two kinetic forms have often been used in phenomenological descriptions of the relaxation process of amorphous materials. One is a non-linear kinetic form expressed as

$$\frac{P(T, t) - P_\infty}{P_0 - P_\infty} = \psi = \exp[-(t/\tau_m)^n] \quad (1)$$

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

where P_0 and P_∞ are initial and equilibrium physical properties in amorphous materials, τ_m is the mean relaxation time, n is a constant with $0 \leqslant n \leqslant 1$ and means the width of the distribution of relaxation times, τ_0 is the pre-exponential factor, E_a is the activation energy of the relaxation process and k_B is the Boltzmann constant. This non-linear kinetic form has been widely used not only in the relaxation of metallic glasses [2–4] but also in the relaxation of oxide glasses [5, 6] and polymer glasses [7].

The other form is a log normal kinetic form (normal log gaussian distribution in relaxation times) which was developed by Nowick and Berry [8]. According to Nowick and Berry, the relaxation function ψ can be expressed by the following equation

$$\psi = \frac{1}{\pi^{1/2}} \int_{-\infty}^{\infty} \exp(-u^2) \exp[-\exp(y - \beta u)] \, du$$

$$y = \ln(t/\tau_m)$$

$$u = \frac{1}{\beta} \ln(\tau/\tau_m) \quad (3)$$

where β is a parameter representing the width of the distribution of relaxation times and τ_m is the mean relaxation time. A numerical integration of Equation 3 was reported by Nowick and Berry [8]. Although the above equation is very complicated for the fitting of experimental data, several authors [9–14] have used this kinetic form for the study of relaxation process of metallic glasses.

To date, however, no experiment comparing the above two kinetic forms using the same experimental data has been reported. It would be very worthwhile analysing the relaxation process of metallic glasses using the two different kinetic forms and comparing the quality of data fitting and values of kinetic parameters. In this paper, the kinetics of resistivity changes caused by isothermal annealing in the temperature range 280 to 400° C in pre-annealed $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass has been analysed using two different kinetic forms (non-linear and log normal), and the quality of data fitting and values of kinetic parameters have been compared. Because the electrical resistivity is very sensitive to changes in local atomic rearrangements and measurements of resistivity can be made very accurately, the method combining measurements of resistivity changes with quench experiments has been widely used for the study of relaxation in metallic glasses [3, 4, 9, 14–17]. A $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass is zero-magnetostrictive and, therefore, soft magnetic properties of this metallic glass have been studied extensively [11, 18, 19].

2. Experimental procedure

A $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass was prepared in the form of a ribbon, about 20 μm thick and 1.5 mm wide, and rapidly quenched using a single roller casting apparatus. 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 in a furnace at a constant temperature. During annealing, nitrogen or argon gas flowed around the samples to prevent their oxidation. After each predetermined time interval, annealing was interrupted and the samples were quenched in acetone to room temperature. Then, the samples were immersed in liquid nitrogen (77 K) to measure the electrical resistivity. All the measurements were made at the reference temperature 77 K. The relative resistivity changes, $\Delta\varrho/\varrho_0$, were calculated as functions of annealing temperature T_a and time t_a, where ϱ_0 is the initial resistivity ($t_a = 0$) and $\Delta\varrho$ is equal to the resistivity changes caused by annealing, $\Delta\varrho = \varrho(T_a, t_a) - \varrho_0$.

3. Results and discussion

3.1. Resistivity changes caused by isothermal annealing

It is well known that in as-quenched metallic glasses which contain two or more kinds of transition metal atoms, both irreversible and reversible resistivity changes occur during structural relaxation, while in pre-annealed metallic glasses which were annealed near the glass transition temperature, virtually only reversible resistivity changes occur on annealing at temperatures below the pre-annealing temperature [3, 4, 14–17]. The scope of the present paper is limited to consideration of kinetics of reversible resistivity changes in pre-annealed samples. It has been reported [19] that the resistivity changes due to thermal annealing in $Co_{58.3}Fe_{4.7}Ni_{10}Si_{11}B_{16}$ metallic glass pre-annealed at 470° C for 60 min, are almost reversible, and, therefore, the pre-annealing of $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass which was used in the present study was carried out at 470° C for 60 min. The crystallization temperature of this metallic glass is 525° C, which was determined by differential scanning calorimetry at a heating rate of 10° C min^{-1}.

The resistivity changes caused by isothermal

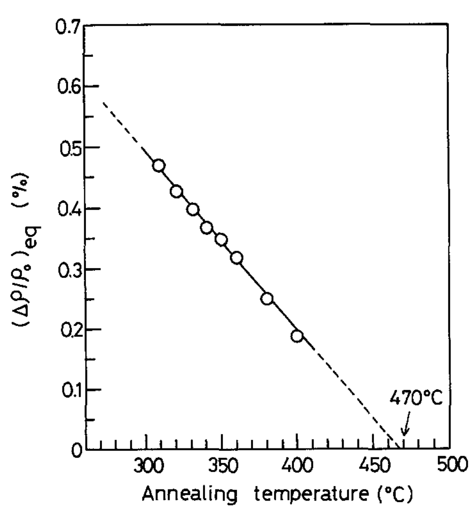

Figure 1 Equilibrium resistivity changes $(\Delta\varrho/\varrho_0)_{eq}$ as a function of annealing temperature in pre-annealed $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass.

annealing in pre-annealed $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass were measured at various temperatures ranging from 280 to 400° C and it was found that the values of resistivity changes increase as a function of annealing time toward an equilibrium value $(\Delta\varrho/\varrho_0)_{eq}$ which depends on the annealing temperature. The equilibrium values of resistivity changes in isothermal annealing are plotted in Fig. 1 as a function of annealing temperature. As can be seen in Fig. 1, the equilibrium values lie on the same straight line for the annealing temperature range from 310 to 400° C and its line intercepts the annealing temperature of 470° C, which is the pre-annealing temperature of this metallic glass. Using equilibrium values shown in Fig. 1, the resistivity changes caused by isothermal annealing were normalized and the normalized resistivity changes $(\Delta\varrho/\varrho_0)/(\Delta\varrho/\varrho_0)_{eq}$ are shown in Fig. 2. The equilibrium values at T_a = 280, 290 and 300° C were obtained by extrapolating the equilibrium values at high annealing temperatures.

3.2. Analysis of experimental data

The normalized resistivity changes shown in Fig. 2 were first analysed using the non-linear kinetic form expressed as Equation 1. As the values of mean relaxation time, τ_m, at each annealing temperature, T_a, three relaxation times which are equal to the time at $\psi = 1/e$, 0.5 and $1 - 1/e$ were taken, where ψ is the relaxation function and corresponds to the values of $1 - (\Delta\varrho/\varrho_0)/(\Delta\varrho/\varrho_0)_{eq}$ and the value of e is 2.718. The relationship between τ_m and T_a is shown in Fig. 3, and it is clear that the mean relaxation time obeys an Arrhenius law. The values of the constant n in Equation 1 were estimated from the relationship between $\log(-\ln\psi)$ and $\log(t/\tau_m)$ shown in Fig. 4. The obtained values of activation energy, E_a, pre-exponential factor, τ_0, and the constant n, are summarized in Table I. The quality of fitting of experimental data to the theoretical curve expressed by Equation 1 is shown in Fig. 5, where the values of τ_m correspond to the time at $\psi = 1/e$. It can be seen from Fig. 6 that the resistivity changes at the different annealing temperatures can be brought into a single master curve with the value of $n = 0.35$ and the quality of fitting is excellent. As can be seen in Table I, the values of E_a, τ_0 and n are almost the same irrespective of the method of determining the values of mean relaxation time, τ_m. The mean values of E_a, τ_0 and n are 1.84 eV, 2.88×10^{-13} sec and 0.35, respectively.

Next, the normalized resistivity changes shown in Fig. 2 were analysed using the log normal kinetic form expressed as Equation 3. It was found that the value of β lies in the range 4.2 and 4.6, depending on the annealing temperature, T_a. The values of τ_m which were estimated from the time at $\psi = 0.5$ and the values of β are plotted against $1/T_a$ in Fig. 6. As can be seen in Fig. 6, the mean relaxation time obeys an Arrhenius law. The estimated values of mean activation energy, E_a, and mean pre-exponential factor τ_0 are 1.75 eV and 2.4×10^{-12} sec, respectively. The quality of fitting of experimental data to the theoretical curve with $\beta = 4.5$ expressed by Equation 3 is shown in Fig. 7. The quality of fitting of experimental

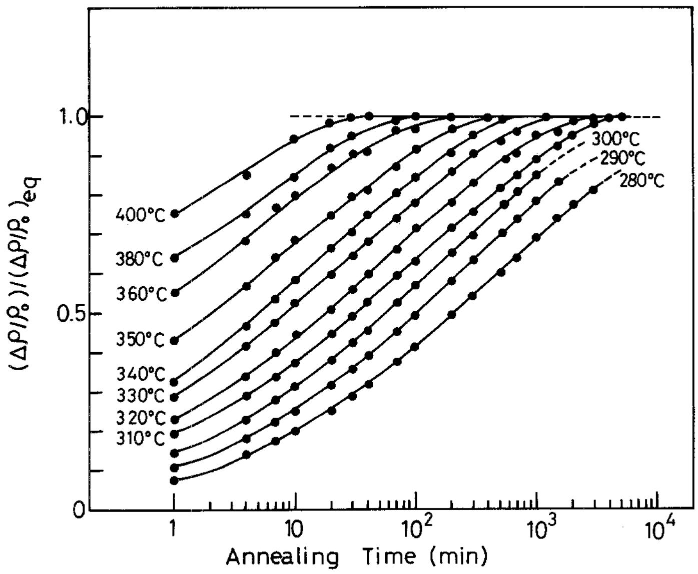

Figure 2 Normalized resistivity changes $(\Delta\varrho/\varrho_0)/(\Delta\varrho/\varrho_0)_{eq}$ in isothermal annealing in pre-annealed $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass.

data is good except for the slight deviation in the large values of $\log(t/\tau_m)$.

3.3. Comparison of two different kinetic forms

From the quality of data fitting shown in Fig. 5, it is clear that the resistivity changes due to thermal annealing in pre-annealed $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass can be well described using the non-linear kinetic form with a constant value of $n = 0.35$. The log normal kinetic form is also good as shown in Fig. 7. It is very interesting that the relaxation process of $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$. metallic glass can be described satisfactorily using the non-linear kinetic form which is very simple compared with the log normal kinetic form, as well as in the case of oxide and polymer glasses, and this indicates that the non-linear kinetic form is useful as a common relaxation function for the comparison of relaxation processes in various amorphous materials.

The values of mean activation energy, E_a, and mean pre-exponential factor, τ_0, estimated using the non-linear kinetic form ($E_a = 1.84\,\text{eV}$, $\tau_0 = 2.88 \times 10^{-13}$ sec) are somewhat different from those estimated using the log normal kinetic form ($E_a = 1.75\,\text{eV}$, $\tau_0 = 2.4 \times 10^{-12}$ sec). This difference would arise from the differences in the method of determining the values of mean relaxation time, τ_m. That is, in the non-linear kinetic form, the mean relaxation time corresponds straightforwardly to the time at $\psi = 1/e$ (or $\psi = 0.5$, $\psi = 1 - 1/e$), while in the log normal kinetic form, the mean relaxation time is determined from the time at $\psi = 0.5$ and the values of β, where the value of β changes with annealing temperature.

Several authors [2–4, 10–13] have examined the kinetics of property changes such as resistivity and field-induced magnetic anisotropy in various metallic glasses using the non-linear kinetic form or the log normal kinetic form. The reported kinetic parameters are summarized in Table II. It can be seen from

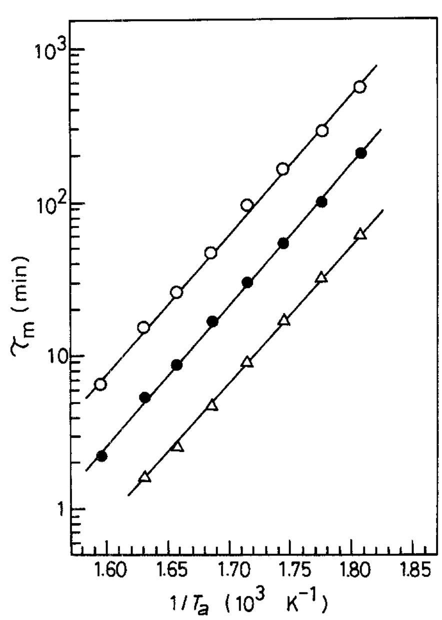

Figure 3 Dependence of the mean relaxation time, τ_m, on the annealing temperature, T_a, for resistivity changes in pre-annealed $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass. The values of τ_m correspond to the time at $\psi = 1/e$ (○), $\psi = 0.5$ (●) and $\psi = 1 - 1/e$ (△).

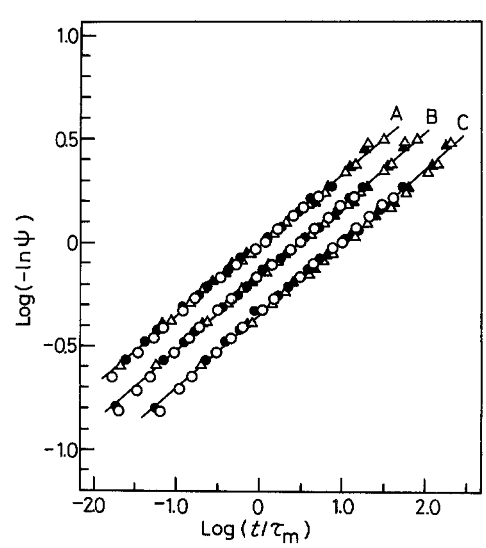

Figure 4 Relation between $\log(-\ln\psi)$ and $\log(t/\tau_m)$ in pre-annealed $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass. ψ is the relaxation function and corresponds to the values of $1 - (\Delta\varrho/\varrho_0)/(\Delta\varrho/\varrho_0)_{eq}$. τ_m corresponds to the time at $\psi = 1/e$ (line A), $\psi = 0.5$ (line B) and $\psi = 1 - 1/e$ (line C). (○) 280° C, (●) 300° C, (△) 320° C, (▲) 340° C.

TABLE I Kinetic parameters estimated using the non-linear kinetic form $\psi = \exp[-(t/\tau_m)^n]$ for resistivity changes in the temperature range 280 to 350° C in pre-annealed $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass. E_a is the activation energy, τ_0 is the pre-exponential factor and n is the constant of the relaxation function.

	τ_m		
	$\psi = 1/e$	$\psi = 0.5$	$\psi = 1 - 1/e$
E_a (eV)	1.84	1.86	1.81
τ_0 (sec)	6.00×10^{-13}	1.40×10^{-13}	1.25×10^{-13}
n	0.35	0.35	0.35

Table II that the value of n in the non-linear kinetic form is around 0.4 almost irrespective of the composition of metallic glasses, while the value of β in the log normal kinetic form is distributed widely in the range of 3 and 6. Chambron and Chamberod [11] have examined the kinetics of the formation of field-induced magnetic anisotropy in $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass pre-annealed at 480° C for 20 min using the log normal kinetic form and reported the values of $E_a = 1.85$ eV and $\tau_0 = 5 \times 10^{-16}$ sec. These values are somewhat different from those for resistivity changes obtained in the present study.

Yokota *et al.* [19] have suggested that the resistivity changes in pre-annealed $Co_{58.3}Fe_{4.7}Ni_{10}Si_{11}B_{16}$ metallic glass are due to the chemical short-range ordering among transition metal atoms. Recently, Komatsu *et al.* [17] 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 (SRO) between cobalt and iron atoms. Komatsu *et al.* [4, 15] have also suggested that the resistivity changes in pre-annealed Fe–Ni based metallic glasses are due to reversible changes in the degree of SRO between iron and nickel atoms.

From these previous studies, it is considered that the resistivity changes caused by isothermal annealing in pre-annealed $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass shown in Fig. 2 are due to changes in the degree of SRO among cobalt, iron and nickel atoms and, thus,

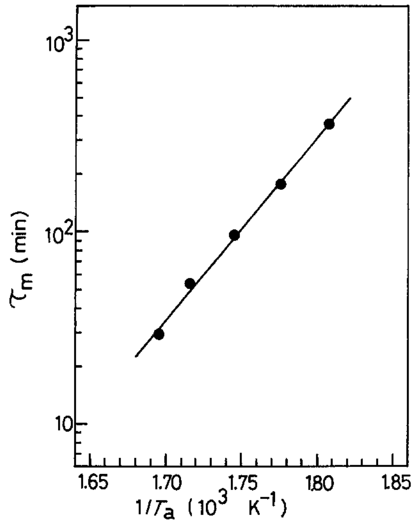

Figure 6 Dependence of the mean relaxation time, τ_m, on the annealing temperature, T_a, for resistivity changes in pre-annealed $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass.

the kinetic parameters of resistivity changes obtained in the present study may correspond to those of the formation of short-range order.

4. Conclusions

Resistivity changes caused by isothermal annealing in pre-annealed $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass were measured and the kinetics of resistivity changes were analysed using two different kinetic forms. In the case of the non-linear kinetic form, the values of mean activation energy, E_a, and mean pre-exponential factor, τ_0, are 1.84 eV and 2.88×10^{-13} sec, respectively, and it was found that the quality of data fitting to the calculated curve with a constant value of $n = 0.35$ was excellent. In the case of the log normal kinetic form, the values of E_a and τ_0 are 1.75 eV and 2.4×10^{-12} sec, respectively. The value of β is in the range 4.2 to 4.6 and the quality of data fitting to the calculated curve with a constant value of $\beta = 4.5$ was also good, except for the slight deviation in the large value of log (t/τ_m).

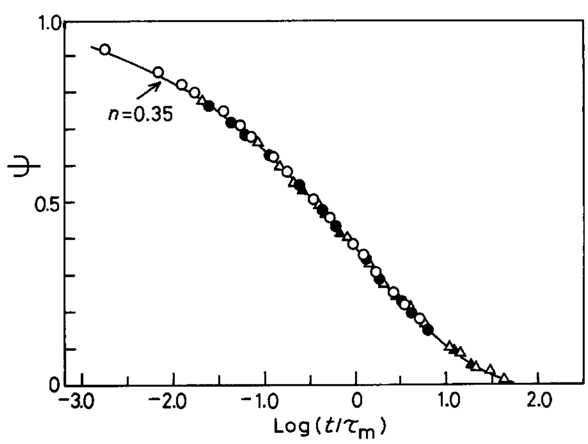

Figure 5 Resistivity changes $\psi = 1 - (\Delta\varrho/\varrho_0)/(\Delta\varrho/\varrho_0)_{eq}$ caused by isothermal annealing at various temperatures as a function of log (t/τ_m) in pre-annealed $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass. τ_m corresponds to the time at $\psi = 1/e$. Solid line is a theoretical curve expressed by Equation 1. (○) 280° C, (●) 300° C, (△) 320° C, (▲) 340° C.

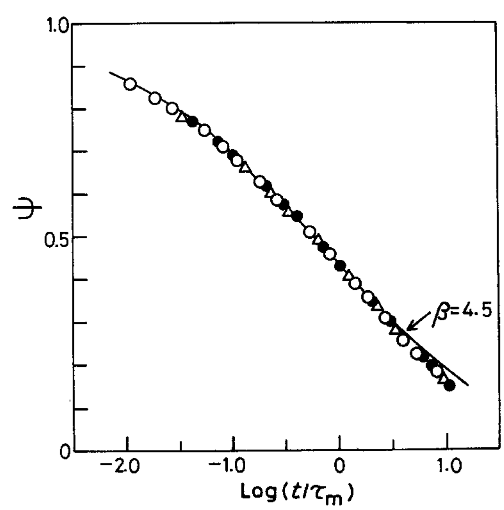

Figure 7 Resistivity changes $\psi = 1 - (\Delta\varrho/\varrho_0)/(\Delta\varrho/\varrho_0)_{eq}$ caused by isothermal annealing at various temperatures as a function of log (t/τ_m) in pre-annealed $Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$ metallic glass. Solid line is a theoretical curve expressed by Equation 3. (○) 280° C, (●) 300° C, (△) 320° C.

TABLE II Kinetic parameters estimated using the non-linear and log normal kinetic forms for reversible properties changes during structural relaxation in various metallic glasses. n (non-linear) and β (log normal) are the parameters representing the width of distribution of relaxation times, E_a is the mean activation energy and τ_0 is the mean pre-exponential factor

Composition	n, β	E_a(eV)	τ_0(sec)	Method*	Reference
Non-linear					
$Co_{58}Fe_5Ni_{10}Si_{11}B_{16}$	0.35	1.84	2.88×10^{-13}	a	This work
$Co_{38}Fe_5Ni_{30}Si_{11}B_{16}$	0.4	1.82	5.46×10^{-14}	a	[3]
$Fe_{15}Ni_{63}Si_8B_{14}$	0.43	1.93	8.6×10^{-16}	a	[4]
$Fe_{40}Ni_{40}B_{20}$	0.4	1.76		b	[2]
Log normal					
$Co_{58}Fe_5Ni_{10}Si_{11}B_{15}$:	4.2–4.6	1.75	2.4×10^{-12}	a	This work
		1.85	5×10^{-16}	c	[11]
$Co_{70.3}Fe_{4.7}Si_{15}B_{10}$	4–6	2.0	7.8×10^{-17}	c	[12]
$Co_{72.1}Fe_{5.9}Si_5B_{15}Mo_2$	3–5	2.0		c	[13]
$Fe_{40}Ni_{40}P_{14}B_6$	4	1.74	6.7×10^{-16}	c	[10]

*a: resistivity, b: Young's modulus, c: field-induced magnetic anistropy.

Acknowledgements

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