# Elinvar Characteristics of Amorphous Alloys and Their Applications

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# Elinvar Characteristics of Amorphous Alloys and Their Applications*

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Synopsis

The elastic properties and the Elinvar characteristics of various kinds of amorphous alloys are introduced. The Elinvar characteristics of Fe-base ferromagnetic amorphous alloys arises from their large ΔE effect. The elastic properties are sensitively affected by the internal stress, and the Elinvar characteristics is also obtained even in nonferromagnetic amorphous alloys such as Pd-Si and Ni-Si-B alloy systems by annealing or cold-rolling. A large stiffening is observed in Fe-base amorphous alloys in the saturated magnetic field, being different from the pole effect. The applications of the amorphous Elinvar alloys to mechanical vibrators and delay lines are described as examples, and then the merits and problems for their applications are pointed out from the practical point of view.

## I. Introduction

In recent years, growing attention has been paid to prominent characteristics of amorphous alloys as practical materials. The most active fields of applied researches at present are magnetic materials. The present authors have also paid attention to magnetic properties of Fe-base amorphous alloys and found that most of them exhibit both characters of Invar[1∼3] and Elinvar[4∼6] around room temperature. In the case of ferromagnetic materials, it is well known that the Invar characteristics is caused by a large spontaneous volume magnetostriction and the Elinvar one by a large ΔE effect below the Curie temperature. According to studies[4∼13] reported so far on the elastic properties of amorphous alloys, the Elinvar characteristics was

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found in Fe base and even in nonferromagnetic amorphous alloys by controlling metalloid contents, preparation conditions or heat-treatments. On the other hand, Co-base ferromagnetic amorphous alloys exhibit no large spontaneous volume magnetostriction and no large ΔE effect, resulting in no Invar and Elinvar characteristics[1,14].

The present paper reviews the recent results on the Elinvar characteristics and the ΔE effect of several kinds of Fe-base ferromagnetic amorphous alloys, and on the Elinvar characteristics of nonferromagnetic amorphous alloys. The stiffening of Young's modulus [14∼16] which is often confused with the pole effect[12,17] is also briefly discussed. Some typical devices applying the Elinvar characteristics of amorphous alloys such as mechanical vibrators and delay lines[18] are demonstrated. Finally, from the practical point of view, the merits and problems for applications of the amorphous alloys such as productivity, aging and anisotropy are discussed.

## II. Elasticity of Amorphous Alloys

In the case of crystalline materials, the crystalline anisotropy in elastic constants is generally remarkable. In contrast with them, the amorphous alloys have an isotropic nature from lack of long-range ordering in atomic arrangement. As is well known, the elastic properties in an isotropic material are expressed by the following equation;

$$\frac{1}{E} = \frac{1}{G} + \frac{1}{3K} \quad \text{.....(1)}$$

where E is Young's modulus, G the shear modulus and K the bulk modulus. Then, E is given by

$$E = \frac{9GK}{3K + G} \quad \text{.....(2)}$$

and also $E = 2(1 + \nu)G = 3(1 - 2\nu)K$ .....(3)
where $\nu$ is Poisson's ratio.

Elastic moduli of amorphous alloys have been measured by the following methods;

(a) stress-strain curve[19]
(b) electrostatic vibration[4]
(c) ultrasonic sound[20]
(d) Brillouin light scattering[21]

Generally, E, G and K of amorphous alloys are smaller than those of crystalline alloys, and E slightly increases by heat-treatments due to the structural relaxation[22]. Elastic moduli are more or less affected by the addition of solute elements. Figure 1 shows the concentration dependences of Young's modulus E and the density $\rho$ of Fe-Si-B amorphous alloys. The value of E increases and $\rho$ decreases with increasing boron content. Similar behaviors have been observed in Pd-Ni-Si and Pd-Fe-P amorphous alloys[9,23,24]. As a general feature, the amorphous alloys have fairly high values in hardness and tensile strength, which are proportional to E and G[25]. Young's modulus E is reduced by cold-rolling and restored substantially by annealing[26]. The values of K for Fe-base amorphous alloys are relatively small as compared with those of other amorphous alloys[27∿29] because of the Invar effects.

## III. Elinvar Characteristics of Ferromagnetic Amorphous Alloys -Fe-base Alloy Systems-

(1) Fe-B alloy system

Distinct Elinvar characteristics in Fe-B amorphous alloys was observed in wide temperature range[6∿15]. In this alloy system, the magnetic moment per Fe atom decreases below 15at%B[3,30] and the Curie temperature lowers with a decrease in the boron content[2,31]. The spontaneous volume magnetostriction is as large as about $2 \times 10^{-2}$ at 15at%B[16]. Such magnetic behaviors are almost the same as those of Fe-Ni crystalline Invar alloys[3,16,32].

Figure 2 shows the temperature dependence of Young's modulus E of Fe-B amorphous alloys annealed at 200°C for 2 hr[15]. With increasing boron content, the Curie temperature $T_c$ rises and approaches to the crystallization temperature $T_x$. As seen from the figure, Young's modulus hardly depends on the temperature in a wide temperature range below $T_c$. Especially, the alloys containing boron from 15 to 18at% indicate a very small value of the temperature coefficient given by

$$e = \frac{1}{E}\frac{dE}{dT} \quad .....(4)$$

Such an Elinvar behavior arises from a large $\Delta E$ effect and its magnitude is defined by

$$\frac{E_S - E_D}{E_D} = \frac{\Delta E}{E_D} \quad .....(5)$$

where $E_D$ and $E_S$ are Young's moduli measured in zero and saturated magnetic fields, respectively. The $\Delta E$ effect of this alloy system is extremely large as about 0.4∿0.6. Young's modulus drastically changes around $T_x$ and the Elinvar characteristics disappears as shown

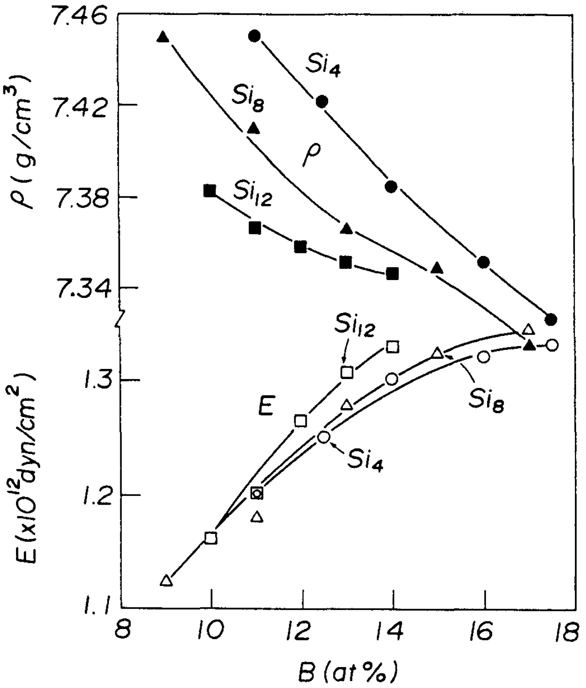


Fig. 1 Relationship among Young's modulus E, density ρ at room temperature and the boron content for the Fe-Si-B amorphous alloys with a constant content of Si ( = 4, 8, 12 at% ).

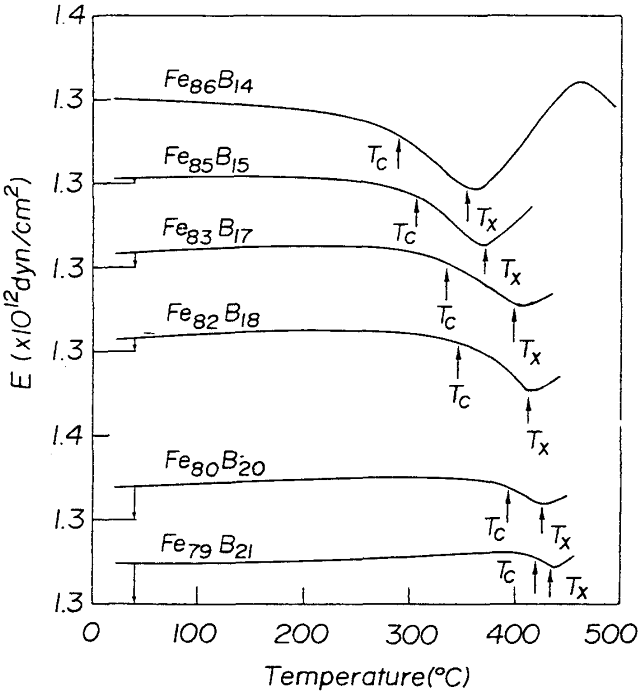


Fig. 2 Temperature dependence of Young's modulus E for amorphous Fe-B alloys annealed at 200°C for 2 hr. $T_x$ and $T_c$ show the crystallization and the Curie temperature, respectively.

in the figure. Hausch and Török have also measured the temperature dependence of Young's modulus of $Fe_{80}B_{20}$ amorphous alloy as a function of annealing temperature[33], and observed the Elinvar characteristics in an amorphous state.

(2) Fe-P alloy system

Fe-P amorphous alloys also exhibit the Invar characteristics due to a large spontaneous volume magnetostriction[5,34]. The temperature dependence of the shear and Young's moduli of $Fe_{85}P_{15}$ amorphous alloy is shown in Fig. 3[35]. This alloy shows the Elinvar characteristics over a wide temperature range below the Curie temperature $T_c$ in as-prepared and annealed states. The $\Delta G$ effect is given by

$$\frac{\Delta G}{G_D} = \frac{G_S - G_D}{G_D} \quad \text{.....(6)}$$

where $G_D$ and $G_s$ are the shear moduli at zero and saturate magnetic fields, respectively. The $\Delta E$ and $\Delta G$ effects calculated from Eqs. (5) and (6) for this alloy are 0.14 and 0.16, respectively, showing almost the same values. However, these values are relatively small as compared with those of Fe-B amorphous alloys.

(3) M-Zr alloy systems (M = Fe, Co and/or Ni)

The elastic properties of amorphous alloys consisting of only transition metals such as $(Fe, Co, Ni)_{90}Zr_{10}$ amorphous alloys have been investigated and the Elinvar characteristics has been observed in $Fe_{90}Zr_{10}$ alloy[36], although its temperature range is not so wide as that of Fe-B and Fe-P amorphous alloys. It has been found that $Fe_{90}Zr_{10}$ and $(FeCo)_{90}Zr_{10}$ amorphous alloys also exhibit the Invar characteristics due to a relatively large spontaneous volume magnetostriction[37,38].

(4) Fe-X-B alloy systems (X = Si, Cr or Mo)

One expects that Fe-base ternary amorphous alloys may exhibit the Elinvar characteristics. Figure 4 shows the temperature dependence of the square of the relative in frequency for Fe-Si-B amorphous alloys quenched (dotted line) and annealed at 400°C for 1 hr in the magnetic field of 400 Oe (solid line)[4]. The values of $f_0$ and $f_t$ are the frequencies at 0°C and t°C, respectively. From the practical point of view, the data around room temperature are shown in the figure. By adequate selection of the composition and heat-treatment, excellent Elinvar characteristics are obtainable.

The temperature dependence of Young's modulus of $(Fe_{1-x}Cr_x)_{85}B_{15}$ amorphous alloys is shown in Fig. 5[39]. Chromium was added in order to improve the corrosion resistance and mechanical properties. With increasing Cr, the Curie temperature $T_c$ decreases and the crystalli-

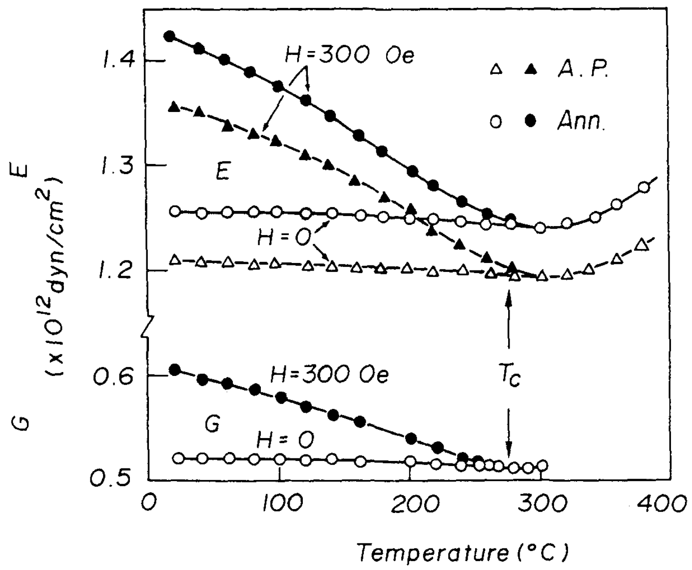


Fig. 3 Temperature dependence of Young's modulus and the shear modulus for $Fe_{85}P_{15}$ alloys as-prepared and annealed in zero or saturated field.

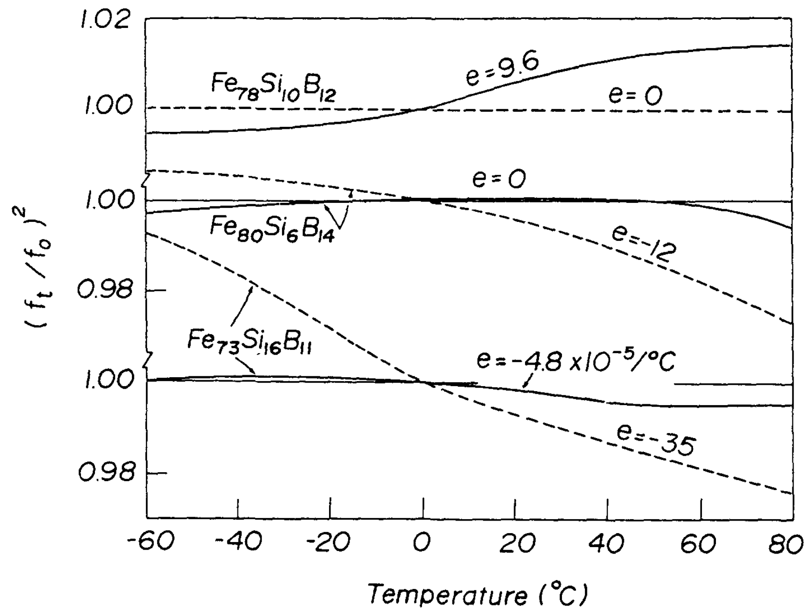


Fig. 4 Fractional change in the square of frequency $(f_t/f_o)^2$ as a function of the temperature for several amorphous Fe-Si-B alloys. $f_t$ and $f_o$ are resonant frequencies at certain temperature t and at 0°C, respectively. dashed lines; as-prepared state, solid lines; annealed state under magnetic field (400 Oe).

zation temperature $T_x$ oppositely increases. Since the Elinvar characteristics is obtained below $T_c$, the temperature range showing this behavior becomes narrower with increasing Cr content, therefore the content of Cr is limited to about 8% from the practical point of view. The addition of Cr is effective in increase of Young's modulus and the corrosion resistance. Therefore, this alloy system is useful for practical applications.

Tyagi and Lord Jr. have measured the temperature dependence of $f_t/f_0$ of $Fe_{78}Mo_2B_{20}$ amorphous alloy annealed at various temperatures [40]. They have found that the elastic property is affected by annealing temperature, and the alloy annealed at 490°C for 20 min exhibits the Elinvar characteristics. However, this alloy becomes brittle because the heat-treatment temperature is close to the crystallization temperature.

(5) Fe-Ni-P-B alloy system

The temperature dependence of Young's modulus of $Fe_{40}Ni_{40}P_{14}B_6$ amorphous alloy has been investigated by Török and Hausch[12]. The temperature coefficient for the as-prepared alloy is negative around room temperature, but that of the alloy annealed at 300°C for 2 hr is positive. Therefore, it is expected that the Elinvar characteristics may be obtained by controlling the heat-treatment condition. After crystallization, no Elinvar characteristics is observed in this alloy and Young's modulus becomes larger by 30 ∿ 40% than that in the amorphous state.

## IV. Elinvar Characteristics of Nonferromagnetic Amorphous Alloys

(1) Pd-Si alloy system

The elastic properties are sensitively affected by internal stresses. Then, the Elinvar characteristics in amorphous alloys is often obtained by controlling the preparation conditions because the internal stresses are induced by rapid-quenching. Figure 6 shows the relationship between the revolution number of roller and the temperature coefficient of Young's modulus at room temperature for $Pd_{80-x}Si_{20}Ag_x$ amorphous alloys[13]. The coefficient becomes small when the roller with 20 cm in diameter is revoluted at 3000 r.p.m.. This means that the magnitude of the internal stresses depends on the quenching speed from the liquid state. Figure 7 shows the annealing time dependence of the temperature coefficient of Young's modulus $e$ at room temperature for $Pd_{80}Si_{20}$ amorphous alloy annealed at 100°C after preparing at various revolution numbers of roller with 20 cm in diameter[13]. The value of $e$ for the specimen prepared at 2000 r.p.m.

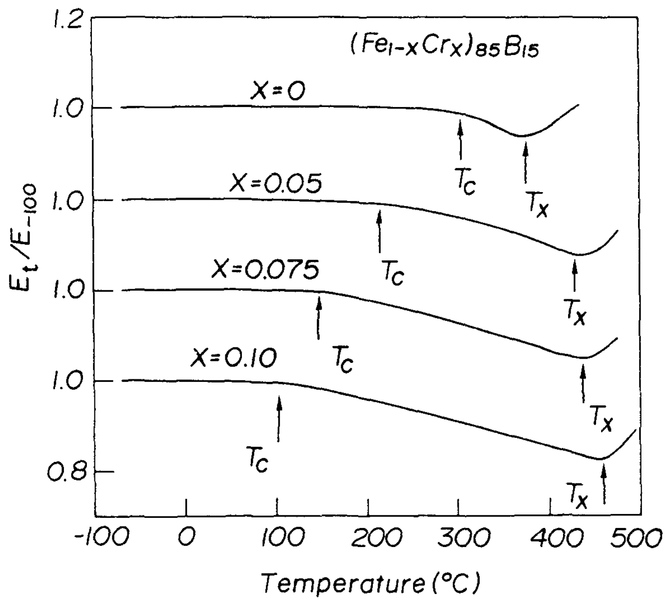


Fig. 5 Temperature dependence of Young's modulus for amorphous $(Fe_{1-x}Cr_x)_{85}B_{15}$ alloys annealed at 200°C for 2 hr. $E_t$ and $E_{-100}$ are Young's modulus at temperature t and at -100°C, respectively.

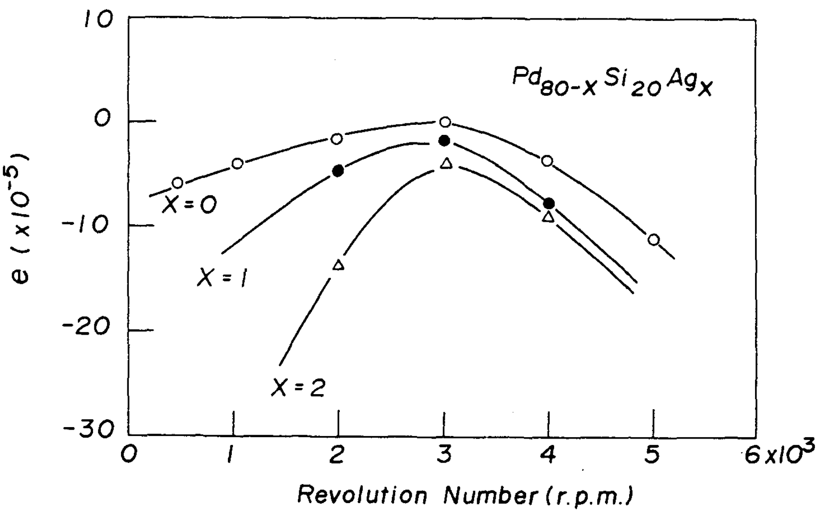


Fig. 6 Revolution number of the roller vs. the temperature coefficient of Young's modulus at room temperature for amorphous $Pd_{80-x}Si_{20}Ag_x$ alloys $(0 \leq x \leq 2)$.

is hardly changed by annealing at 100°C, attaining to the Elinvar characteristics. On the other hand, the value of $e$ for the alloy prepared at 4000 r.p.m. remarkably depends on the annealing time and the Elinvar characteristics is no longer observed after annealing at 100°C for more than 1 hr. From these results, it is concluded that the Elinvar characteristics of Pd-Si amorphous alloys is obtained by controlling the magnitude of internal stresses, depending on the quenching rate and heat-treatment.

(2) Ni-Si-B alloy system

Most of Ni-Si-B amorphous alloys are paramagnetic at room temperature, and their elastic properties strongly depend on the preparation conditions[18]. Smaller values of the temperature dependence of Young's modulus, $e$, are obtained when the alloy is prepared at the rate of 3∿4000 r.p.m. by using a roller with 20 cm in diameter. Figure 8 shows the relationship between the reduction ratio by cold rolling and the value of $e$ for Ni-Si-B amorphous alloys. The magnitude of $e$ for $Ni_{67}Si_{13}B_{20}$ amorphous alloy gradually becomes smaller with increasing the reduction ratio and reaches to $-4 \times 10^{-5}$ at 7%. On the other hand, the magnitude of $e$ for $Ni_{67}Si_{10}B_{23}$ amorphous alloy becomes larger with an increase of the reduction ratio. Therefore, the elastic properties of the cold rolled Ni-Si-B amorphous alloys sensitively depend on the composition of metalloids.

## V. The ΔE and Pole Effects

Since the elastic properties of ferromagnetic materials are affected by the magnetostriction, Young's modulus becomes smaller by ΔE than the value of a hypothetical paramagnetic state as given in Eq. (5). Generally speaking, the more the saturation magnetostriction $\lambda_s$ increases, the more the ΔE effect increases because $\lambda_s$ is directly correlated to the ΔE effect. It is empirically well known that the saturation magnetostriction $\lambda_s$ of Fe-base amorphous alloys is associated with the saturation magnetization $M_s$ and can be written as[41],

$$\lambda_s \propto M_s^2 \quad .....(7)$$

Berry et. al. have been studied the ΔE effect and $\lambda_s$ of $Fe_{75}P_{15}C_{10}$ amorphous alloy and obtained quite large values of 0.25 for $\Delta E/E_D$ and of $25 \times 10^{-6}$ for $\lambda_s$ at room temperature in the as-prepared state[42]. Furthermore, Arai et. al. have measured the magnetic field dependence of Young's modulus and the magnetostriction of Fe-Si-B amorphous alloys, and obtained the remarkably large $\Delta E/E_D$ value of 1.91 for

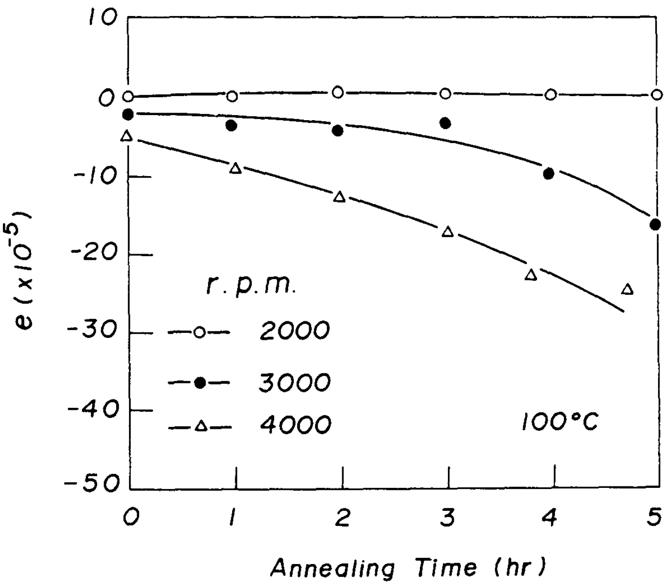


Fig. 7 Effect of annealing time on the temperature coefficient of Young's modulus at room temperature for $Pd_{80}Si_{20}$ amorphous ribbons prepared at 2000∿4000 r. p. m..

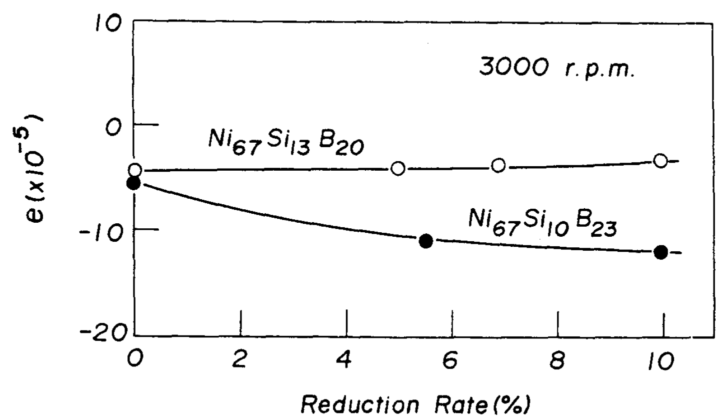


Fig. 8 Effect of reduction ratio by cold rolling on the temperature coefficient of Young's modulus for $Ni_{67}Si_{13}B_{20}$ and $Ni_{67}Si_{10}B_{23}$ amorphous alloys.

$Fe_{78}Si_{10}B_{12}$ amorphous alloy[43] and the large $\lambda_s$ value of $35 \times 10^{-6}$ for $Fe_{78}Si_8B_{14}$ amorphous alloy[44].

We have investigated systematically how the ΔE effect does contribute to the Elinvar characteristics in Fe-base amorphous alloys[4, 15]. In Fig. 9, $Fe_{85}B_{15}$ amorphous alloy exhibits a large value of 0.4 for $\Delta E/E_D$ at room temperature, while the value of $Fe_{83}P_{17}$ amorphous alloy is only 0.1[15], although both alloys show the Elinvar characteristics in a wide temperature range. In contrast with the ΔE effect, the saturation magnetostrictions $\lambda_s$ of both amorphous alloys are extremely large, attaining to $30 \sim 40 \times 10^{-6}$ as shown in Fig. 10. The internal stress $\sigma_i$ in Fe-base amorphous alloys is very large[42] and the crystalline anisotropy K is very small[42]. Under such a circumstance, the rotational process of the magnetic domains is predominant. When the energy of internal strain $\lambda_s\sigma_i$ is larger than the energy of crystalline anisotropy K[45],

$$\frac{\Delta E}{E_D} = \frac{2}{5}\left(\frac{E_s\lambda_s}{\sigma_i}\right) \qquad .....(8)$$

$$\mu_0 = \frac{8}{9}\pi\left(\frac{M_s^2}{\lambda_s\sigma_i}\right) \qquad .....(9)$$

where $\mu_0$ is the initial permeability and $M_s$ is the saturation magnetization. Eliminating $\sigma_i$ from Eqs. (7) and (8), we get the following equation;

$$\frac{\Delta E}{E_D} = \frac{9}{20\pi}\left(\frac{E_s\lambda_s^2}{M_s^2}\mu_0\right) \qquad .....(10)$$

From Eq. (10), the value of $\Delta E/E_D$ is proportional to $\mu_0$. By using the measured values of $M_s$, $\lambda_s$ and $\mu_0$, we have calculated the value of $\Delta E/E_D$ for $Fe_{85}B_{15}$ and $Fe_{83}P_{17}$ amorphous alloys, and the results are given in Table 1. The calculated values agree fairly well with the measured ones. Accordingly, it is concluded that the reason why such a remarkable difference in the ΔE effect occurs is attributed to the difference of the value of $\mu_0$ between both amorphous alloys.

In the research on the ΔE effect, one should keep in mind the "Pole effect" which is often confused with the ΔE effect. The pole effect have been found when the measurement is carried out under the magnetic field using the thin sheet sample at low frequency modes. With increasing of external magnetic field the frequency increases linearly due to the magnetic pole occured on the edge of sample, then the apparent Young's modulus becomes large. This phenomenon was named "Pole effect" by Berry et al.[46]

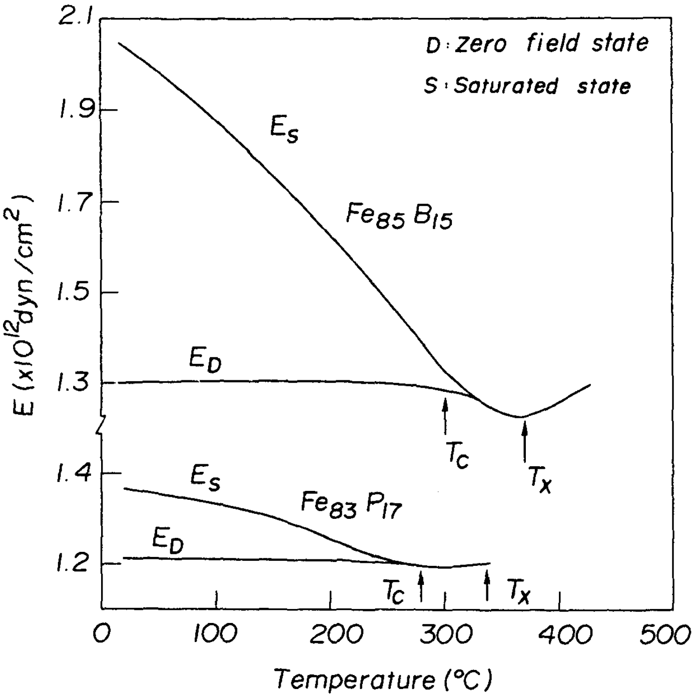


Fig. 9 Temperature dependence of Young's modulus under zero or saturated magnetic field for annealed $Fe_{85}B_{15}$ and $Fe_{83}P_{17}$ amorphous alloys.

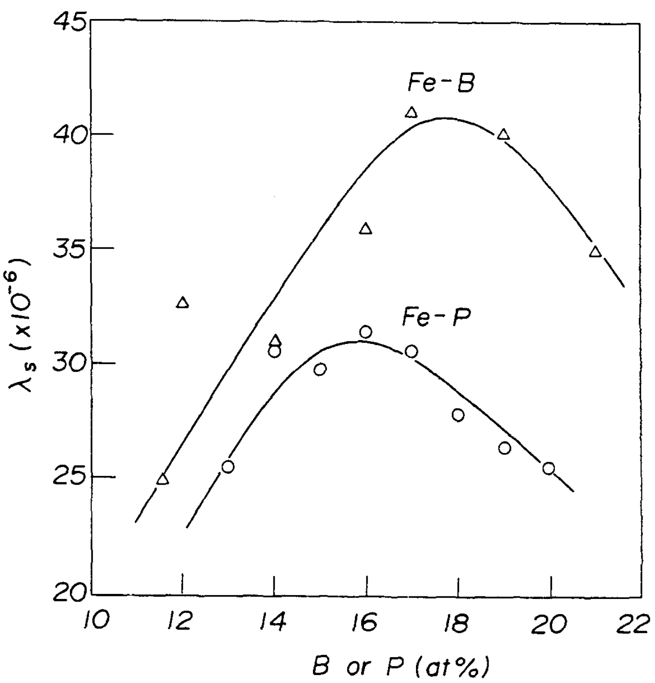


Fig. 10 Concentration dependence of the saturation magnetostriction for as-prepared Fe-B and Fe-P amorphous alloys.

Table 1 Saturation magnetostriction $\lambda_s$ initial permeability $\mu_0$, the Curie temperature $T_c$, Young's modulus at the saturated state $E_s$ and the measured and calculated $\Delta E$ effect for $Fe_{83}P_{17}$ and $Fe_{86}B_{14}$ amorphous alloys in as-prepared and annealed states.

| Alloy | $\lambda_s$ ($\times 10^{-6}$) | $\mu_0$ | $E_s$ ($\times 10^{12}$dyn/cm$^2$) | $(\Delta E/E_D)_{meas}$ | $(\Delta E/E_D)_{calc}$ |
|---|---|---|---|---|---|
| $Fe_{83}P_{17}$ | 30 | 900 | 1.35 | 0.13 | 0.12 |
| $Fe_{83}P^*_{17}$ | 32 | 860 | 1.42 | 0.14 | 0.14 |
| $Fe_{86}B_{14}$ | 31 | 3500 | 1.78 | 0.43 | 0.40 |
| $Fe_{86}B^*_{14}$ | 49 | 1800 | 2.02 | 0.55 | 0.52 |

*Annealed at 200°C for 2 hr.

The value of pole effect which makes an apparent large $\Delta E$ effect is given by the 2nd term of the equation expressed by[46)]

$$f_n^2 = \frac{\alpha_n^2 d^2 E}{3\pi^2 \ell^4 \rho} + \frac{2\beta_n MH}{\rho\pi^2\ell^2} \qquad .....(11)$$

where d, $\ell$ and $\rho$ are the thickness, the length and density of the specimen, and M and H are the saturation magnetization and the external magnetic field, respectively. The values of $\alpha_n$ and $\beta_n$ are the constants which depend on the mode of oscillation. Furthermore, when the pole effect occurs, the natural frequency in as-saturated states is given by

$$f_{ns} = \left(\frac{\alpha_n}{\ell}\right)^2 \frac{d}{\pi} \frac{E_s}{3\rho} \qquad .....(12)$$

From Eqs. (11) and (12), the following equation is given,

$$\frac{f_n^2}{f_{ns}^2} = 1 + \frac{6\gamma_n M_s \ell^2}{E_s d^2} H \qquad .....(13)$$

where $\gamma_n$ is represented by $\gamma_n = \beta_n/\alpha_n^4$, and their values are given by $\gamma_1 = 0.891$, $\gamma_2 = 0.0788$, $\gamma_3 = 0.0165$ and $\gamma_4 = 0.00602$ for each oscillation mode.

Figure 11 shows the magnetic field dependence of Young's modulus (designated by $[f_n/f_{ns}]^2$, n = 1, 2, 3, ...) for $Fe_{83}B_{17}$ amorphous alloy [13,47]. The value of $(f_n/f_{ns})^2$ measured at low frequency such as fundamental oscillation $f_1$ gives normal $E/E_D$ vs. H curve under the low fields below 100 Oe. However, in more higher fields, it increases linearly and does not saturate. On the other hand, even at the field of 100 Oe or more, $E/E_D$ value saturates easily with increasing the frequency by heightening the oscillation mode like $f_2$, $f_3$, .... In other words, the pole effect becomes vanishingly smaller at higher frequencies[48]. Therefore, the $\Delta E/E_D$ value obtained by using the higher order oscillation modes is considered to be a real value.

The pole effect described above appears not only in amorphous alloys but also in crystalline alloys when a thin and long sample is used as presumed from equation[14]. The data measured for crystalline $Fe_{63.5}Ni_{36.5}$ Invar alloy with 60 μm thick and $\ell/d = 100$ and 300 is shown in Fig. 12[46]. The value of $(f_t/f_{20})^2$ (—o—) at the first mode oscillation under the external field of 700 Oe changes with a negative gradient even below $T_c$ and its value is larger than the paramagnetic value $E_p$ obtained by extrapolating from temperature above $T_c$ as shown with a dotted-dashed line. It is found that this is obvious influence of the pole effect and the apparent Young's

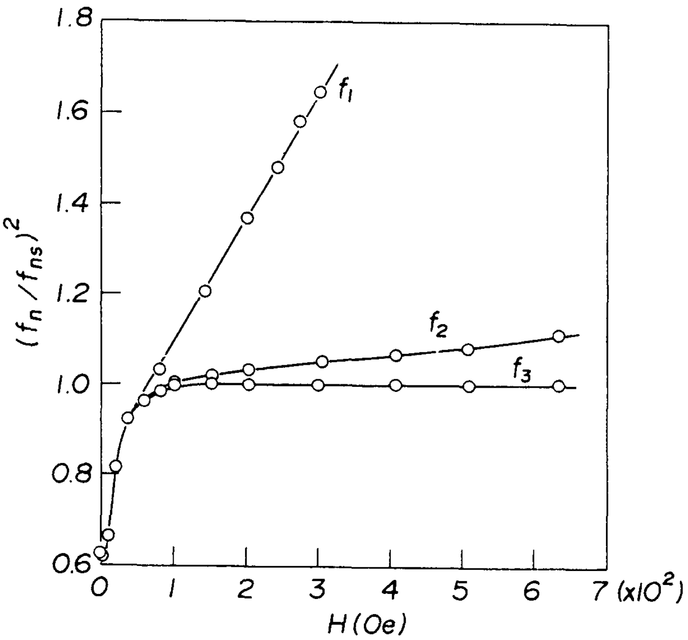


Fig. 11 Dependence of the $(f_n/f_{ns})^2$ on the magnetic field for annealed $Fe_{83}B_{17}$ amorphous alloy at the fundamental, second and third frequency modes.

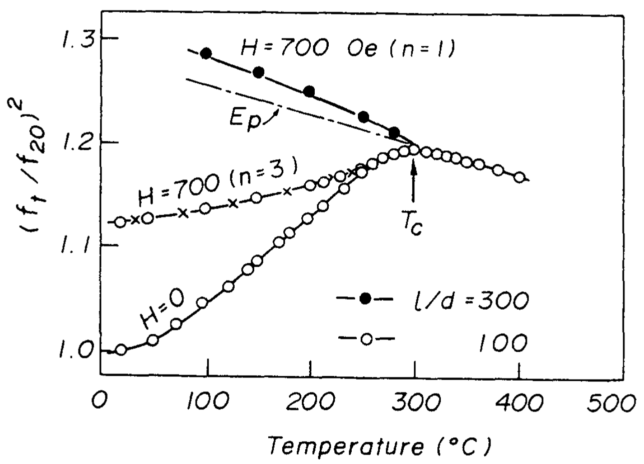


Fig. 12 Temperature dependence of $(f_t/f_{20})^2$ for annealed $Fe_{63.5}Ni_{36.5}$ crystalline alloy under the fields of 0 and 700 Oe. The length-thickness ratios are 100 and 300.

modulus becomes remarkably large. The curve (—x—) obtained from the 3rd mode oscillation takes positive gradient below $T_c$ (softening phenomenon), and this result agrees with the temperature dependence of Young's modulus measured at saturated field ($E_s$) for the Invar alloy of a bulk sample (—o—)[49].

In order to know more precisely the relation between the pole effect and ΔE effect, the temperature dependence of Young's modulus of $Fe_{75}Cr_5B_{20}$[18] and $Co_{70}B_{30}$ amorphous alloys with and without the magnetic field are investigated[14,47]. As shown in Fig. 13, $Fe_{75}Cr_5$-$B_{20}$ amorphous alloy indicates a remarkable Elinvar characteristics and a quite large ΔE effect, while $Co_{70}B_{30}$ amorphous alloy does not show the Elinvar characteristics and the ΔE effect is extremely small. In considering of Young's modulus in the magnetically saturated state ($E_s$) and in the paramagnetic state (Ep), $E_s$ value is higher than $E_p$ in Fe-base amorphous alloys (stiffening phenomenon) but Co-base amorphous alloys do not show such a phenomenon. In addition, the pole effect observed by measuring with low frequencies is shown in the same figure, and this effect is commonly appeared in both alloys. Therefore, it is clear that the large ΔE effect observed in Fe-base amorphous alloys does not have any relations to the pole effect, and this ΔE effect essentially accompanies a stiffening phenomenon which is noticed only in Fe-base amorphous alloys. After all, we conclude that such a phenomenon is not connected with the amorphous structure because the stiffening is not observed in Co-base amorphous alloys as described above.

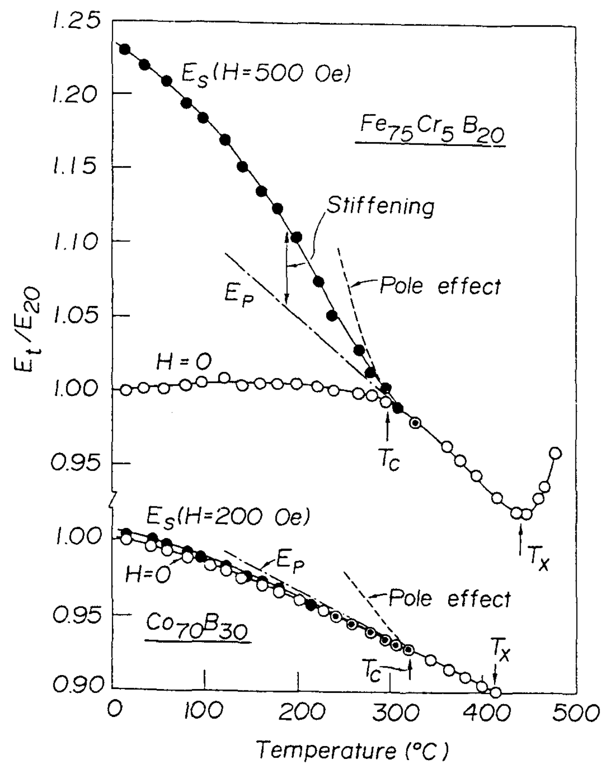


Fig. 13 Temperature dependence of $E_t/E_{20}$ for $Fe_{75}Cr_5B_{20}$ and $Co_{70}B_{30}$ amorphous alloys with and without field ($E_t$ and $E_{20}$ are Young's modulus at temperature t and 20°C, respectively).

## VI. Applications of Amorphous Elinvar Alloys

Elinvar alloys are widely applied to many kinds of electromagnetic devices and precision instruments. Typical applications of Elinvar alloys are listed in Table 2[50]. The amorphous alloys have generally excellent mechanical properties such as a high tensile strength and a high hardness, however the applicable fields are limited because that the shape of amorphous alloys produced is a thin ribbon or a fine wire. The possibility of various applications of amorphous Elinvar alloys has been proposed[51]. In the present paper, we demonstrate typical applications for mechanical vibrators and delay lines.

(1) Mechanical Vibrators

In application of the Elinvar alloys for vibrator of functional parts such as a vibrating reed and a mechanical filter, the appropriate frequency range is from several Hz to M Hz. Especially, they are

Table 2 Applications of Elinvar alloys

| | |
|---|---|
| Measuring Instruments | Seismograph, Gravity meter, Flow meter, Accelerometer, Torque meter, Manometer, Spring-balance, Dial gauge, Tuning fork, Vibrating reed, Hair spring |
| Electro-magnetic Instruments | Mechanical filter, Delay line, Magnetostrictive vibrator, reed relay, Standard oscillator, Bourdon's tube. |
| Others | Shutters of camera, Bellow, Membrane, Various precise spring. |

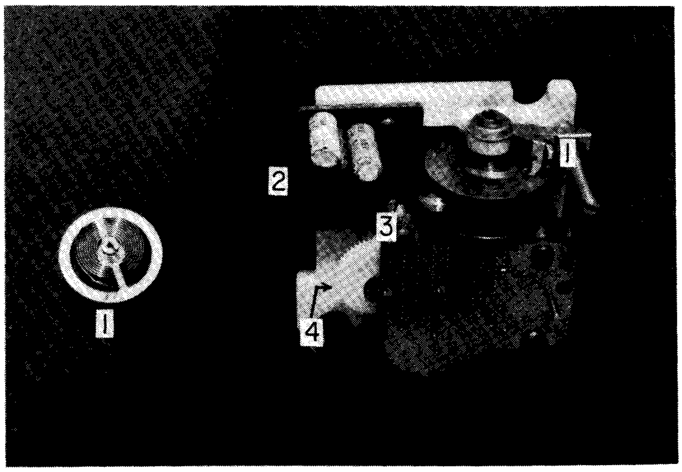


Photo. 1 Hair spring made of $Ni_{67}Si_{13}B_{20}$ amorphous alloy and its application to clock. (1. hair spring, 2. source of electric power, 3. driving coil, 4. gear.)

most suited to small size vibrators for watches and clocks. By improving in frequency accuracy ($\Delta f/f_0$), the vibrators for many watches and clocks are displaced by quartz having a very high accuracy of $10^{-7} \sim 10^{-8}$ order. However, the Elinvar alloys are still suitable for clocks using a tuning fork with accuracy of $10^{-5} \sim 10^{-6}$ and watches using a hair spring with accuracy of $10^{-4} \sim 10^{-6}$.

The hair spring materials used recently are Fe-base and Co-base crystalline Elinvar alloys, but they are not used in a magnetic field because their ferromagnetism brings about a time error. On the contrary, Pd-Si and Ni-Si-B amorphous Elinvar alloys are nonferromagnetic and suitable for the hair spring materials of watches because the temperature coefficient of Young's modulus can be controlled to almost zero. The hair spring made of $Ni_{67}Si_{13}B_{20}$ amorphous alloy and the clock assembled by it are shown in Photo. 1. The most principle problem in applying them as tuning fork and a vibrating reed is to keep on a constant vibration between 0.1 and 1 kHz for long time at particular temperature range, then the material with a high mechanical strength and a high fatigue limit is requested. Most of amorphous alloys are suitable to these applications[52]. However, the mechanical vibration quality factor Q necessary for tuning forks is somewhat lower than 3000[7,53]. In addition to above applications, the amorphous alloys with a high mechanical strength are useful as the materials for ligament and suspension wires.

(2) Delay lines

Ultrasonic wave delay lines make use of property that the propagation velocity of ultrasonic wave is late by the order of about $10^5$ than that of electromagnetic wave[54]. The delay mediums generally have the delay time of several μs, and it is required that the temperature coefficient of delay time and the attenuation coefficient of ultrasonic wave are as small as possible. The temperature coefficient of delay time $t$ is given by

$$t = -\frac{1}{2}(e + \alpha) \quad .....(14)$$

where $e$ is the temperature coefficient of Young's modulus and $\alpha$ is the thermal expansion coefficient. As seen from Fig. 6, the value of $e$ can be controlled by preparation conditions, then $t$ becomes very small. In nonferromagnetic crystalline materials they accompany the following dampings, depending the grain size;

$$a \propto f^4 \ (\zeta \geq 2\pi\bar{D}) \quad .....(15)$$

$$a \propto f^2 \ (\zeta \leq 2\pi\bar{D}) \quad .....(16)$$

where $a$ is the attenuation coefficient, $\zeta$ the wave length and $\bar{D}$ the mean diameter of grain. In amorphous alloy, there are no grain boundary scattering losses. In fact, Pd-Si amorphous alloys exhibit a extremely small attenuation coefficient[54] similar to that of a fused silica which is used as delay lines[55]. Therefore, it is promised that Pd-Si amorphous alloys are used as a delay line up to higher frequency range in contrast to ferromagnetic materials.

Since sound waves in the ferromagnetic materials accompany the various damping phenomena depending on the frequency $f$ and the stress $\sigma$[56], these ferromagnetic amorphous alloys should be used in a relatively low frequency range. Fe-base amorphous alloys exhibit simultaneously the Invar and Elinvar characteristics and the value of $t$ becomes small as shown in Table 3. Then these amorphous alloys are considered to be suitable as materials for delay lines[51].

In Fig. 9, it has been pointed out that Young's modulus of Fe-base amorphous alloys is easily affected by a external magnetic field. Therefore, it is clear that the sound velocity is readily controlled by applying the external magnetic field. Arai et al. have shown that Fe-base amorphous alloys are suitable for variable magnetostrictive delay lines[43]. They have demonstrated that the delay time is controlled easily by changing the bias magnetic field and shown that the delay characteristics are effectively improved by annealing just below the crystallization temperature[11].

Table 3 Temperature coefficient of Young's modulus, $e$, thermal expansion coefficient, $\alpha$, and temperature coefficient of delay time, $t$, for some Fe-B amorphous alloys. Each value is the average from 0 to 40°C.

| Alloy | heat treatment | $e$ ($\times 10^{-5}$) | $\alpha$ ($\times 10^{-6}$) | $t$ ($\times 10^{-6}$) |
|---|---|---|---|---|
| $Fe_{86}B_{14}$ | as-prepared | -1.5 | -1.5 | +8.3 |
| $Fe_{85}B_{15}$ | 200°C, 2 hr | +1.5 | -1.0 | -7.0 |
| $Fe_{79.5}B_{20.5}$ | 200°C, 2 hr | +1.0 | +4.1 | -7.0 |
| $Fe_{84}B_{16}$ | 300°C, 30 min*) | -0.2 | -0.1 | +1.1 |
| $Fe_{87}B_{13}$ | 200°C, 30 min**) | -0.5 | -1.5 | +3.3 |
| $Fe_{83}P_{17}$ | 200°C, 2 hr | -0.5 | +4.6 | +0.2 |

*) Cooled at the rate of 200°C/hr in longitudinal magnetic field of 400 Oe.
**) Cooled at the rate of 200°C/hr in transverse magnetic field of 400 Oe.

## VII. Merits and Problems for Applications

(1) Merits

As compared with crystalline alloys, amorphous alloys have a merit of easy production. For instance, in production of crystalline thin sheets, many manufacturing processes are necessary, that is, repeated rolling processes are necessary to produce thin materials after casting and forging. On the contrary, the productions of amorphous alloys have such merits that the object is directly obtained from the melt using simple equipments with low costs, which is a convenient method from the standpoint of the energy saving, although they are limited to small dimentions such as thin sheets and fine wires.

(2) Problems

There are some problems for applications of amorphous alloys. In the present paper, the aging effect and anisotropy of elastic properties are described.

(a) Aging Effect

As is well known, the amorphous structure is a nonequilibrium metastable state, then elastic properties may change by aging. Figure 14 shows the time dependence of $\Delta e$ value for $(Fe_{1-x}Cr_x)_{85}B_{15}$ $(x = 0.025)$ amorphous alloys, where $\Delta e$ is a difference between the temperature coefficient of Young's modulus at zero hour, $e_0$, and that at t hours, $e_t$[17]. The value of $\Delta e$ for the sample melt quenched or annealed at a temperature (300°C) near the crystallization temperature tends to decrease with time, and the decrement of the former sample is above twice in comparison with the value of the latter. These behaviors are connected with relaxations of internal stresses induced by rapidly quenching from melts. By annealing at a temperature (200°C) enough below the crystallization temperature, the value of $\Delta e$ becomes constant after 100 days as shown in the figure. Therefore, an adequate heat-treatment is necessary to stabilize the elastic properties of amorphous alloys.

(b) Anisotropy Effect

It is well known in crystalline alloys that elastic properties exhibit a remarkable anisotropy along a crystal axis. This anisotropy is enhanced by cold-rolling due to a fiber structure. On the other hand, amorphous alloys without grain boundaries do not form such a fiber structure as those of crystalline alloys. However, it is considered that some anisotropy occurs due to inhomogeneous distribution of internal stresses induced by rapidly quenching. In fact, it has been reported that the ferromagnetic amorphous alloys take a

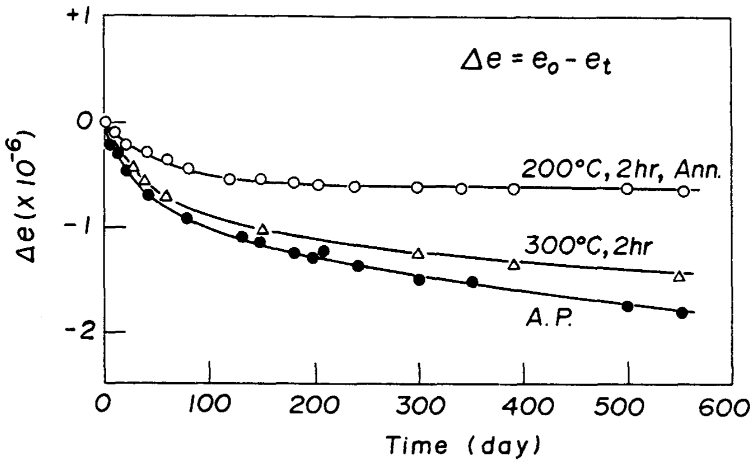


Fig. 14 Time dependence of Δe for as-prepared and annealed $(Fe_{1-x}Cr_x)_{85}B_{15}$ (x = 0.025) amorphous samples.

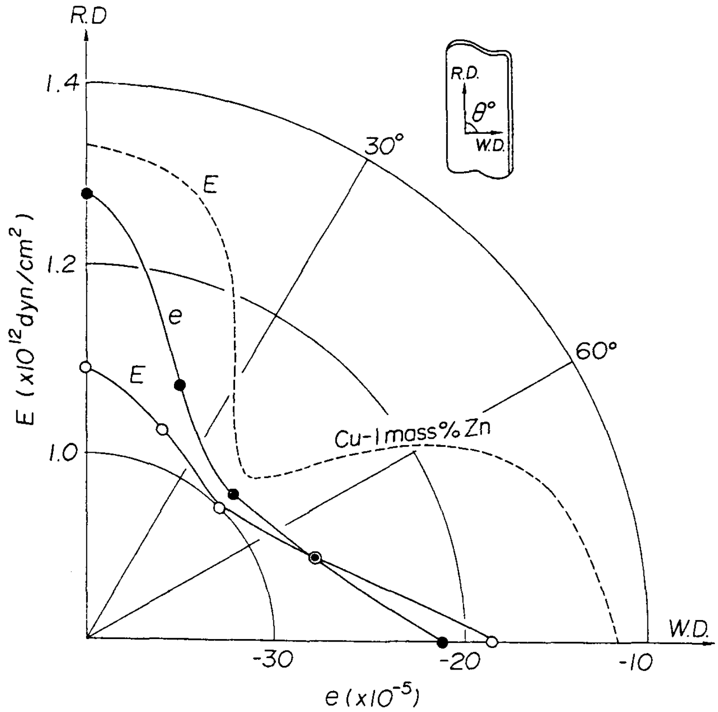


Fig. 15 Anisotropy in Young's modulus and its temperature coefficient for as-prepared $Ni_{78}Si_{10}B_{12}$ amorphous alloy and rolled Cu-1 mass%Zn crystalline[60] alloy. R. D. and W. D. show the directions of length and width of ribbon, respectively. In crystalline alloy, the rolling and perpendicular directions are shown by R. D. and W. D., respectively.

uniaxial anisotropy with the value of about $10^2 \sim 10^3$ J/$m^3$ [57,58]. Recently, a structural anisotropy in a Mo-Si sputtered amorphous alloy has been confirmed by spallation pulsed neutrons[59]. In order to investigate the anisotropy of Young's modulus, $Ni_{78}Si_{10}B_{12}$ amorphous alloy with 21 mm wide was prepared. This alloy has no contribution from magnetic domains due to paramagnetic. Young's modulus was measured between the length direction and width one as shown in Fig. 15, together with that of a rolled crystalline Cu-1%Zn alloy[60] for comparison. The amorphous alloy does not show such a large elastic anomaly as that of the crystalline alloy. However, Young's modulus exhibits a minimum value of $1.0 \times 10^{12}$ dyn/$cm^2$ in the direction of 45° and a maximum value of $1.2 \times 10^{12}$ dyn/$cm^2$ in the direction of width, and its difference is about 20%. It is therefore considered that an analogous elastic anisotropy also occurs in the direction of thickness. The temperature coefficient of Young's modulus also takes a similar angle dependence as shown in the same figure. Similar results have been obtained in Pd-Si amorphous alloys, and have shown that the anisotropy is enhanced by cold-rolling and reduced by annealing[61]. Such relatively large anisotropy would not be ignored when the amorphous alloys are used to precise measurement apparatuses.

## Conclusion

The elastic properties and the Elinvar characteristics of ferromagnetic and nonferromagnetic amorphous alloys have been introduced and some practical applications of the amorphous Elinvar alloys have been demonstrated. Since the amorphous Elinvar alloys exhibit various excellent properties which can not be obtained in crystalline Elinvar alloys, their applicable fields in electromagnetic and precise measuring devices are considered to be remarkably wide. When ones are going to use these amorphous alloys, ones have to choice the alloy composition, heat-treatment and cold-rolling suitable for each usage. In their practical use, one should pay attention to the demerits such as aging effect and anisotropy in elastic properties.

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