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Young's Modulus and Delay Time Characteristics of Ferromagnetic Fe-Si-B Amorphous Alloys*

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Synopsis

The temperature dependence of thermal expansion and Young's modulus of amorphous Fe-Si-B alloys prepared by the roller quenching technique was measured in order to examine their delay time characteristics. The thermal expansion coefficient of as-prepared alloys was in the order of $7\sim 9\times 10^{-6}$/°C depending on the content of metalloids. The temperature coefficient of Young's modulus varied from 0 to -40×10^{-5}/°C with ordinary annealing and magnetic annealing, and the Elinvar characteristics caused by a large ΔE effect was obtained for several alloys.

The temperature coefficient of the delay time calculated from thermal expansion and Young's modulus was nearly zero for several alloys. Therefore, these amorphous alloys are expected to be useful for ultrasonic delay lines.

I. Introduction

Elastic properties of amorphous alloys have been investigated by many workers(1)-(6), and it has been known that the elastic moduli of amorphous phase are generally about 20~30% lower than those of crystalline phase and also that Pd-base amorphous alloys exhibit a large anharmonicity.

As is well known, elastic properties are easily affected by metallurgical treatments because they are very structure-sensitive. We have already reported that the temperature coefficient of Young's modulus of Pd-Si amorphous alloys varies with alloy compositions, conditions for preparing the alloys, heat-treatments and cold workings. From the results, the Elinvar characteristics has been observed in the amorphous $Pd_{80}Si_{20}$ and $Pd_{79}Si_{20}Ag_1$ alloys, and it has been concluded that they are useful for delay lines(7).

In the case of some ferromagnetic crystalline alloys, elastic properties change

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anomalously due to the ΔE effect below the Curie temperature, showing the Elinvar characteristics(8),(9). Accordingly, the same Elinvar characteristics is expected even in ferromagnetic amorphous alloys.

Elinvar alloys are widely used as a delay line because they exhibit a small temperature coefficient of the delay time. The temperature coefficient of the delay time can be calculated from the temperature coefficient of the thermal expansion and Young's modulus. In the present study, therefore, the thermal expansion and Young's modulus of ferromagnetic Fe-Si-B amorphous alloys are measured and the delay time characteristics are estimated from these data.

II. Experimental

Fe-Si-B amorphous alloys were prepared by the roller quenching method.(10) The velocity of the roller (50 mm in diameter) was 3000～5000 rpm. The amorphous state of specimens was confirmed by the X-ray diffraction with Mo-Kα radiation.

The crystallization temperature of amorphous alloys was determined from the temperature dependence of the electrical resistivity and the magnetization.

Amorphous specimens were vacuum-sealed in a quartz ampoule, and then ordinary and magnetic annealing were carried out.

The thermal expansion curve was measured with a dilatometer of a differential transformer type. The temperature dependence of Young's modulus was measured with a vibrator controlled oscillator system vibrating at 120～200 Hz.

The temperature coefficient of the delay time was calculated from the temperature coefficients of the thermal expansion and Young's modulus curves.

III. Results and discussion

1. *Thermal expansion characteristics*

The thermal expansion curves of several kinds of Fe-Si-B amorphous alloys are shown in Fig. 1. The thermal expansion coefficient in the vicinity of room temperature plays a significant role in the delay time characteristics, thus the curves are drawn from -60°C to 80°C. All the specimens are ferromagnetic in this temperature range, and therefore, as seen in the figure, the curves are slightly convex upward owing to the spontaneous volume magnetostriction(11). The thermal expansion coefficient α of $Fe_{80}Si_8B_{12}$ amorphous alloys is about 7×10^{-6}/°C at room temperature, and it becomes larger with increase in the total concentration of metalloids, reaching a value of 9×10^{-6}/°C for $Fe_{73}Si_{12}B_{15}$ amorphous alloy.

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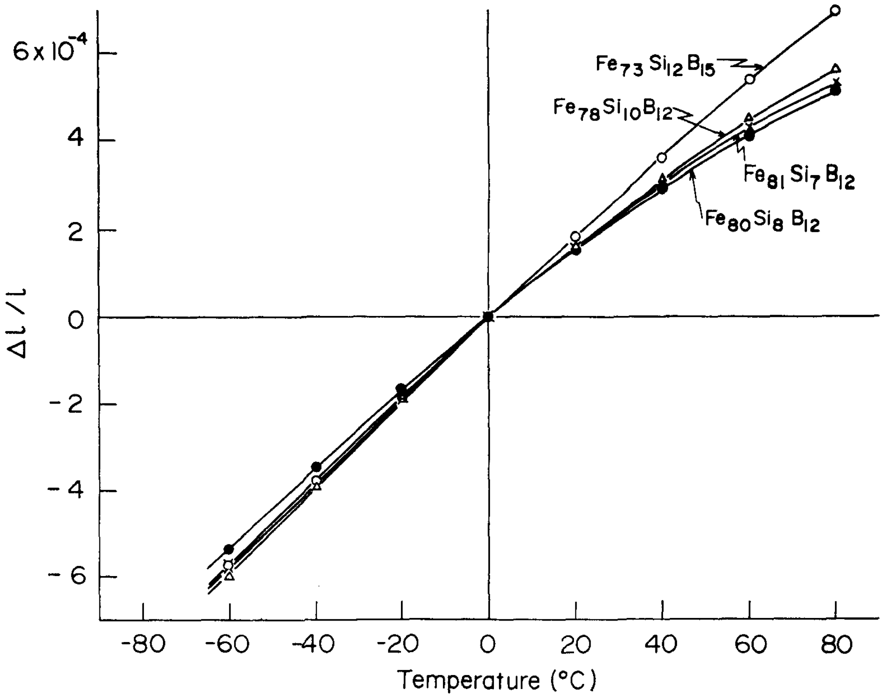

Fig. 1. Thermal expansion curves of the amorphous Fe-Si-B alloys in as-prepared state.

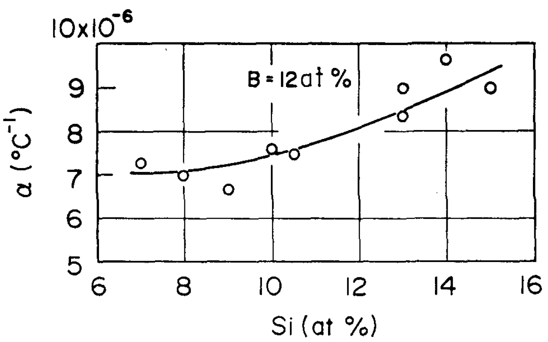

Fig. 2. Relationship between thermal expansion coefficient (α) and Si content for the Fe-Si-B amorphous alloys with a constant content of B(=12 at%).

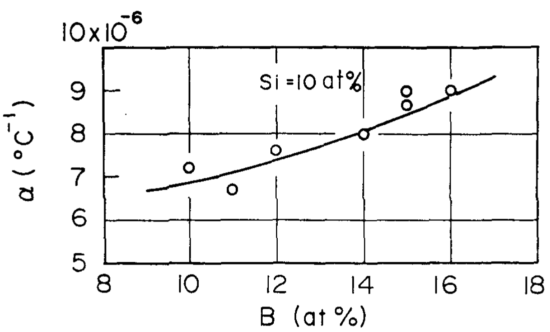

Fig. 3. Relationship between thermal expansion coefficient (α) and B content for the Fe-Si-B amorphous alloys with a constant content of Si (=10 at%).

Figure 2 shows the thermal expansion coefficient α vs. the Si content for the as-prepared Fe-Si-B amorphous alloys containing 12 at%B. The coefficient α is the mean value between 0°C and 40°C. The value of α becomes larger from 7×10^{-6}/°C to 9×10^{-6}/°C with increase in the Si content.

Figure 3 also shows the relation between the value of α and the B content for a fixed Si content (10 at%Si), where the effect of the B content on α is almost similar with that of the Si content.

Elastic properties are easily affected by metallurgical treatments, but the value of α of annealed or cold worked amorphous alloys is substantially equal with that of as-prepared alloys, and therefore, the thermal expansion characteristics of

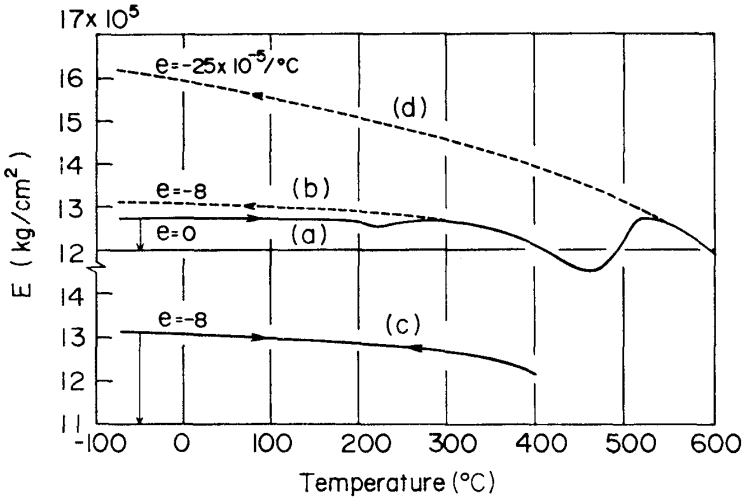

Fig. 4. Temperature dependence of Young's modulus (e) for the amorphous $Fe_{78}Si_{10}B_{12}$ alloy: (a) heating curve of as-prepared specimen, (b) cooling curve from 400°C, (c) heating and cooling curves of specimen annealed for 1 hr at 400°C, (d) cooling curve from 600°C.

Fe-Si-B amorphous alloys are scarcely affected by metallurgical treatments.

2. *Properties of Young's modulus*

Young's modulus E of the as-prepared amorphous alloys does not change monotonically during heating. Figure 4 shows the typical curves of the temperature dependence of Young's modulus for $Fe_{78}Si_{10}B_{12}$ amorphous alloy. The curve (a) of as-prepared specimen exhibits the Elinvar characteristics around room temperature, i.e., the temperature coefficient of Young's modulus e is zero. In this curve two minimum points are seen in the vicinity of 220°C and 460°C, respectively. Such a behavior of Young's modulus has also been observed in other amorphous alloys(7),(12). The minimum point at lower temperature shifts from 200°C to 300°C with increase in the total content of metalloids. The curve (b) obtained by cooling the sample from 400°C shows a monotonic change without the minimum at 220°C and it does not coincide with the curve (a). Heating and cooling curves (c) of the specimen annealed at 250°C for 5 hr change reversibly without the minimum at 220°C. From these results and other data(13), the minimum point observed in the curve (a) may be due to the relaxation of internal strains, introduced into the specimen during rapid solidification. The minimum point at 460°C agrees with the starting temperature of crystallization determined from the X-ray analyses, so that the increase in Young's modulus in the temperature range from 460°C to 520°C is due to the transformation of amorphous phase to crystalline phase. The curve (d) obtained by cooling the sample from 600°C shows the temperature dependence of E of a crystallized specimen. At room temperature, the value of E for the crystalline state is about 25% larger than that

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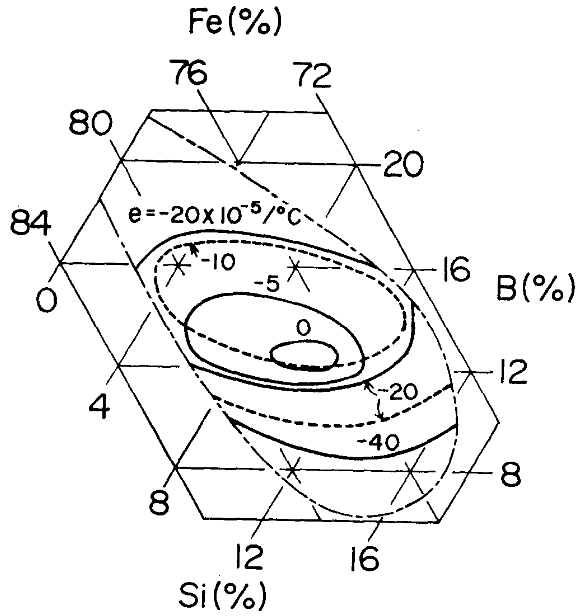

Fig. 5. Equi-value curve of temperature coefficient of Young's modulus (e) at 0°C~40°C in Fe-Si-B ternary diagram. Solid lines: as-prepared alloy, dashed lines: annealed alloy at 250°C for 5 hr.

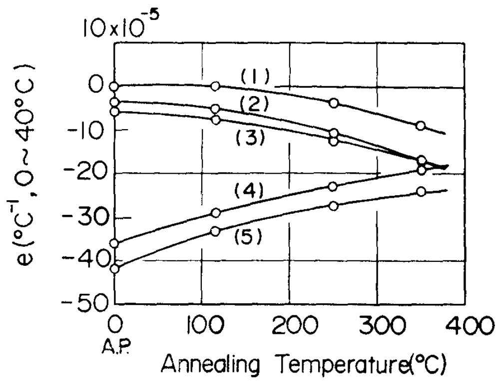

Fig. 6. The temperature coefficient of Young's modulus (e) for various amorphous Fe-Si-B alloys after 2 hr of annealing at temperature T.
(1) $Fe_{77}Si_{10}B_{13}$, (2) $Fe_{80}Si_{6}B_{14}$, (3) $Fe_{73}Si_{12}B_{15}$, (4) $Fe_{77.5}Si_{12.5}B_{10}$, (5) $Fe_{77}Si_{15}B_{8}$.

of the amorphous state.

The mean value of e in the range of 0°C to 40°C was plotted in Fig. 5 of the compositional diagram for Fe-Si-B ternary system, wherein the solid and dashed lines are the equi-value curves of e in the as-prepared and annealed (250°C×5 hr) states, respectively. As shown in the figure, the Elinvar characteristics is obtained within the limited compositions about 76~79 at%Fe, 9~11 at%Si and 12~13 at% B only in the as-prepared state. In the annealed state, on the other hand, it is absent within this compositional diagram.

Figure 6 shows the effect of annealing temperature on e of the Fe-Si-B amorphous alloys with different contents of Si and B. The specimens were annealed for 2 hr at each temperature. With an increase in the annealing temperature, the value of e decreases for the specimens of (1)~(3), and, on the contrary, it increases for the specimens of (4) and (5), all of them have a tendency to converge to about -20×10^{-5}/°C.

Figure 7 shows the effect of magnetic field (1.5 kOe) on the temperature dependence of E, namely the ΔE effect, of the $Fe_{78}Si_{10}B_{12}$ amorphous alloy, wherein (1) and (3) are for the specimens annealed at 250°C for 5 hr and (2) and (4) are for the specimens annealed at 400°C for 1 hr under magnetic field (400 Oe). The magnetic field is applied in the longitudinal direction of the specimen. In the figure, it is seen that Young's modulus E is considerably affected by the magnetic

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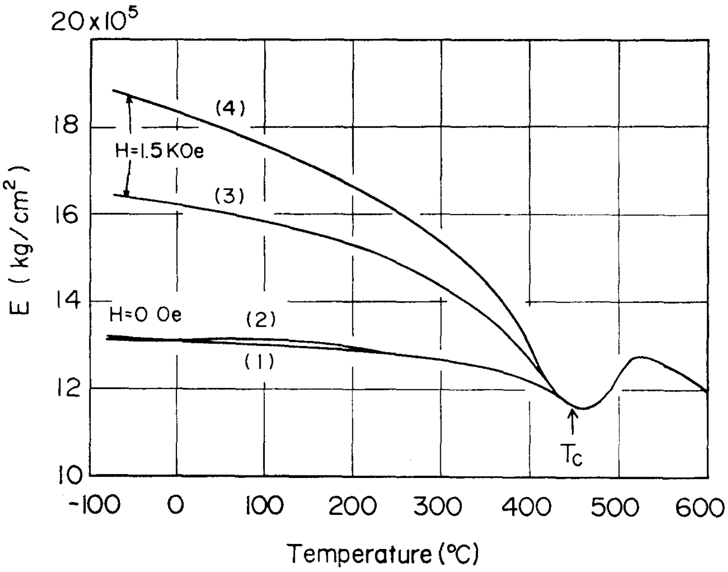

Fig. 7. Effect of magnetic field on the temperature dependence of Young's modulus for the amorphous $Fe_{78}Si_{10}B_{12}$ alloy. (1) (3) annealed at 250°C for 5 hr, (2) (4) annealed at 400°C for 1 hr under magnetic field of 400 Oe.

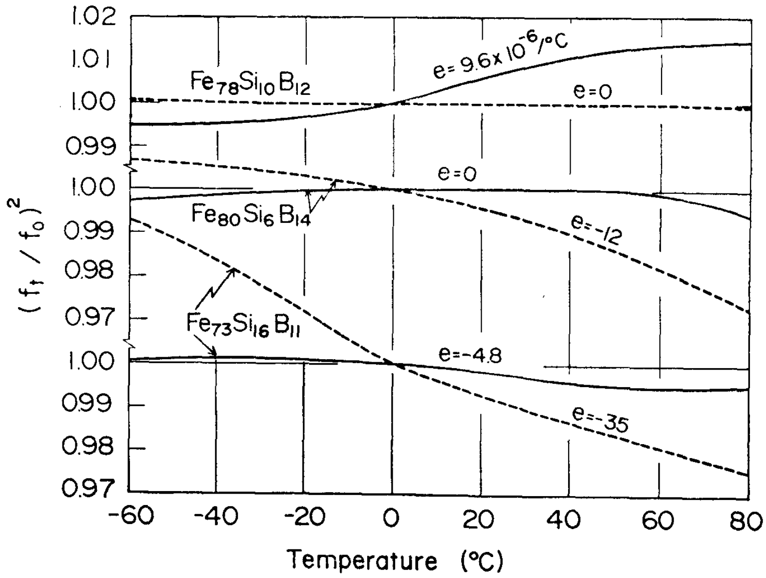

Fig. 8. Fractional change in square of frequency $(f_t/f_0)^2$ as a function of temperature for several amorphous Fe-Si-B alloy. f_t and f_0 is resonant frequency at each temperature and at 0°C, respectively. dashed lines; as-prepared state, solid lines; annealed state under magnetic field (400 Oe).

field and this ΔE effect is remarkable in the magnetic annealed specimen. For the specimen (4) the value of E is larger than that of pure iron and $\Delta E/E$ is about 0.4. Such large ΔE effect of the Fe-Si-B amorphous alloy should be closely related with the large magnetostriction of this alloy. In fact, it was confirmed that the magnetostriction of this alloy is about 30×10^{-6}. A similar large ΔE effect of amorphous alloys has already been reported for Fe-P-C system(14),(15).

The magnetic annealing improves the Elinvar characteristics of the amorphous alloys. Figure 8 shows the effect of magnetic annealing on the temperature dependence of E for three typical alloys. It is seen from the figure that the value of e of some alloys approaches zero by the magnetic annealing. Particularly, $Fe_{80}Si_6B_{14}$ alloy shows the most excellent Elinvar characteristics over the temperature range from -40°C to 50°C. The relationships between the ΔE effect and the magnetic annealing and the magnetostriction will be reported in more details in the near future.

3. *Temperature coefficient of delay time*

Recently, it has been reported by the present authors that the Pd-Si alloy system exhibits a small temperature coefficient of delay time(7). Tsuya et al. have also shown that Fe-base amorphous alloys have superior poperties for the application to the magnetostrictive delay line(15).

In general, the temperature coefficient of delay time, t, is represented by the following equation;

$$t = -\frac{1}{2}(a+e) ,$$

where a is the thermal expansion coefficient and e is the temperature coefficient of Young's modulus. The term $(a+e)$ is often called the thermoelastic coefficient. Therefore, t can be simply calculated by using the present values of a and e. For a delay line t is required to be as small as possible, and thus $(a+e)$ should be made very small or zero. In Table 1, the values of t for three kinds of alloys are listed with Young's modulus and density. The value of t varies sensitively with the preparing conditions of specimens and heat-treatments. This table shows that a better delay time characteristics can be obtained even in as-prepared state or by adequate heat-treatments.

At present, ferromagnetic crystalline alloys of Elinvar type are widely used for delay lines. In these crystalline alloys, however, the scattering loss resulting in a

Table 1. Young's modulus (E), density (ρ) and temperature coefficient of delay time (t) for amorphous Fe-Si-B alloys.

	E (kg/cm^2)	ρ (g/cm^3)	t ($\times 10^{-6}$/°C)	Heat-treatment
$Fe_{78}Si_{10}B_{12}$	12.7×10^5	7.4	~0	As-prepared
$Fe_{77}Si_{11}B_{12}$	12.7	7.4	0.5	〃
$Fe_{77}Si_{10}B_{13}$	12.8	7.4	~0	Annealed at 115°C for 2 hr
$Fe_{80}Si_6B_{14}$	12.8	7.4	−0.3	Annealed at 400°C for 1 hr under magnetic field of 400 Oe.

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(15) K.I. Arai, N. Tsuya and M. Yamada, IEEE Trans. Mag., MAG-**12** (1976), 936.

large damping may not be neglected owing to the presence of grain boundaries(16). In the amorphous alloys, on the other hand, this loss does not occur because they essentially have no grain boundary. Such a characteristic nature in the amorphous alloys may result in a small damping of ultrasonic waves. Then the Fe-Si-B amorphous alloys are suitable for use in delay lines, especially in the higher frequency range of ultrasonic waves.

IV. Conclusions

Amorphous alloys of Fe-Si-B system were prepared by the roller quenching method and their thermal expansion and Young's modulus were examined as a function of temperature, and then the temperature coefficient of delay time was calculated. The results are summarized as follows:

(1) Thermal expansion coefficient of the amorphous alloys used in the present work is in the order of $7 \sim 9 \times 10^{-6}/°C$ varying with the content of metalloids.

(2) Young's modulus of an $Fe_{78}Si_{10}B_{12}$ amorphous alloy exhibits two minimum points in the vicinity of 220°C and 460°C. The first minimum is probably caused by relaxation of internal strains in the specimen, and the second one by the crystallization from the amorphous phase.

(3) Temperature coefficient of Young's modulus changes sensitively by the preparing condition of specimens and heat-treatments, and in several kinds of Fe-Si-B amorphous alloys a superior Elinvar characteristics has been found in the vicinity of room temperature.

(4) Very small temperature coefficients of the delay time have been obtained for some amorphous alloys in as-prepared state or by adequate heat-treatments.

Acknowledgement

The authors are grateful to Mr. Y. Kobayashi of the Research Institute of Electric and Magnetic Alloys for the preparation of the amorphous specimens.

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