Thermal Expansion Anomaly in Some Ferromagnetic Amorphous Alloys*

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Synopsis

Amorphous samples have been made by the roller quenching and the centrifugal solidification techniques in the form of ribbons 20∼40 μm thick and 0.5∼1 mm wide.

Thermal expansion properties of the ferromagnetic amorphous alloys have been examined for various Fe-base and Co-base alloys. In the thermal expansion curves, the Fe-base amorphous alloys exhibit a large anomaly below the Curie temperature, while the Co-base amorphous alloys exhibit no distinct anomaly in the vicinity of the Curie temperature. It is concluded that the anomaly in the thermal expansion of Fe-base alloys is closely connected with a large spontaneous volume magnetostriction.

I. Introduction

In the recent years the transition-metal based amorphous alloys made by continuous rapid quenching methods have been attracting an increasing interest because of their characteristic properties[(1)~(3)]. For instance, the thermal expansion property is one of the interesting properties of amorphous alloys. Up to now, this property has been studied for paramagnetic amorphous alloys such as Pd-Ni-P and Pt-Ni-P systems[(4)], and it has been found that the thermal expansion coefficients of the amorphous alloys are higher than those of their pure crystalline metals by 10 to 20%. On the other hand, study on the thermal expansion property of ferromagnetic amorphous alloys has not been done.

The present work is designed to obtain information on the thermal expansion properties of the Fe-base and Co-base ferromagnetic amorphous alloys, in particular, to know the possibility of a large thermal expansion anomaly below the Curie temperature, which is found in some ferromagnetic crystalline alloys.

II. Experimental

Amorphous samples were prepared by the the roller quenching and the centri-

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(1) T. Masumoto and R. Maddin, Mat. Sci. Eng., **19** (1975), 1.

(2) J.J. Gilman, J. Appl. Phys., **46** (1975), 1625.

(3) T. Masumoto et al., Bull. Japan Inst. Metals, **15** (1976), 155.

(4) H.S. Chen, J.T. Krause and E.A. Sigety, J. Non-Cryst. Solids, **13** (1973/74), 321.

fugal solidification techniques[5] in the form of ribbons 0.5~1 mm wide and 20~40 μm thick. The amorphous nature of samples was confirmed by X-ray diffraction. The specimens were annealed at 250°C for 5 hr in order to relieve internal strains caused by rapid quenching.

The thermal expansion curves were measured by a differential transformer method (Rigaku Thermoflex Cat. No. 8561 Al) with a heating rate of 2.5°C/min. A dead weight applied to the specimens was 10 g, corresponding to a stress level of 200~800 g/mm².

In order to determine the Curie temperature, the measurement of magnetization against temperature was carried out with a magnetic balance under a field of 10 kOe using about 5 mg of samples.

The electrical resistivity of the alloys was measured up to 600°C by the usual four-terminal method in order to estimate the crystallization temperature.

III. Results

Figure 1 shows the thermal expansion curves of the Fe-P-C amorphous alloys. The Curie temperature T_c decreases with increasing Fe content, and all heating curves change anomalously below T_c. In particular, the $Fe_{80}P_{13}C_7$ and $Fe_{85.5}P_{7.5}C_7$ amorphous alloys exhibit a large negative thermal expansion coefficient below T_c.

Thermal expansion curve of the $Fe_{83}P_{17}$ amorphous alloy is shown in Fig. 2. With increasing temperature, the curve also changes anomalously below T_c, but not so remarkable as in the case of Fe-P-C amorphous alloys.

Figure 3 shows the thermal expansion curves of several kinds of Fe-Si-B

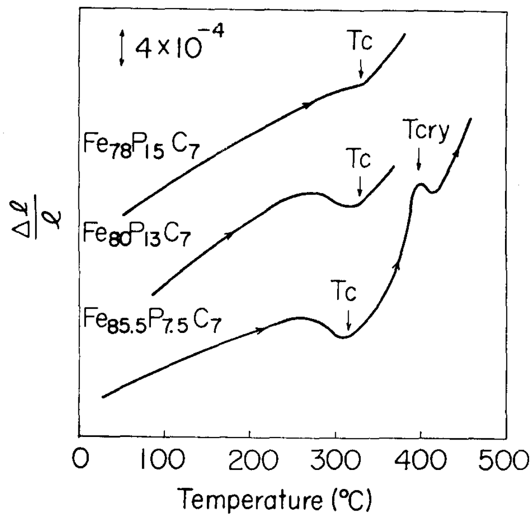

Fig. 1. Thermal expansion curves of Fe-P-C amorphous alloys.

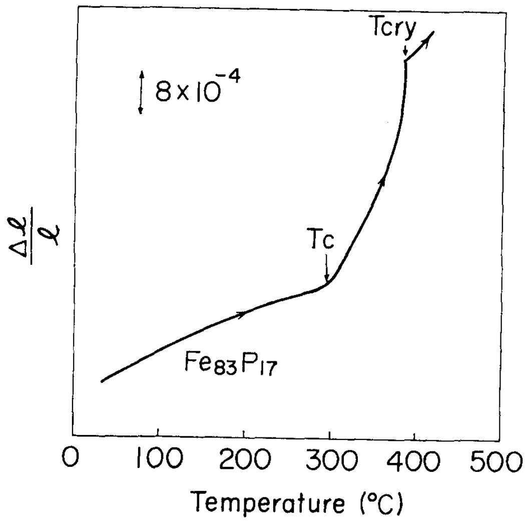

Fig. 2. Thermal expansion curve of the $Fe_{83}P_{17}$ amorphous alloy.

(5) R. Pond and R. Maddin, Trans. AIME, **245** (1969), 2475.

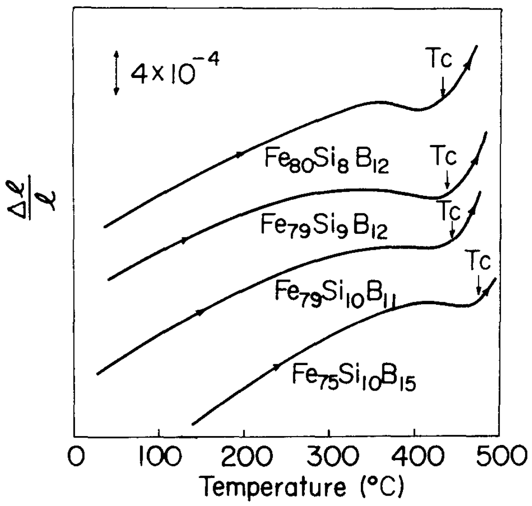

Fig. 3. Thermal expansion curves of Fe-Si-B amorphous alloys.

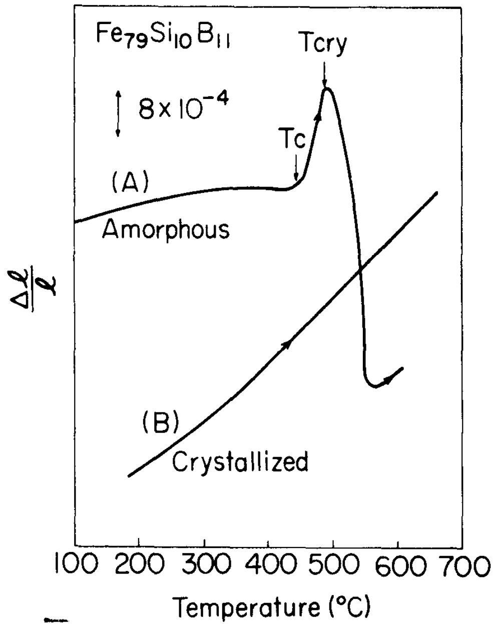

Fig. 4. Thermal expansion curves of the $Fe_{79}Si_{10}B_{11}$ alloy in the amorphous state and crystallized state, respectively.

amorphous alloys. In this system, T_c increases with a decrease in Fe content, and as shown in the figure, all curves behave in a similar way and the anomalous change also occurs in the vicinity of T_c with a large negative thermal expansion coefficient.

Figure 4 shows the thermal expansion curves of the $Fe_{79}Si_{10}B_{11}$ alloy in the amorphous state and the crystallized state, respectively. As temperature increases, the thermal expansion curve of amorphous specimen (A) exhibits a large anomaly below T_c, a steep elongation above T_c, and then shrinks drastically around the crystallization temperature T_{cry}. On the other hand, the curve of crystallized specimen (B) exhibits a monotonic expansion without any anomalous change.

Figure 5 shows the effect of B content on the Curie temperature T_c and the crystallization temperature T_{cry} in the Co-B system amorphous alloys. As the B content increases, T_{cry} increases linearly from about 370°C to about 420°C, and on the contrary, T_c decreases greatly from about 400°C at 28 at% B to about 250°C at 32 at% B. These two curves cross at the content of about 28 at%. Fig. 6 shows typical thermal expansion curves of two kinds of the Co-B amorphous alloys with B contents below and above 28 at%. The curve of $Co_{82}B_{18}$ alloy with T_c higher than T_{cry} changes monotonically below 370°C where the crystallization of amorphous phase occurs. On the other hand, for the $Co_{68}B_{32}$ alloy with T_c lower than T_{cry} no change in the thermal expansion exhibits in the temperature range below T_{cry}, that is, the anomalous change observed in the Fe-base amorphous alloys is not observed in the Co-base amorphous alloys. In Fig. 7 the thermal

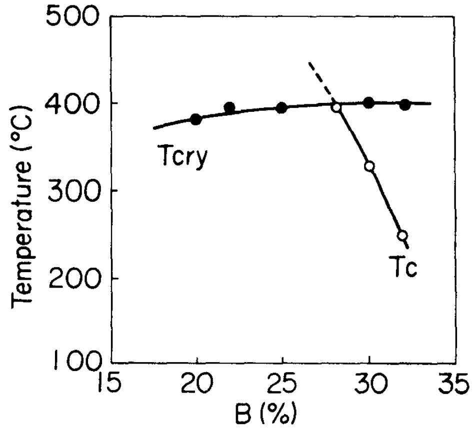

Fig. 5. Effect of B content on the Curie temperature T_c and the crystallization temperature T_{cry} in the Co-B system amorphous alloys.

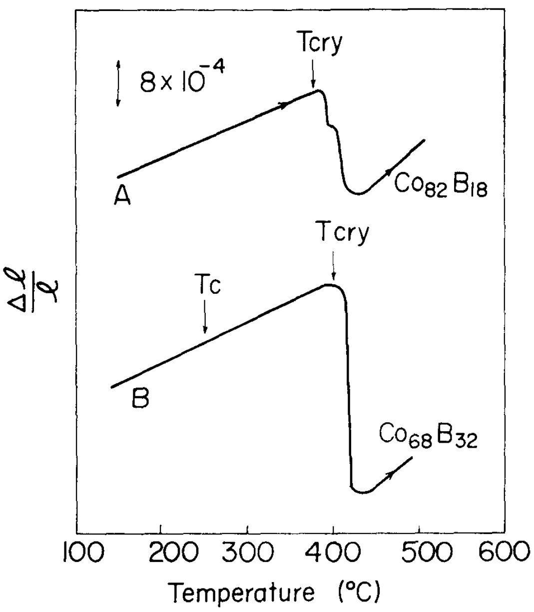

Fig. 6. Thermal expansion curves of the Co-B amorphous alloys with B contents below and above 28 at%.

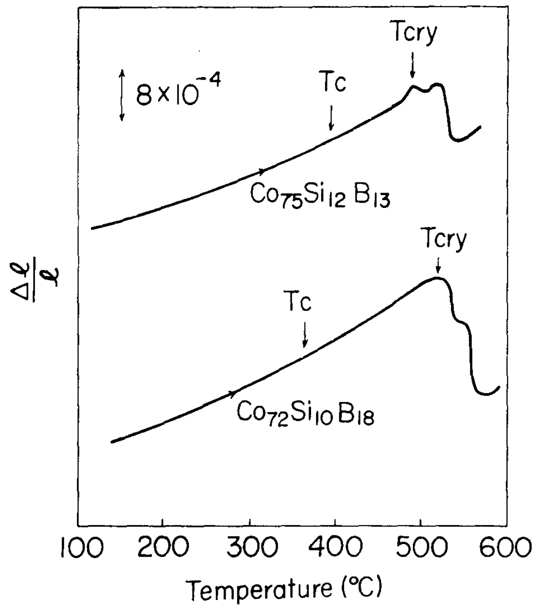

Fig. 7. Thermal expansion curves of Co-Si-B amorphous alloys.

expansion curves of the Co-Si-B system are shown as the other Co-base amorphous alloys. Again no distinct anomaly is observed near T_c.

As is well known, pure Ni metal is ferromagnetic at room temperature. However, the Ni base amorphous alloys with a large amount of glass former elements are all paramagnetic above the liquid nitrogen temperature.

From the present experiments on the thermal expansion, it is evident that Fe-base amorphous alloys exhibit an anomaly in the vicinity of T_c, but Co-base amorphous alloys exhibit no distinct anomaly. This anomalous behavior in the thermal expansion of Fe-base amorphous alloys is easily affected by the content and the sort of metallic or metalloid elements in the alloy system.

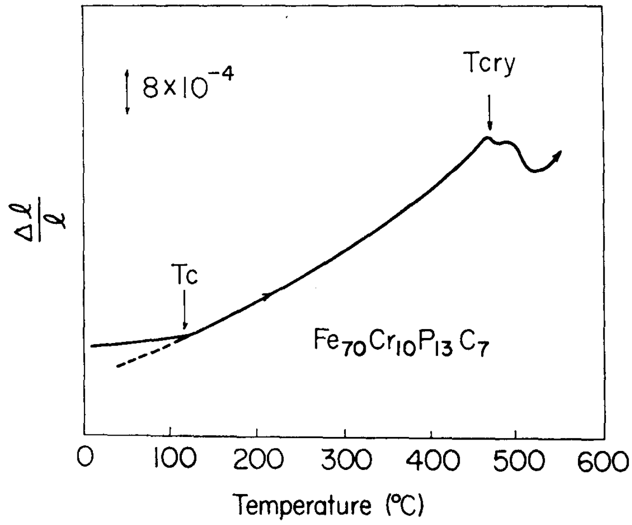

Fig. 8. Thermal expansion curve of the $Fe_{70}Cr_{10}P_{13}C_7$ amorphous alloy.

IV. Discussion

It has been pointed out that the amorphous state is easily affected by aging, even at low temperatures below the crystallization temperature(6),(7). This phenomenon could be a cause of the anomaly in the thermal expansion curves of the Fe-base alloys. However, as shown in Fig. 8, the thermal expansion curve of the $Fe_{70}Cr_{10}P_{13}C_7$ amorphous alloy exhibits no distinct anomaly in the temperature range where Fe-P-C, Fe-P and Fe-Si-B amorphous alloys exhibit the anomaly. In the temperature range below the Curie temperature ($T_c \approx 130°C$), the anomalous change in the thermal expansion is also observed. Therefore, the thermal expansion anomaly of Fe-base amorphous alloys may be related to the spontaneous volume magnetostriction.

The spontaneous volume magnetostriction ω_s is expressed as follows(8);

$$\omega_s = \frac{I_s}{2} \frac{\partial \omega}{\partial H} \bigg/ \frac{\partial I_s}{\partial H}, \tag{1}$$

where I_s is the spontaneous magnetization, H the magnetic field and $\partial\omega/\partial H$ the forced volume magnetostriction. In general, ferromagnetic crystalline metals and alloys exhibit, more or less, an anomaly in the thermal expansion curve below the Curie temperature due to the spontaneous volume magnetostriction. Several kinds of Fe-base crystalline alloys are called "Invar alloys" because they have a very small thermal expansion coefficient at room temperature owing to a large spontaneous volume magnetostriction. These Invar alloys, as is well known, exhibit a very large positive forced volume magnetostriction $\partial\omega/\partial H$(9). In the case of the Fe-base amorphous alloys, the value of $\partial\omega/\partial H$ has been also reported by

(6) Y. Waseda and T. Masumoto, Phys. Status Solidi (a), **31** (1975), 477.
(7) Y. Waseda, Solid State Physics (in Japanese), **10** (1975), 459.
(8) E.W. Lee, Rep. Prog. Phys., **18** (1955), 184.
(9) Y. Nakamura, IEEE Trans. Mag., MAG–**12** (1976), 278.

N. Tsuya et al., and relatively large positive values have been obtained in $Fe_{80}P_{13}C_7$ and $Fe_{70}Cr_{10}P_{13}C_7$ amorphous alloys[(10),(11)].

The relation between the forced volume magnetostriction $\partial\omega/\partial H$ and the pressure dependence of the Curie temperature $\partial T_c/\partial P$ is given as follows[(12)];

$$\left(\frac{\partial\omega}{\partial H}\right)_P \approx \frac{T}{T_c}\left(\frac{\partial M}{\partial T}\right)_P \frac{\partial T_c}{\partial P}, \tag{2}$$

where the subscript P means the constant pressure and M the magnetic moment. The coefficient $T/T_c(\partial M/\partial T)_P$ is always negative. Therefore, the ferromagnetic materials which exhibit a large positive value of $\partial\omega/\partial H$ would accompany with a large negative value of $\partial T_c/\partial P$. In the case of Fe-base amorphous alloys, $\partial T_c/\partial P$ has been observed to have a relatively large negative value of -2K/kbar[(13)]. This value is comparable in the order of magnitude to that of the Fe-Ni crystalline Invar alloy[(9)].

From the above-mentioned results, we can conclude that the thermal expansion anomaly below T_c of the Fe-base amorphous alloys is closely connected with a large spontaneous volume magnetostriction.

In the case of crystalline alloys, the value of the spontaneous volume magnetostriction is often estimated from the Grüneisen relation. In this case it is necessary to measure the thermal expansion coefficient over a wide range of temperature containing the Curie temperature T_c. However, as shown in Figs. 1, 2 and 4, the thermal expansion curves of the Fe-P-C, Fe-P and Fe-Si-B amorphous alloys suffer a remarkable creep elongation above T_c due to the dead weight applied to the specimens during measurement, and furthermore, some of them exhibit a drastic shrinkage in the vicinity of the crystallization temperature T_{cry}. Thus, in the present study, it is difficult to estimate the value of the spontaneous volume magnetostriction using the Grüneisen relation.

V. Conclusion

Several kinds of Fe-base and Co-base ferromagnetic amorphous alloys have been prepared by the roller quenching and the centrifugal solidification techniques. The thermal expansion characteristics of these alloys have been investigated to clarify the behavior in the vicinity of the Curie temperature. The results obtained are summarized as follows:

(1) Thermal expansion curves of the Fe-base alloys exhibit an anomalous change below the Curie temperature. This anomaly is caused by the spontaneous volume magnetostriction. On the other hand, the Co-base amorphous alloys do

(10) N. Tsuya, K.I. Arai, Y. Shiraga, M. Yamada and T. Masumoto, Phys. Status Solidi (a), **31** (1975), 557.
(11) N. Tsuya, K.I. Arai, Y. Shiraga and T. Masumoto, Phys. Lett., **51A** (1975), 121.
(12) W.J. Carr, Jr., *Magnetic Properties of Metals and Alloys*, American Society for Metals, (1959), P. 236.
(13) T. Mizoguchi, IBM Research Report, RC 6054.

not exhibit such a distinct anomaly.

(2) Anomalous changes in the thermal expansion of the Fe-base alloys are affected by the content and the sort of metallic or metalloid elements in the alloy system.

Acknowledgement

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