New Co-Fe Amorphous Alloys as Soft Magnetic Materials

New Co–Fe Amorphous Alloys as Soft Magnetic Materials*

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Synopsis

Amorphous alloys of $(Fe_{1-x}Co_x)_{80}P_{13}C_7$ and $(Fe_{1-x}Co_x)_{75}Si_{15}B_{10}$ were prepared by quenching from the melt by using the centrifugal type and roller type solidification techniques. Specimens were all ribbons in form. Measurements were made of B-H hysteresis loops, effective permeabilities at high frequencies, longitudinal magnetostrictions, electrical resistances, specific gravities and Vickers hardnesses.

These alloys are magnetically very soft. The magnetostriction is zero at a composition near $x=0.94$, being positive in the range of $0 \leq x < 0.94$ and negative in the range of $1 \geq x > 0.94$. The coercive force and the permeability depends on the absolute value of magnetostriction. The alloy ($x=0.94$) having a vanishingly small magnetostriction exhibits the best soft magnetic properties: the coercive force is 0.006 Oe, the maximum permeability is 7.0×10^5 and the effective permeability is about 7×10^3 at higher frequencies up to about 100 KHz. In addition to these, this alloy has a high Vickers hardness of 910. Possible applications of this alloy are discussed.

I. Introduction

In recent years, the ferromagnetic properties of the splat cooled amorphous alloys have been the subject of extensive study by many workers[(1)-(4)]. From the point of view of practical application, it is noteworthy that these alloys are magnetically very soft since amorphous alloys are highly isotropic and homogeneous in their structure of atomic arrangoment. Very low coercive forces of the order of $0.01 \sim 0.1$ Oe have been obtained in these alloys[(1)-(4)]. These values are favorable to the soft magnetic devices. But these alloys have some disadvantages as seen in the following facts: (i) Large Barkhausen jumps are usually observed in magnetization reversal[(1),(2),(3),(5)], (ii) The maze type magnetic domains are often seen in the as-prepared specimens and then the ratio of the remanence to saturation

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(1) H. Fujimori, T. Masumoto, Y. Obi and M. Kikuchi, Japan. J. Appl. Phys., **13** (1974), 1889. H. Fujimori and T. Masumoto, Trans. JIM, **17** (1976), 175.
(2) T. Egami, P.J. Flanders and C.D. Graham, Jr., AIP Conf. Proc., **24** (1975), 697.
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(4) F.E. Luborsky, J.J. Becker and R.O. McCary, IEEE Trans. Magnetics, **11** (1975), 1644.
(5) J.J. Becker, Digests of Intermag Conf. (London, 1975), Paper 31–6.

magnetization is as small as 0.4~0.6 in these specimens(1),(2),(6),(7). The effects of internal strain(1),(6), of alloy-compositional fluctuations(8) and of atomic pair ordering(8) have been reckoned as the cases of the disadvantageous properties mentioned above. But the problem has not yet been solved completely.

The present study deals with an investigation on the contribution of the magnetostriction to the magnetic properties of amorphous alloys in order to obtain more excellent soft magnetic characteristics. It is well known that the sign of the magnetostriction of Fe-Co crystalline alloys changes from positive on the Fe rich side to negative on the Co rich side. On the basis of this experimental fact, amorphous alloys in the Fe-Co system were produced with particular interest in finding the alloy of zero magnetostriction, and the magnetic properties, especially the low-field properties of engineering interest, were investigated. A part of the result has been reported in Ref. 9. This paper reports the details.

II. Experimental

1. Amorphous specimens

Metalloids of P and C were chosen as glass forming elements which best stabilize the amorphous state in the Fe rich Fe-Co alloys, while metalloids of B and Si were chosen as glass forming elements in the Co rich Co-Fe alloys. By using mother alloys of the systems $(Fe_{1-x}Co_x)_{80}P_{13}C_7$ ($x=0\sim0.75$) and $(Fe_{1-x}Co_x)_{75}Si_{15}B_{10}$ ($x=0.73\sim1$), amorphous alloy ribbons (0.5~1 mm in width, 20~30 μm in thickness and 300 mm in length) were prepared by the centrifugal solidification technique(10). The velocity of the rotating drum (300 mm in circumference) was 5000 rpm, the cooling rate being about 10^5 degree/sec. In addition to these short ribbons, long ribbons (1~2 mm in width, 30~40 μm in thickness and 4~5 m in length) were formed by the roller quenching technique(11). The roller (50 mm in diameter) rotated at a rate of 3000 rpm. The result of chemical analysis on some amorphous alloys is listed in Table 1. The ribbon specimens were cut to appropriate lengths for each measurement.

2. Measurements

The B-H hysteresis loops were measured by means of the conventional method using a Cioffi type recording fluxmeter. Single length of ribbon (about 150 mm

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(11) H.S. Chen and C.E. Miller, Rev. Sci. Instrum., **41** (1970), 1237.

Table 1. Analytical results of some amorphous alloys used (at %).

	P	C	Si	B
$Fe_{80}P_{13}C_7$	12.5	6.8	—	—
$Fe_{45}Co_{35}P_{13}C_7$	12.7	6.9	—	—
$Fe_5Co_{70}Si_{15}B_{10}$	—	—	14.6	9.7
$Co_{75}Si_{15}B_{10}$	—	—	14.5	9.5

long) was used for the measurement in most cases. In the case of $Fe_{4.7}Co_{70.3}Si_{15}B_{10}$ alloy, a troid was used in order to obtain an accurate value of permeability. Effective permeability at high frequency of this alloy was measured by means of the Maxwell bridge method using the same troid. Magnetostriction was measured in a field of $0.05 \sim 500$ Oe by using a modified dilatometer of suspension type. Density (specific gravity) measurements were made in carbon tetrachloride by using a pyconometer. X-ray diffraction measurements were carried out to confirm that the ribbons are in the amorphous state. Electrical resistance and saturation magnetization were measured at temperatures between room temperature and 800°C in order to see the crystallization process. Hardness was measured by using a micro-Vickers hardness tester.

III. Results and discussions

1. Amorphous state and crystallization

The as-prepared ribbon of $Fe_{80}P_{13}C_7$ alloy has been confirmed to be in the amorphous state and its crystallization process has also been studied in detail(12). Only the results on Co rich alloys are described here.

Figure 1 shows the curve of intensity factor obtained by the X-ray diffraction intensities of $Co_{75}Si_{15}B_{10}$ ribbon. As can be seen in the figure, this curve is quite similar in form to that of liquid Co(13), indicating that the ribbon is in the amorphous state. A similar $S(Q)$ curve has been obtained in the cases of Fe-Co-P-C and Fe-Co-Si-B alloys.

Figure 2 shows the temperature dependence of electrical resistance and saturation magnetization of $Fe_5Co_{70}Si_{15}B_{10}$ ribbon as measured at a rate of temperature change 150 degree/hr. Both curves are markedly irreversible on heating and cooling. The curve of resistance vs. temperature has a maximum at 480°C and a minimum near 600°C, forming a sharp drop in resistance around 480°C. The saturation magnetization per gramme (σ_s) first decreases with increasing temperature from room temperature. The Curie temperature can be estimated to be 430°C. When heated further, σ_s increases suddenly at 480°C. The curve of

(12) T. Masumoto, Y. Waseda, H. Kimura and A. Inoue, Mater. Sci. Eng., **23** (1976), 141 (Proc. 2nd Internat. Conf. on Rapidly Quenched Metals, (Section II), MIT, Cambridge, Mass., 1975).

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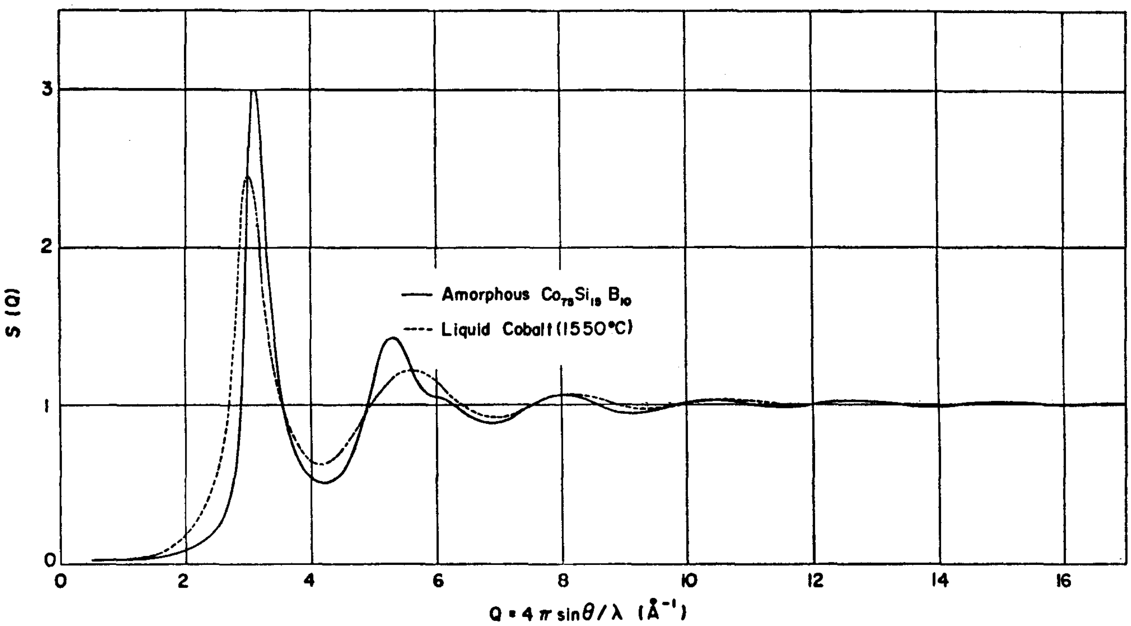

Fig. 1. Intensity factor $S(Q)$ for the amorphous $Co_{75}Si_{15}B_{10}$ alloy (solid line) and liquid cobalt (dashed line).

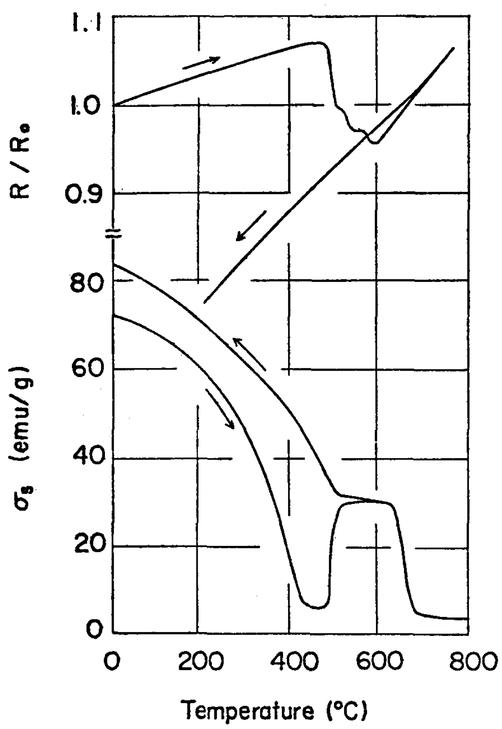

Fig. 2. Temperature dependence of saturation magnetization σ_s and of electrical resistance R/R_0 for the amorphous $Fe_5Co_{70}Si_{15}B_{10}$ alloy.

σ_s vs. temperature on cooling no longer agrees with the initial curve on heating. Such irreversible behaviours are commonly observed at the amorphous-crystalline transition in amorphous materials. In the present case, the temperature 480°C is

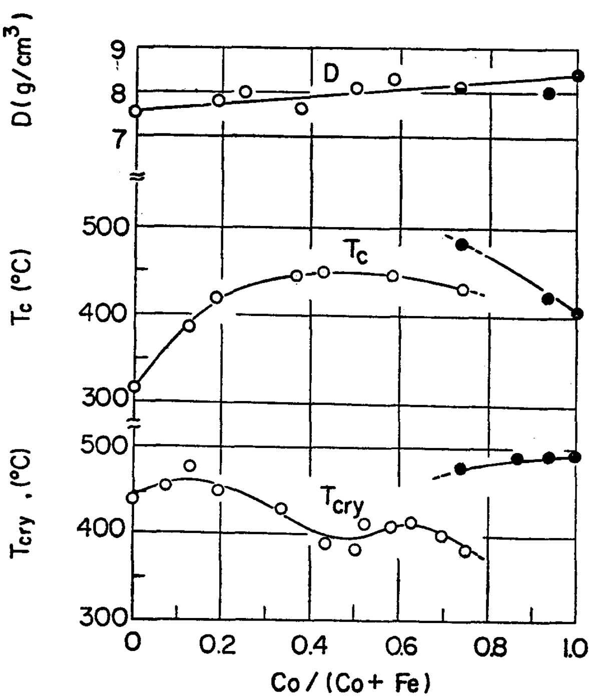

Fig. 3. Density D, Curie temperature T_c and crystallization temperature T_{cry} in the amorphous Co-Fe alloys. ○: $(Fe_{1-x}Co_x)_{80}P_{13}C_7$, ●: $(Fe_{1-x}Co_x)_{75}Si_{15}B_{10}$.

thought to be the crystallization temperature (a specific heat anomaly was observed at the same temperature).

The composition dependence of the crystallization temperature (T_{cry}) thus obtained for all the alloys is shown in Fig. 3. The values of T_{cry} of Co-Fe-Si-B alloys are higher than those of Fe-Co-P-C alloys. The figure also shows the results of the density (D) and the Curie temperature (T_c) in the amorphous state. Irrespective of whether the glass forming elements are the P-C or the Si-B, D increases with the composition x linearly from 7.54 in $Fe_{80}P_{13}C_7$ to 8.65 in $Co_{75}Si_{15}B_{10}$. It should be noted that the values of D are only 3~4% lower than those of pure Fe and pure Co even though each alloy includes about 20~25% of metalloids P-C or Si-B. This fact is consistent with the consideration that the amorphous structure is based on the random dense packing of the constituent atoms. The Curie temperature of $Co_{75}Si_{15}B_{10}$ is 410°C which is 90°C higher than that of $Fe_{80}P_{13}C_7$ (T_c=320°C). The Curie temperature changes in a parabolic way with respect to the composition of x though there is a little discrepancy between the Curie temperatures of the P-C and the Si-B based alloys. The highest Curie temperature (about 450°C) appears in an alloy with $x \simeq 0.5$. But, this Curie temperature is only apparent, having been obtained by an extrapolation of the σ_s vs. temperature curve; the crystallization temperatures of the alloys around x=0.5 are lower than their Curie temperatures.

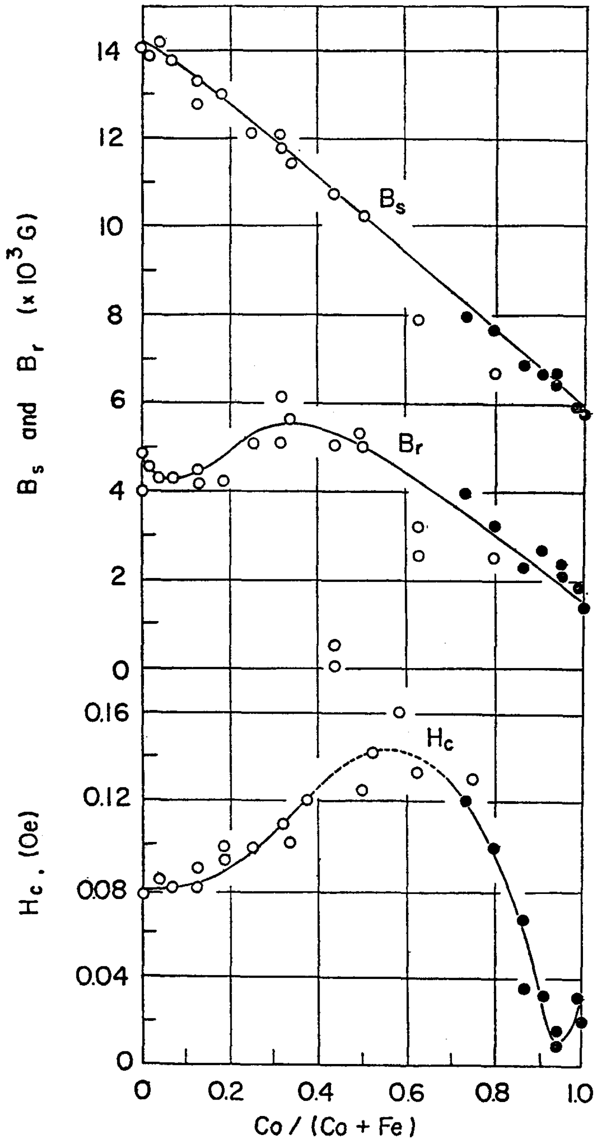

Fig. 4. Compositional dependence of residual magnetization B_r, saturation magnetizatoin B_s and coercive force H_c in the amorphous Co-Fe alloys. o: $(Fe_{1-x}Co_x)_{80}P_{13}C_7$, ●: $(Fe_{1-x}Co_x)_{75}Si_{15}B_{10}$.

2. Magnetic properties of the as-prepared ribbon

(a) B-H hysteresis loop

Figure 4 shows the composition dependence of the saturation magnetization per unit area ($B_s=4\pi I_s$), of the residual magnetization per unit area ($B_r=4\pi I_r$) and of the coercive force (H_c) of all the alloys investigated. The values of B_s and B_r decrease monotonically with increasing composition x, except for a slight increase of B_r in the Fe rich region. The H_c vs. x curve is relatively complicated and has a broad maximum around $x=0.5$ and a sharp minimum around $x=0.94$. The minimum value of H_c is about 0.01 Oe. It has further been found that the maximum permeability (μ_m) of the alloys with $x\simeq0.94$ is very large (the values are

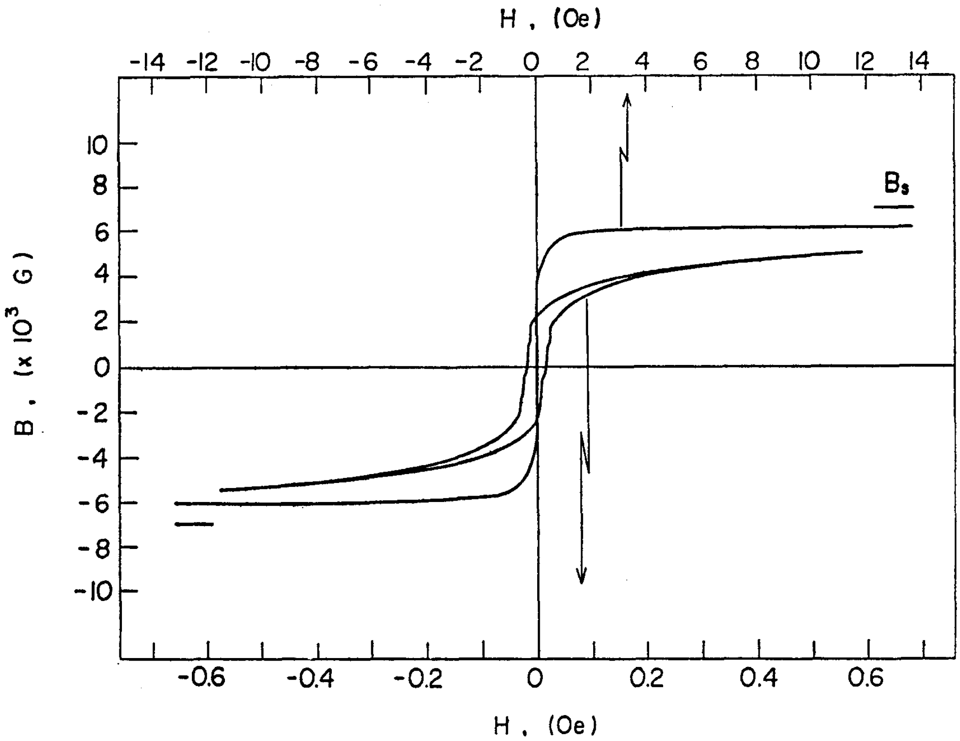

Fig. 5. Magnetization curve and B-H hysteresis loop for the amorphous $Fe_5Co_{70}Si_{15}B_{10}$ alloy.

of the order of 10^5) and the Barkhausen effect of these alloys is weaker than that of the alloys in the Fe rich region. As a typical example of such remarkable low-field properties, the hysteresis loop of an $Fe_5Co_{70}Si_{15}B_{10}$ ribbon (150 mm long) is shown in Fig. 5. The loop is nearly square (the loop is slightly inclined by the demagnetization effect, because of 150 mm long ribbon). H_c is as small as 0.01 Oe, and μ_m is as large as 1.8×10^5 (no correction of demagnetization was made).

It is well known that crystalline Co-base alloys generally have high values of coercive force due to their large crystalline magnetic anisotropies and do not exhibit soft magnetic properties (only Borocube-compound is exceptive[(14)]). Contrary to this empirical fact, the present alloys have excellent soft magnetic properties even in Co rich alloys as seen above. This is obviously due to the amorphous nature of the specimens. The amorphous structure is free from the magnetocrystalline anisotropy and structural defects such as grain boundaries. It should, however, be noted that the coercive force of the Fe rich alloys is rather large (in the next paragraph, a correlation between the coercive force and the magnetostriction will be found).

As can be seen in Figures 4 and 5, the ratio B_r/B_s is always small ($0.4\sim0.6$) in the whole composition range. In relation to the small B_r/B_s ratio, the field required to reach saturation of magnetization is always large (about 10^3 times as large as H_c) in the whole composition range. These properties are unfavorable

(14) H. Hirota, Y. Tawara and Y. Komatsu, National Technical Report, **14** (1968), 197.

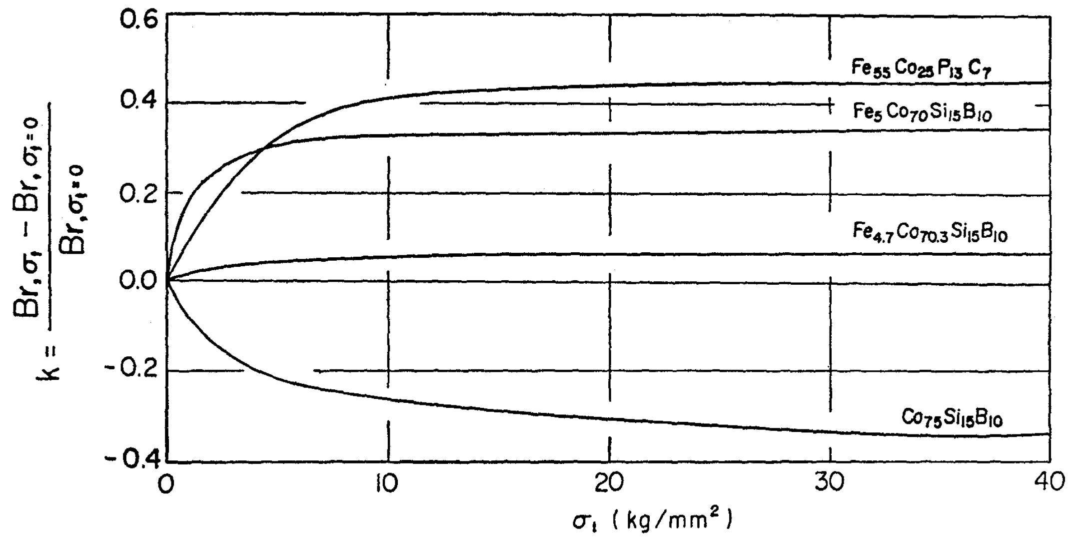

Fig. 6. Effect of tension (σ_t) on residual magnetization of various Co-Fe amorphous alloys.

to the soft magnetic devices, but these can be improved by means of magnetic field cooling (see section 3).

(b) Stress effect and magnetostriction

Figure 6 shows the dependence of B_r on the tensile stress (σ_t) applied along the ribbon axis. A striking point in this result is that B_r of $Co_{75}Si_{15}B_{10}$ decreases by the application of σ_t while B_r of the alloys including Fe increases. The compositional dependence of the B_r-σ_t curves suggests that there is a certain composition, at which the sign of magnetostriciton changes from positive to negative, on the Co rich side. A direct measurement of magnetostriction was made in order to confirm the presence of the alloy with zero magnetostriction. Fig. 7 shows the composition dependence of the longitudinal magentostriciton (λ_s) measured along the ribbon axis. It is clearly seen that λ_s is zero at a composition $x \simeq 0.94$, being positive in the range of $0 \leq x < 0.94$ and negative in the range of $x > 0.94$.

A comparison of H_c in Fig. 4 with λ_s in Fig. 7 shows that H_c is extremely small at a composition where λ_s is just zero, while H_c of the magnetostrictive alloys is rather large. Thus, it is suggested that the zero magnetostriction is effective for reducing the B-H hysteresis energy loss in amorphous alloys, similarly to the situation in crystalline soft magnetic materials. More quantitative argument concerning the correlation between the observed H_c and λ_s is made in Ref. 15.

From this magnetostriction study, it is found that an alloy of $Fe_{4.7}Co_{70.3}Si_{15}$-B_{10} has a vanishingly small magnetostriction, maybe less than 10^{-7} in the absolute value.

(15) H. Fujimori, Y. Obi, T. Masumoto and H. Saito, Mater. Sci. Eng., **23** (1976), 281 (Proc. 2nd Internat. Conf. on Rapidly Quenched Metals (Section II), MIT, Cambridge, Mass., 1975).

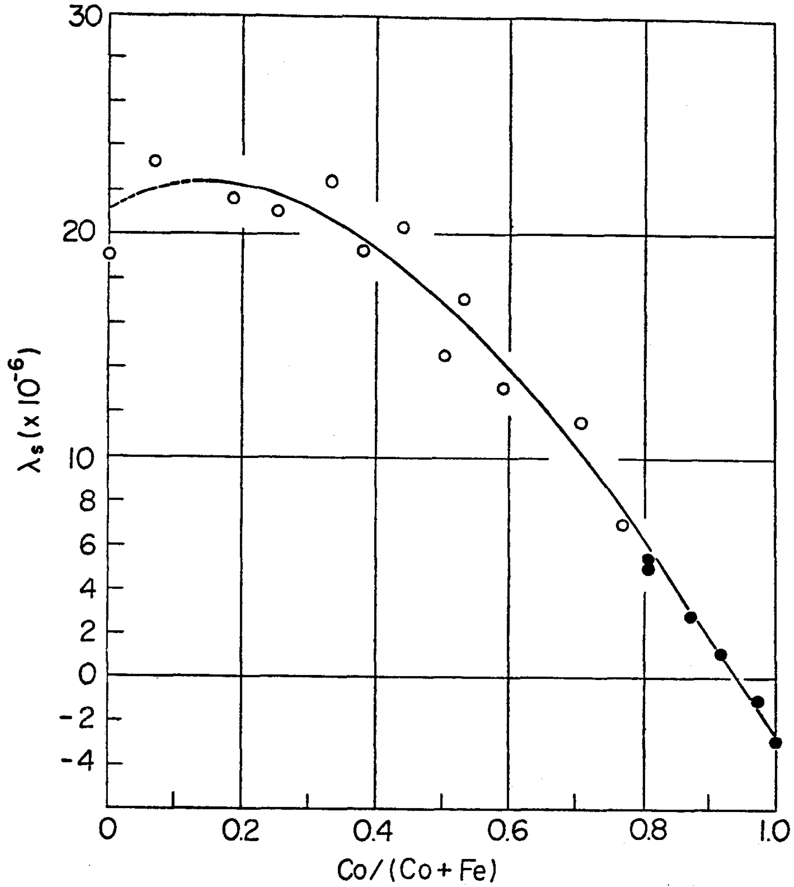

Fig. 7. Saturation magnetostriction λ_s vs Co/(Co-Fe) curve in the amorphous Co-Fe alloys. ○: $(Fe_{1-x}Co_x)_{80}P_{13}C_7$, ●: $(Fe_{1-x}Co_x)_{75}Si_{15}B_{10}$.

Table 2. Some magnetical and physical properties of several amorphous alloys and of commercial crystalline materials.

	$\mu_m (\times 10^3)$	H_c (Oe)	B_r (KG)	B_r/B_s	$\lambda_s (\times 10^{-6})$	T_c (°C)	$\rho \mu\Omega$-cm)	H_V
$Fe_{80}P_{13}C_7$ (1)	130	0.08	6.0	0.42	+19.1	310	135	770
〃 (*)	180	0.018	13.0	0.36	—	—	—	—
$Fe_{45}Co_{35}P_{13}C_7$	40	0.19	5.4	0.51	+20.4	440	270	980
$Fe_{4.7}Co_{70.3}Si_{15}B_{10}$	181	0.013	2.3	0.36	− 0.1	430	134	910
〃 (**)	700	0.006	4.2	0.63	—	—	—	—
$Co_{75}Si_{15}B_{10}$	30	0.03	2.0	0.30	− 3.0	400	120	920
$Fe_3Co_{72}P_{16}B_6Al_3$ (3)	—	0.013	4.5	0.71	—	—	130	—
78 Permalloy (16)	400	0.007		0.65	+ 3.5	600	60	130

(*) Cooled from 330°C to R.T. at a rate of 175°C/hr in an external field of 400 Oe.
(**) Annealed at 180°C for 30 min in an external field of 400 Oe.

3. Effect of magnetic field cooling on the static magnetic properties of an amorphous $Fe_{4.7}Co_{70.3}Si_{15}B_{10}$ ribbon

It has already been known that the B-H hysteresis properties of $Fe_{80}P_{13}C_7$ are greatly improved by magnetic field cooling (see the typical values in Table 2). A

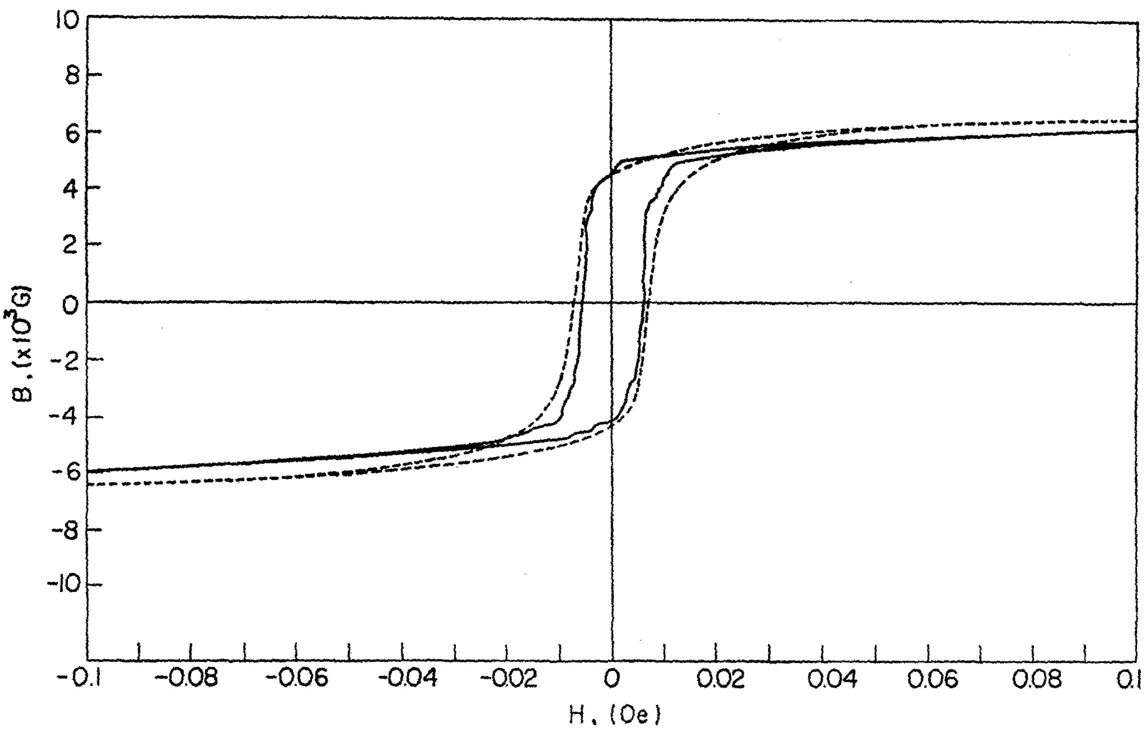

Fig. 8. B-H hysteresis loops of the amorphous $Fe_{4.7}Co_{70.3}Si_{15}B_{10}$ alloy annealed at 180°C for 30 min in a magnetic field (solid line) and Permalloy[16] (dashed line).

similar magnetic field cooling was performed on $Fe_{4.7}Co_{70.3}Si_{15}B_{10}$. In this experiment, a troid made of an amorphous ribbon (about one meter long) produced by the roller quenching technique was used in order to eliminate the demagnetization effect completely. The B-H hysteresis loop of this specimen is shown in Fig. 8. The magnetic properties are listed in Table 2. Note that the magnetic properties are substantially improved by the magnetic field cooling. The best soft magnetic properties: H_c of 0.006 Oe, μ_m of 7.0×10^5 and B_r of 4200 G are comparable to those of commercial 4–78 Mo Permalloy[16].

The improvement in the soft magnetic properties by means of magnetic field cooling may be attributed to the internal stress relief as well as to the induced uniaxial magnetic anisotropy.

4. Permeability of an amorphous $Fe_{4.7}Co_{70.3}Si_{15}B_{10}$ ribbon at high frequencies

For engineering applications of the present alloy as soft magnetic materials, the magnetic properties at high frequencies are important as well. Figure 9 shows the frequency dependence of effective permeability (μ_{eff}) of an as-prepared ribbon (25 μ_m thick) of the $Fe_{4.7}Co_{70.3}Si_{15}B_{10}$ alloy. The value of μ_{eff} is of the order of 7×10^3 at frequencies up to about 100 KHz. Compared with data of available commercial alloys, the value of μ_{eff} of this ribbon is larger than that of Alperm, and the frequency dependence of μ_{eff} is smaller than that of Permalloy.

(16) Tohoku Metal Industries, Ltd. Catalogue, (1974).

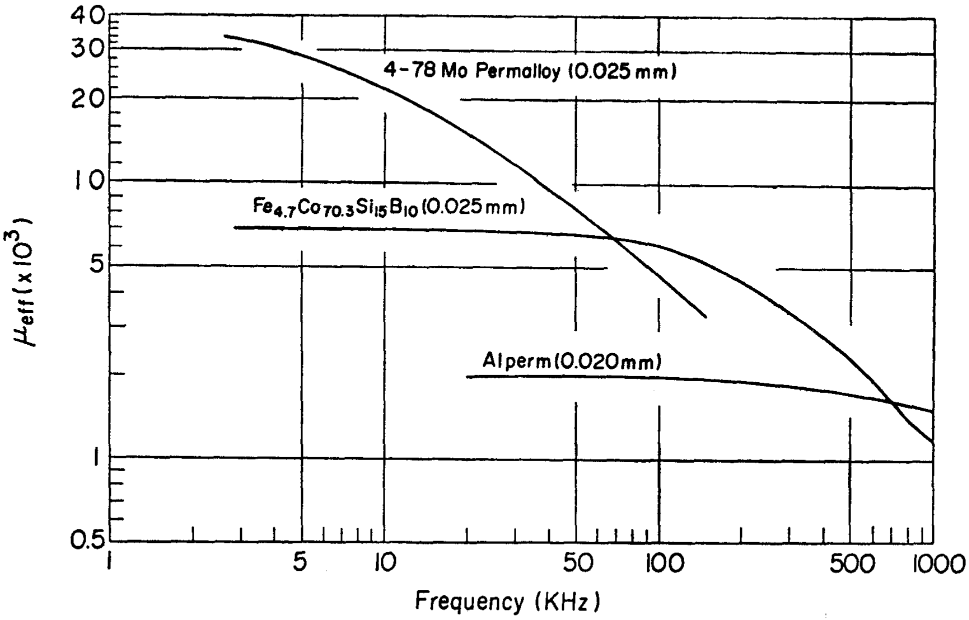

Fig. 9. Frequency dependence of effective permeability of the amorphous $Fe_{4.7}Co_{70.3}Si_{15}B_{10}$, alloy, Permalloy, and Alperm. Values in parenthesis indicate the thickness of specimens. An amplitude of AC field of 10 m Oe was used for the measurement.

The AC core loss is 0.055 W/kg at a flux density of 200 G and at a frequency of 10 KHz, being as small as that of Permalloy. The reason for such good frequency dependence of μ_{eff} seems to lie in the high electrical resistance (see Table 2) together with the high static permeability; the static permeability can be retained up to high frequencies because of suppressed eddy current loss. The high electrical resistance may arise from the characteristics of amorphous structure.

In addition to the magnetic properties, the present amorphous ribbons are mechanically very hard. The obtained value of Vickers hardness is of the order of 700$\sim$900 in the case of the Co rich Co-Fe-Si-B alloys. Generally speaking, there is a tendency that when a material has high value in hardness it is at the same time highly resistive against wear. A preliminary test shows that the resistance against wear of an $Fe_{4.7}Co_{70.3}Si_{15}B_{10}$ ribbon is of the same order as that of Fe-Si-Al (Sendust). Accordingly, the amorphous $Fe_{4.7}Co_{70.3}Si_{15}B_{10}$ alloy may be useful as the material for magnetic recording heads, for example. The high crystallization temperature (see Fig. 3) and the high stability of permeability against external mechanical shock (see the small effect of stress in Fig. 6 for example) should also make these amorphous alloys useful not only for magnetic recording heads but also for general soft-magnetic devices.

IV. Conclusions

Magnetic, electrical and mechanical properties of Fe-Co based amorphous alloys, prepared by the centrifugal and roller quenching methods, were studied. The results obtained are as follows:

1) Amorphous alloys in the Co-Fe system are stable at compositions of $x=0\sim0.75$ in the system $(Fe_{1-x}Co_x)_{80}P_{13}C_7$ and $x=0.73\sim1$ in the system $(Fe_{1-x}Co_x)_{75}$-$Si_{15}B_{10}$. Crystallization temperatures of the P-C based alloys (380∼480°C) are lower than those of the Si-B based alloys (480∼500°C).

2) The Curie temperature changes in a parabolic way with respect to composition x, having a maximum value of about 450°C near $x=0.5$. Specific gravity increases linearly from 7.54 in $Fe_{80}P_{13}C_7$ to 8.65 in $Co_{75}Si_{15}B_{10}$. Electrical resistivity in the amorphous state is as high as 130∼270 $\mu\Omega$-cm.

3) Saturation magnetization (B_s) and residual magnetization (B_r) decrease monotonically with increasing composition x, except for a slight increase of B_r in the Fe rich region. The coercive force (H_c) vs. x curve has a broad maximum around $x=0.5$ and a sharp minimum around $x=0.94$.

4) Magnetostriction is zero near $x=0.94$, being positive in the range of $x<0.94$ and negative in the range of $x>0.94$.

5) The amorphous $Fe_{4.7}Co_{70.3}Si_{15}B_{10}$ alloy has nearly zero magnetostriction and exhibits the best soft magnetic properties. H_c of 0.006 Oe and a maximum permeability of 7.0×10^5 can be obtained by means of magnetic field cooling. As-prepared ribbon of this alloy has a high effective permeability (about 7×10^3) at high frequencies, a low AC core loss (0.055 W/kg at 200G and at 100 KHz) and a high value of Vickers hardness (910). Therefore, this amorphous alloy is very promising for the material as various soft-magnetic devices such as magnetic recording heads.