Amorphous Magnetic Alloys

著者	Masumoto Tsuyoshi
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Amorphous Magnetic Alloys*

Tsuyoshi Masumoto

The Research Institute for Iron, Steel and Other Metals

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Synopsis

The alloy systems for amorphous magnetic alloys are devided into the metal-metalloid type and the metal-metal type. The former alloys consist of ferromagnetic transition metals (TM: Fe, Co and Ni) and metalloid elements (B, C, Si, P and Ge). On the other hand, the amorphous alloys belonging to the latter type are limited to several alloy systems of TM-Zr and TM-Hf. In this paper, the subjects covered include the composition dependence of the magnetization, Curie temperature, magnetostriction, coercive force and permeability for two types of amorphous magnetic alloys. Finally, the examples of the alloy design for some applications and their magnetic characteristics are briefly introduced.

I. Introduction

The amorphous ferromagnetic alloys produced by continuous melt-quenching techniques are strongly expected as various soft magnetic materials for power transformers and magnetic and electronic devices such as tape-recorder heads, amplifiers, inverters and transducers.[1-7] In selecting an alloy for a specific application, however, considerations in multitude of areas are required. For instance, the properties of the amorphous alloys depend not only upon the chemical composition but also upon the quenching condition and the post-quench heat treatment. Fortunately, the amorphous alloys can be produced in a wide composition range and they are sensitive to mild heat treatments. Therefore, there are ample opportunities to design the composition and heat treatment of the alloy talored for specific applications.

This paper reviews recent data on magnetic properties of two types of amorphous alloys and the characteristics of the alloys designed for some applications.

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II. Alloy Systems of Amorphous Magnetic Alloys

Amorphous alloys have been found in a large number of alloy systems by means of melt-quenching.[8] Amongst these alloys, the alloy systems having strong-ferromagnetic nature are classified generally into two categories; namely, the TM-metalloid type and the TM-TM type. Most of amorphous magnetic alloys found so far belong to the former type and they contain various kinds of metalloids such as B, C, Si, P and Ge in the range of about 15-30 at%. On the other hand, the alloys belonging to the latter type are extremely limited to several alloy systems consisting of early transition metals (TM: Fe, Co, and Ni) and late transition metals (TM: Zr and Hf).[9,10]

At present, the TM-metalloid type alloys are most extensively studied in the fields of scientific researches and industrial applications.[1-7] In contrast with this system, the TM-TM type alloys have not been taken any interest in magnetic materials because of relatively low concentrations of ferromagnetic metals. However, it has recently been found that the amorphous alloys are formed near low compositions of Zr and Hf and they have higher thermal stability and almost similar soft-magnetic properties compared with the TM-metalloid type alloys.[11] In binary systems, the Zr content forming amorphous single phase is about 9-11 for Fe-Zr, about 9-16 for Co-Zr and about 10-11 at% for Ni-Zr system. In ternary and quaternary systems, the amorphous phase is formed only around 10 at% Zr. However, this limited composition range is extended by small additions of Metalloids.

III. Magnetic Properties

1. TM-metalloid type amorphous magnetic alloys

A large amount of data on magnetic poperties of this-type alloys has been compiled and reviewed in several articles.[1-7] However, there is considerable scatter and disagreement among them, so that it may be useful to reassess the effect of metalloid composition on the intrinsic properties qualitatively, using limited but consistent sources of date.

Figure 1 shows the composition dependence of saturation magnetization at room temperature σ_s and the Curie temperature T_c for the binary amorphous alloys of Fe-B, Fe-P and Co-B[12]. Both σ_s and T_c of Co-base alloys decrease as the concentration of B is increased, due to the magnetic dilution by a charge transfer from B atoms. On the contrary, T_c of Fe-base alloys increases as the metalloid concentration of B and P is increased. Such an unusual behavior of σ_s and T_c in Fe-rich alloys is related closely with their invar behaviors.[13]

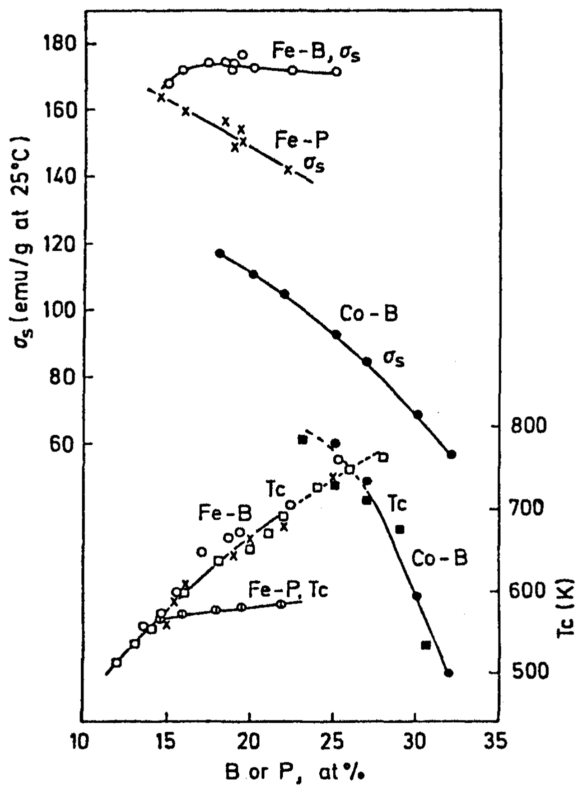

Fig. 1. Saturation magnetization σ_s and Curie temperature T_c of binary Fe- and Co-base alloys.

Variations in σ_s and T_c of Fe- and Co-base alloys with various combinations of two metalloids are also shown in Figs. 2 and 3.[12] In terms of enhancing the value of T_c of Fe-base alloys, the metalloids rank in the order of Ge, Si, B, C and P. On the other hand, the value of σ_s is of the same order among B, C and Si, and is less with Ge and P. For Co-base alloys, the effects of metalloids are similar for T_c and σ_s as shown in Fig. 3. Both of them are reduced in the order of C, B, Si, Ge and As.

For applications which require high magnetic induction, therefore, the Fe-base alloys with combinations of B, C and Si are optimum. Figure 4 shows the composition dependence of σ_s in Fe-B-C and Fe-B-Si systems.[14] It is seen that the maximum value is located around $Fe_{80}B_{20}$ composition. However, the Fe -B and Fe-B-C alloys are not necessarily the best one for application in terms of the ease of formation and thermal stability. As a result, the optimum combination of metalloids is of the B-Si or B-Si-C.

The systematic studies on magnetic properties of the amorphous Fe-Co-Ni alloys have been carried out by Ohnuma et al.[15,16] Figures 5 and 6 represent the saturation magnetic induction (B_s) at room temperature and Curie temperature (T_c) for $(Fe, Co, Ni)_{78}Si_8B_{14}$ system. In the figures, both values change continuously and monotonically with respect to the composition, in contrast to the discontinuous changes in B_s and T_c at the boundaries between different crystal structures in the crystalline ternary system. Figure 7 shows the saturation magnetostriction (λ_s) of the same alloys.[17] the value of λ_s is as large as about 30×10^{-6} in the region of the Fe-rich alloys and takes a maximum of 35×10^{-6} at $Fe_{0.83}Co_{0.17}$. The λ_s decreases with decreasing Fe content and approaches to zero value and then changes to a negative sign at Co-Ni side. Therefore, the Zero magnetostriction is obtained on a composition line connected smoothly from $Co_{0.95}Fe_{0.05}$ to $Ni_{0.8}Fe_{0.2}$. This line is different from that for the crystalline alloys as shown by the dotted line in the figure. This zero-magnetostriction line is displaced by addition of other transition metals as shown in Fig. 8, while it is hardly changed by combinations of metalloids.

Figures 9 and 10 show the coercive force (H_c) and effective permeability (μ_e) of the same alloys in as-quenched state.[16] As can be seen in the figures, H_c decreases and μ_e increases gradually with a decrease of the absolute value of λ_s, and H_c lower than 5 mOe and μ_e higher than 10^4 are obtained in the vicinity of the zero-magnetostriction line. Thus the zero-magnetostrictive amorphous alloys have high permeability comparable to permalloy even in the as-prepared state. Further improvement of the permeability is possible by controlling the alloy composition and post-quench heat treatment. As an example, Fig. 11 shows the effects of alloy composition and heat treatment on permeability for (Co, Fe)$_{70}$(Si, B)$_{30}$ amorphous alloys.[16] In the vicinity of $(Fe_{0.06}Co_{0.94})_{70}(Si_{0.4}B_{0.6})_{30}$, the values higher than 4×10^3 are obtained in as-quenched state and after annealing it increases until 5×10^5 or more. The $(Fe_{0.06}Co_{0.94})_{70}B_{30}$ alloy does not show a high

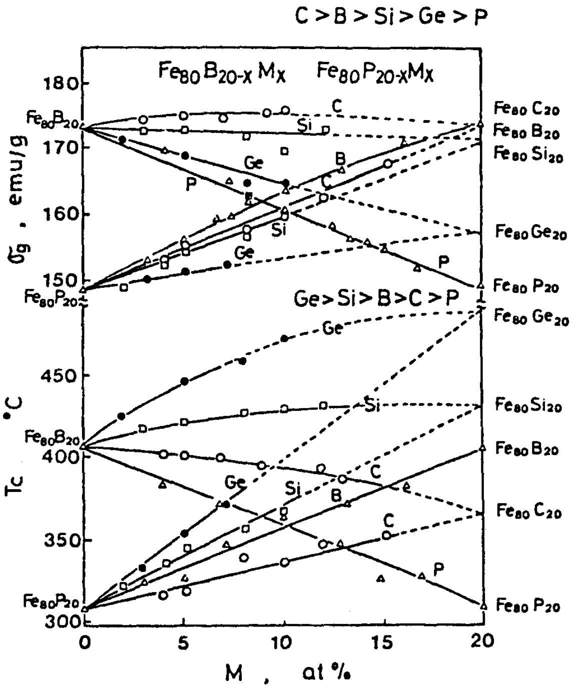

Fig. 2. Saturation magnetization σ_s and Curie temperature T_c of ternary Fe-base alloys. Dashed lines indicate extrapolations.

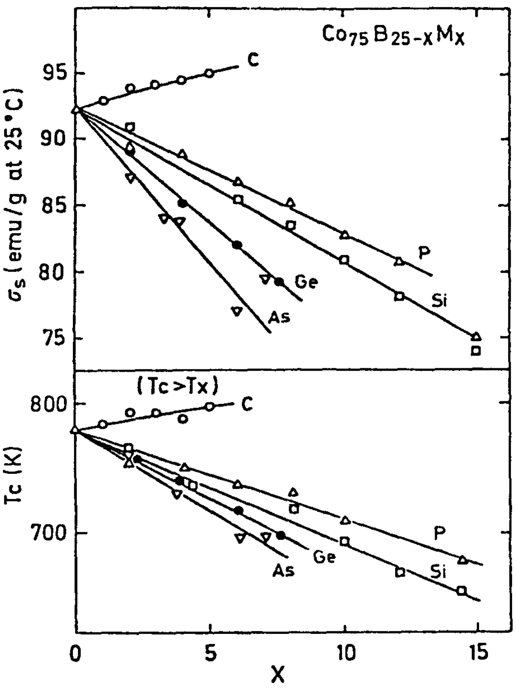

Fig. 3. Saturation magnetization σ_s and Curie temperature T_c of $Co_{75}B_{25-x}M_x$ (M=C, P, Si, Ge and As).

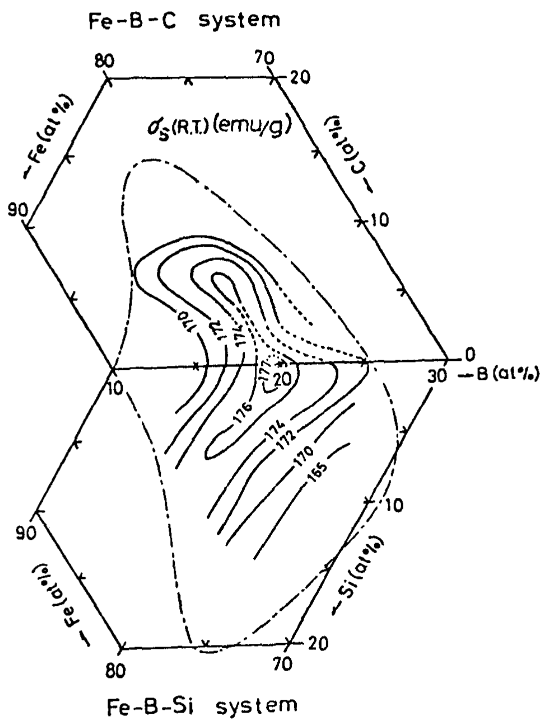

Fig. 4. Composition dependence of saturation magnetization σ_s in Fe-B-C and Fe-B-Si systems.

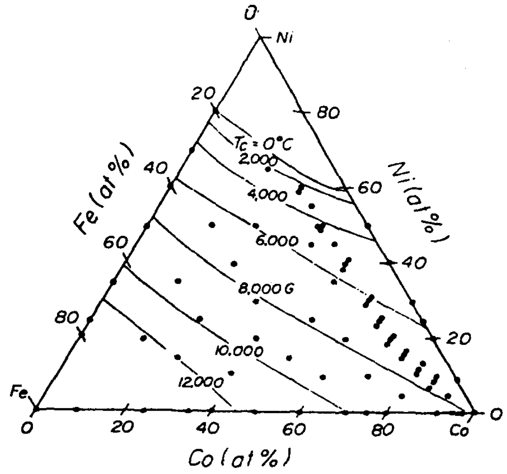

Fig. 5. Saturation magnetic induction B_s at room temperature of (Fe, Co, Ni)$_{78}$Si$_8$B$_{14}$ amorphous alloys.

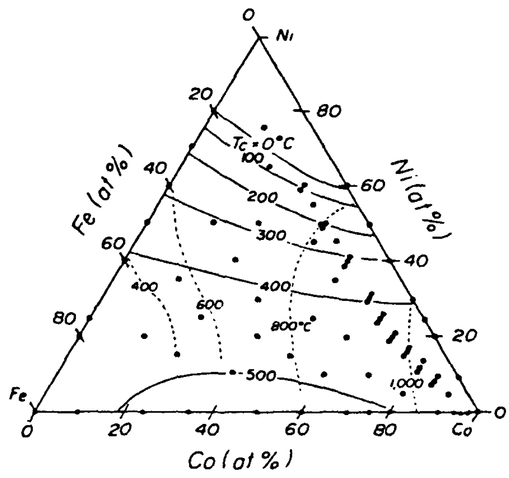

Fig. 6. Curie temperature T_c of (Fe, Co, Ni)$_{78}$Si$_8$B$_{14}$ amorphous alloys. Dashed lines indicate T_c of crystalline Fe-Co-Ni ternary alloys.

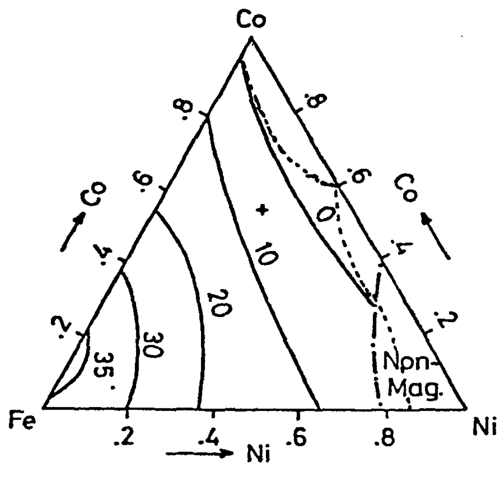

Fig. 7. Saturation magnetostriction λ_s of (Fe, Co, Ni)$_{78}$Si$_8$B$_{14}$ amorphous alloys. Dashed lines indicate λ_s of crystalline Fe-Co-Ni ternary alloys.

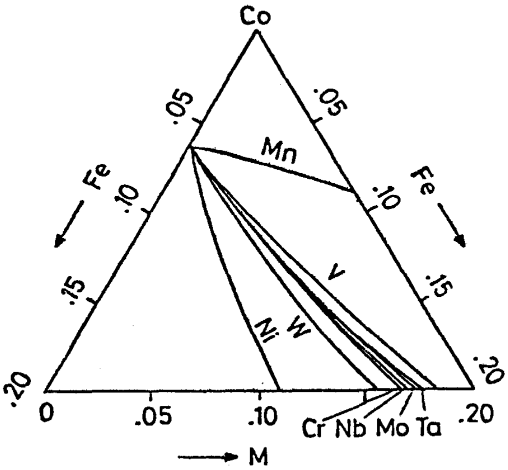

Fig. 8. Zero-magnetostriction lines of $(Fe, Co, M)_{78}Si_8B_{14}$ amorphous alloys (M:Mn, Ni, Cr, Mo, W, V, Ta and Nb).

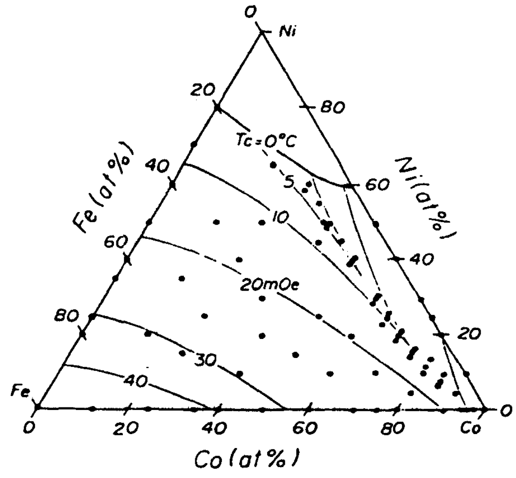

Fig. 9. Coercive force H_c of $(Fe, Co, Ni)_{78}Si_8B_{14}$ amorphous alloys.

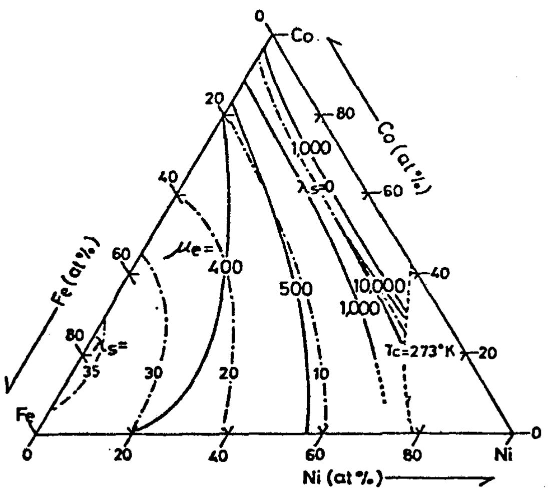

Fig. 10. Effective permeability μ_e at 1 kHz and 3 mOe (solid lines) and magnetostriction λ_s (dashed lines) of $(Fe, Co, Ni)_{78}Si_8B_{14}$ amorphous phous alloys.

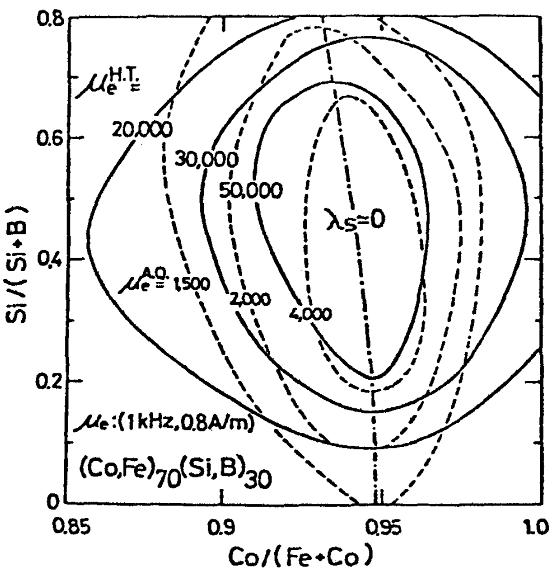

Fig. 11. Effective permeability μ_e at 1 kHz and 3 mOe for as-quenched (dashed lines) and annealed (solid lines) amorphous $(Co, Fe)_{70}(Si, B)_{30}$ alloys. Chain line indicates zero-magnetostriction.

value because of T_c higher than T_x. Therefore, the highest permeability can be obtained only near the compositions having zero-magnetostriction and T_c lower than T_x in Fe-Co-Si-B system.

2. TM-TM type amorphous magnetic alloys

Magnetic properties of the TM-TM type amorphous alloys have extensively been studied by ourselves.[19-21] Figures 12 and 13 shows the T_c and n_B of amorphous TM-Zr binary alloys. In Co-Zr system, it is found that n_B decreases monotonically with increasing Zr content in a manner similar to Co-P and Co-B system. The n_B of "pure" amorphous Co atom is estimated to have almost the same value (about 1.75 μ_B) as crystalline Co atom. The T_c value in Co-Zr system could not be measured because they were significantly higher than T_x. The n_B of Ni-Zr alloys is negligibly samll at 11 at% Zr. The compositional dependence of n_B and T_c in Fe-Zr system shows abnormal behavior; namely, both the values decrease monotonically with a decrease in Zr content and when extrapolating the measured value of n_B to x=0 the n_B of "pure" amorphous atom is estimated to be almost of 0 μ_B. Such behaviors of T_c and n_B may provide instructive information on magnetic properties of "pure" amorphous Fe.

Figure 14 shows the compositional dependence of saturation magnetization at 0 K and

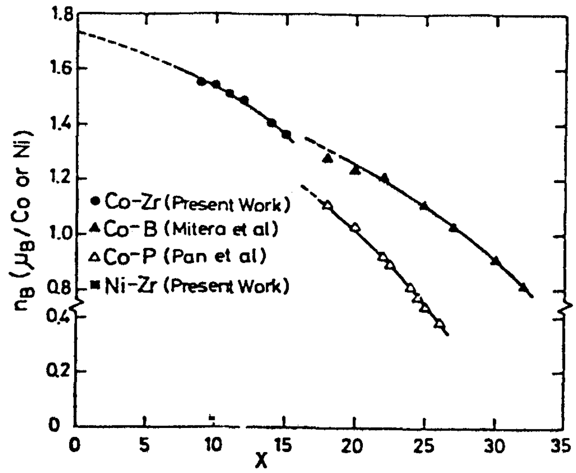

Fig. 12. Magnetic moment n_B of $TM_{100-x}Zr_x$ (TM=Co, Ni) and TM-metalloid ternary alloys.

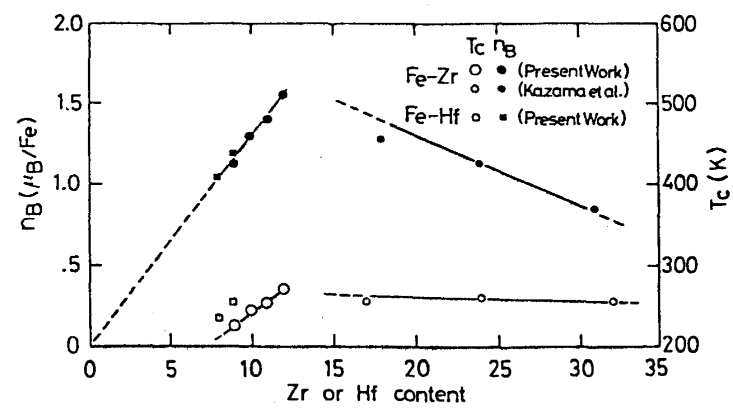

Fig. 13. Magnetic moment n_B and Curie temperature T_c of $Fe_{100-x}M_x$ (M=Zr, Hf) binary alloys.

10 kOe (Ms) for pseudo-ternary Fe-Co-Ni system fixed at Zr=10. The variation of Ms in Ni-rich region shows a tendency similar to that of (Fe, Co, Ni)-Si-B alloys. On the contrary, the behavior of Ms value in the Fe-rich region is entirely different and the value of $Fe_{90}Zr_{10}$ alloy is about 109 emu/g markedly lower than those for previous Fe-metalloid type alloys. This low value increases by substituting Fe by Ni or Co and shows the maximum value at about 20-30 at% Co or Ni. In addition to the unusual feature of Ms, the Fe-rich alloys also exhibit a different behavior of T_c from the TM-metalloid type alloys. As seen in Fig. 15, the T_c value in Fe-rich region decreases monotonically with increasing Fe content. These Fe-rich alloys also have a remarkable invar effect.[20] Such magnetically anomalous behaviors in the present alloys may be understood from a stand-point of coexistence of an antiferro- and ferro-magnetic state in amorphous matrix. The present alloys also provide an interesting behavior in the magnetostriction. Figure 16 shows the compositional dependence of λ_s in pseude-ternary Fe-Co-Ni system for fixed Zr content.[19] The λ_s value of the Fe-rich TM-Zr alloys decreases drastically with increasing Fe content in the opposite way to TM-metalloid alloys. As a peculiarity of TM-Zr system, we can find the following; for the $Co_{90}Zr_{10}$ alloy λ_s has a value of 3×10^{-6} and its

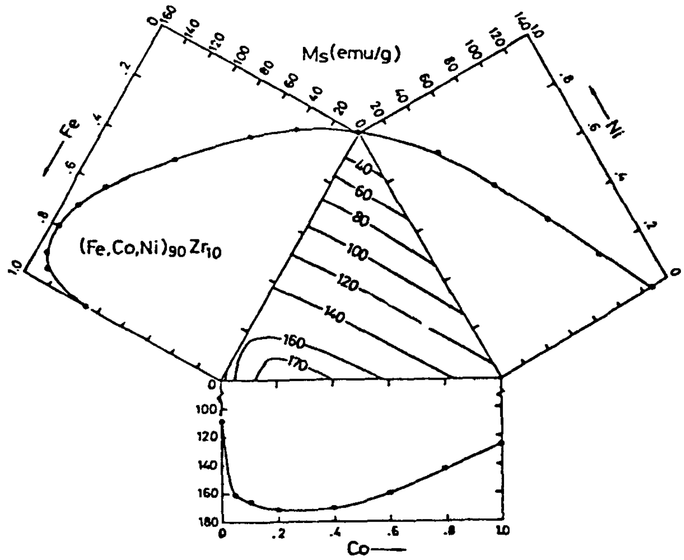

Fig. 14. Saturation magnetization Ms at 0 K of (Fe, Co, Ni)$_{90}$Zr$_{10}$ alloys.

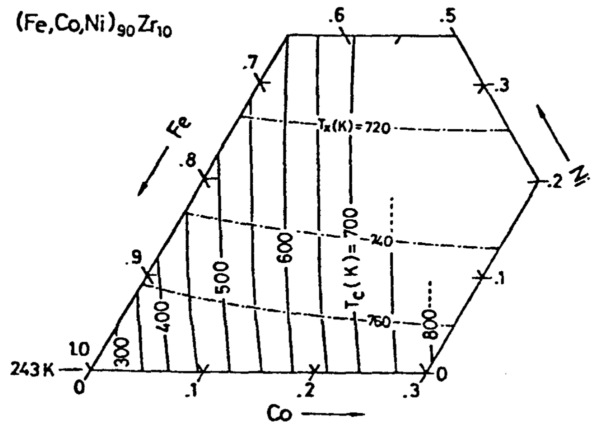

Fig. 15. Curie temperature T_c of (Fe, Co, Ni)$_{90}$Zr$_{10}$ alloys. Chain lines indicate crystallization temperature T_x.

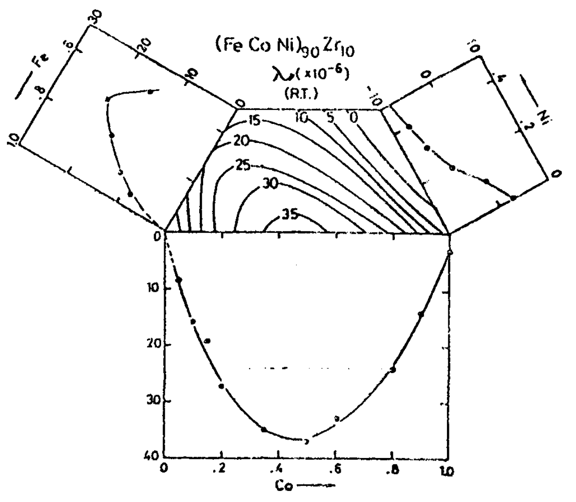

Fig. 16. Saturation magnetostriction λ_s of (Fe, Co, Ni)$_{90}$ Zr_{10} alloys.

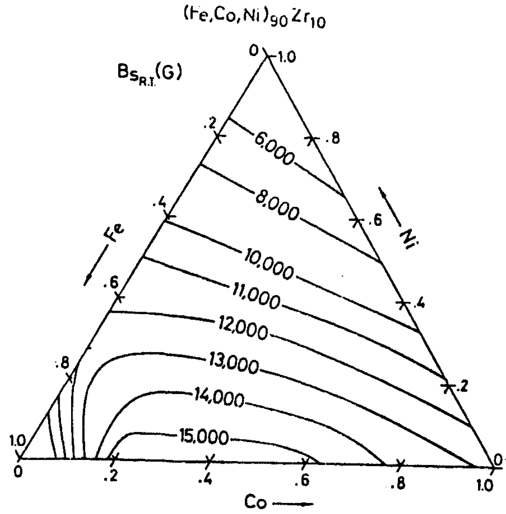

Fig. 17. Saturation magnetic induction Bs at room temperature of (Fe, Co, Ni)$_{90}Zr_{10}$ alloys.

sign is not negative but positive. The zero-magnetostriction composition lies near $(Co_{0.88}Ni_{0.12})_{90}Zr_{10}$ and shifts to the Fe-rich side with increasing Ni content.

The compositional dependence of Bs is shown in Fig. 17[9]. The maximum value of about 16.7 kG obtained around $(Fe_{0.7}Co_{0.3})_{90}Zr_{10}$ and the value decreases with an increase in Ni content.

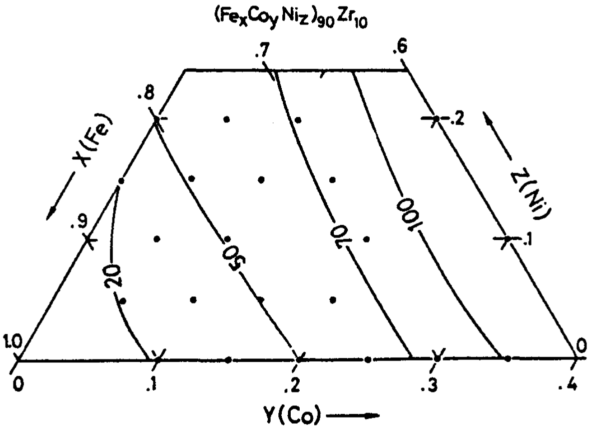

Fig. 18. Coercive force H_c of (Fe, Co, Ni)$_{90}Zr_{10}$ alloys annealed at 350-400 °C for 20 min under 600 Oe.

Figure 18 shows the compositional dependence of H_c for $TM_{90}Zr_{10}$ alloys annealed at 350-400 °C for 20 min under a magnetic field of 600 Oe. The H_c value increases from 20 to 100 mOe gradually with increasing Co content.

From these results, one can expect that the TM-TM type amorphous alloys possess a high saturation magnetic induction, a low coercive force and a high permeability, which are required for practical soft -magnetic materials. Table 1 lists the characteristics of several $TM_{90}Zr_{10}$ amorphous alloys with high magnetic induction compared with those of typical TM-metalloid amorphous alloys. Also, it has been found that the zero-magnetostrictive Co-Zr base alloys have extremely

Table 1

Characteristics of several $TM_{90}Zr_{10}$ amorphous alloys with high magnetic induction compared with those of typical TM-metalloid amorphous alloys.

Alloy Composition	Tx (°C)	Tc (°C)	$B_s^{(R.T)}$ (KG)	λ_s ($\times 10^{-6}$)	Hc (mOe)	B_r/B_{10} (%)	ρ (μΩ-cm)
$(Fe_{.8}Co_{.2})_{90}Zr_{10}$	490	347	15.7	27	50	83	140
$(Fe_{.7}Co_{.2}Ni_{.1})_{90}Zr_{10}$	470	445	14.6	29	70	97	130
$(Fe_{.8}Co_{.1}Ni_{.1})_{90}Zr_{10}$	470	277	13.6	24	45	86	150
$(Fe_{.9}Co_{.1})_{90}Zr_{10}$	490	197	11.6	18	20	50	160
$Fe_{80}B_{20}$	380	378	15.8	31	40	78	145
$Fe_{78}Si_{10}B_{12}$	478	460	14.4	33	35	74	128
$Fe_{40}Ni_{40}B_{20}$	451	390	10.0	14	90	68	-
$Fe_{40}Ni_{40}P_{14}B_6$	414	247	7.8	11	20	71	130

Table 2

Typical data of zero-magnetostrictive amorphous alloys

Alloy Composition	T_x (°C)	T_c (°C)	B_s (kG)	B_r/B_s	H_c (mOe)	μe	ρ (μΩ-cm)	H_v
$Co_{77.0}Cr_{11.7}Zr_{11.3}$	549	360	5.4	0.15	7.0	34,800	126	574
$Co_{79.0}Cr_{10.6}Zr_{10.4}$	540	433	6.7	0.31	9.5	14,000	125	564
$Co_{81.5}Mo_{9.5}Zr_{9.0}$	570	498	7.3	0.35	3.0	21,000	125	561
$Co_{82.5}Mo_{9.3}Zr_{8.2}$	526	576	8.5	0.65	19.6	6,800	123	552
$Co_{83.5}W_{6.0}Zr_{10.5}$	578	453	7.2	0.27	9.6	8,800	137	585
$Co_{80.4}V_{9.8}Zr_{9.8}$	520	-	7.7	0.20	7.0	12,600	127	-

low coercivity and high permeability. The typical data are shown in Table 2. These data show clearly that the present alloys possess high qualities as soft-magnetic materials, similar to the TM-metalloid amorphous alloys.

IV. Concluding Remarks

In this paper only the data from a few sources have been used in order to avoid experimental uncertainties. Recent experimental data on magnetic properties of TM-metalloid type and TM-TM type amorphous alloys have been summarized mainly based on our studies. These results suggest that the amorphous magnetic alloys are very interesting materials to scientists from fundamental and practical points of view. However, for practical uses there are still remained many unsolved problems. Particularly, improvements on stability of magnetic properties against aging and mass productions with low cost are strictly required.

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