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著者	Kikuchi Michio, Fukamichi Kazuaki, Kimura Hisamichi, Masumoto Tsuyoshi
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Soft Magnetic Co-Ti-B Amorphous Alloys with High Corrosion Resistance*

Michio Kikuchi**, Kazuaki Fukamichi, Hisamichi Kimura
and Tsuyoshi Masumoto
The Research Institute for Iron, Steel and Other Metals

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Synopsis

Co-Ti-B ternary amorphous ribbons were prepared by the melt-quenching method, and their soft magnetic properties, hardness and corrosion resistance have been investigated. With increasing titanium content, the Curie temperature decreases monotonically, while the crystallization temperature gradually increases. These alloys are magnetically very soft, that is, the coercive force takes a minimum value of 0.01 Oe and the maximum permeability shows a large value of 6×10^4 around $x = 0.05$ for $(Co_{1-x}Ti_x)_{80}B_{20}$ amorphous alloys. Their linear magnetostrictions are also quite small, being of the order of about -2.5×10^{-6}. In addition, these amorphous alloys have a high hardness and an excellent corrosion resistance. Therefore, Co-Ti-B amorphous alloys are promised as the soft magnetic materials for electromagnetic devices.

I. Introduction

As is well known, the crystalline Co and its alloys have a large magnetocrystalline anisotropy and these alloys containing rare earth elements are extensively used as strong hard magnets1). In contrast to these crystalline alloys, Co-base amorphous alloys exhibit a high initial permeability and a low coercive force2,3), therefore, they

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**Permanent address: The Research Institute of Electric and Magnetic Alloys, Sendai 982, Japan.

are considered as attractive soft magnetic materials. Such excellent soft magnetic properties of the amorphous alloys arise from a high mobility of the magnetic domain boundaries due to no magnetocrystalline anisotropy and no grain boundary.

In application of soft magnetic materials to electromagnetic devices, a high resistance against an atmospheric corrosion is required with excellent soft magnetic properties. Recent works[4,5] on sputtered amorphous films of Co-Ti and Co-Ti-B have shown that they have a very small magnetostriction and an excellent corrosion resistance. However, these thin films do not show low coercive forces even after appropriate annealing. In our early work[6], we have found that Co-B melt-quenched amorphous alloys reveal a relatively low magnetostriction and a low coercive force, while they have a low corrosion resistance and a low crystallization temperature. Although the addition of chromium to this alloy system is effective in the improvement of the corrosion resistance, it remarkably decreases the magnetization[7] and the Curie temperature[8]. In order to solve these faults, we have tried to investigate the effect of the addition of titanium to the Co-B amorphous alloys on the soft magnetic properties, the crystallization temperature, the hardness and the corrosion resistance. In the present study, the melt-quenching method has been adopted for the purpose of eliminating the influence of the substrate on the magnetic properties in such a case of the sputtered films.

II. Experimental

By using electrolytic cobalt, spongy titanium and 99.8% pure boron as starting materials, various master alloys of Co-Ti-B system were melted in an argon atmosphere using a high frequency furnace.

The amorphous ribbon samples were prepared in the form of about 1.2 mm width and 30 μm thickness from the melts by a single roller method (200 mm diameter copper roller and 3000 ∿ 5000 r.p.m. revolution speeds). Confirmation of an amorphous state was made using a X-ray diffractometer with Mo-K_α. The compositions of samples used in the present work were in the ranges of 68 ∿ 82 at% cobalt, 16 ∿ 30 at% boron and 0 ∿ 20 at% titanium. Annealing treatments were carried out under the conditions of 200 ∿ 250°C and 0.5 ∿ 2 hr in vacuum.

The B-H hysteresis loop at room temperature was measured by means of a conventional flux-meter using a pair of identical coils wound on the quartz tubes. The temperature dependence of the magnetization was measured at 10 kOe using a magnetic balance. The longitudinal linear magnetostriction was detected in the field of 1 kOe at room temperature by a dilatometric method. The micro-Vickers hardness H_V was obtained under the load of 200g at room temperature.

The corrosion resistance was examined in a 3% NaCl aqueous solution at 20°C using amorphous ribbons with about 1m length. The weight loss after immersing for 2 months was measured by a microbalance. The potentiodynamic polarization measurement was carried out at a potential sweep rate of 0.03 V/min in 3% NaCl aqueous solution and the critical pitting voltage V_c' at which the current density abruptly increases was decided from the curve.

III. Results and Discussion

Figure 1 shows the compositional changes in the Curie temperature T_c and the crystallization temperature T_x of the amorphous alloys in the ternary Co-Ti-B system, wherein the values of T_c above T_x were estimated by extrapolation of the thermomagnetization curves. The value of T_c remarkably depends on not only the titanium but also the boron content; T_c steeply falls with increasing titanium content, and

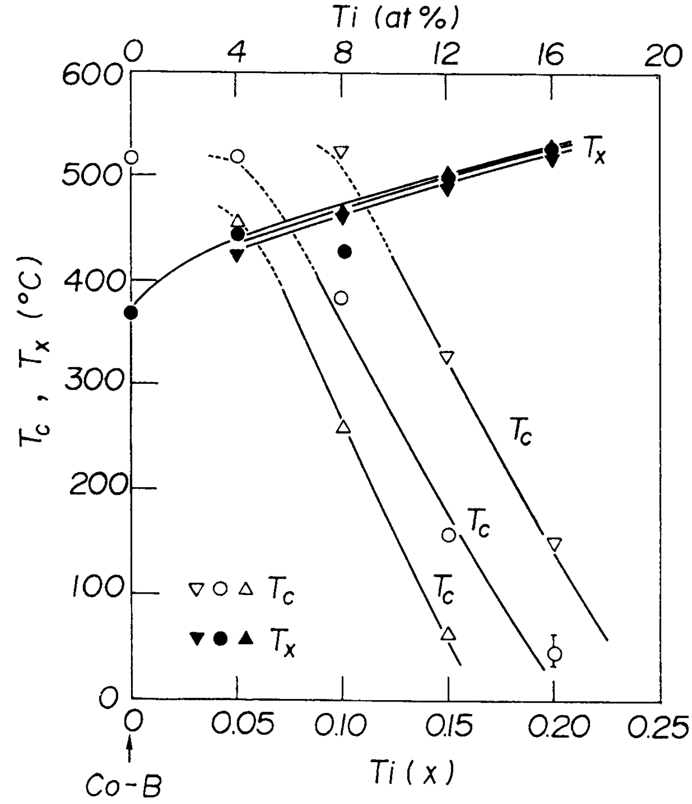

Fig. 1 The Curie temperature T_c and the crystallization temperature T_x of $(Co_{1-x}Ti_x)_{82}B_{18}$ (▽ , ▼), $(Co_{1-x}Ti_x)_{80}B_{20}$ (○ , ●) and $(Co_{1-x}Ti_x)_{78}B_{22}$ (△ , ▲) amorphous alloys.

it is close to room temperautre in the alloy with x = 0.20 for $(Co_{1-x}Ti_x)_{80}B_{20}$ amorphous alloy system. The value of T_c becomes higher than T_x above x = 0.07, and the estimated T_c takes a constant value of about 500°C, though these alloys crystallize before diminishing of their ferromagnetism. On the contrary, T_x gradually increases with increasing titanium content and the increment is almost independent of the boron content. It should be noted that the value of T_x of these amorphous alloys is higher than those of Co-B binary amorphous alloys. With increasing boron content, the Curie temperature T_c linearly decreases and the crystallization temperature T_x slightly increases at a constant titanium content.

Figure 2 shows the composition dependences of the magnetization at the field of 10 Oe, B_{10}, the residual magnetization B_r, the coercive force H_c and the maximum permeability μ_m obtained from the B-H loops in the as-prepared states (solid lines) and the annealed ones at 250°C for 30 min at the magnetic field of 400 Oe (broken lines) for the $(Co_{1-x}Ti_x)_{80}B_{20}$ and $(Co_{1-x}Ti_x)_{82}B_{18}$ alloys. The values of B_{10} and B_r decrease monotonically with increasing titanium content x. This behavior is similar to that of Co-Ti-B sputtered amorphous films$^{5)}$, and B_{10} and B_r values are 7200 and 6500 G, respectively, at the composition of x = 0.05. The value of H_c has a broad minimum with 0.01 Oe around x = 0.05. As shown in the figure, μ_m obtained from the B-H loop takes a characteristic behavior in contrast with H_c; the quite high value of 6×10^5 was found in the annealed alloy with x = 0.05. It is noticed that this large value is the almost same level as the data for Co-base soft magnetic amorphous alloys reported previously$^{6)}$. The values of H_c and B_r of $(Co_{1-x}Ti_x)_{82}B_{18}$ amorphous alloys are higher than those of $(Co_{1-x}Ti_x)_{80}B_{20}$ amorphous alloys. Therefore, the value of μ_m for the former alloys becomes lower than that of the latter ones. As seen from the figure the soft magnetic properties are improved by annealing. Such an annealing effect would be explained as that the internal stresses induced during rapid-quenching are relaxed greatly, resulting in a reduction of the local magnetic anisotropy$^{9,10)}$.

The concentration dependence of the longitudinal linear magnetostriction $\lambda_{/\!/}$ for the $(Co_{1-x}Ti_x)_{80}B_{20}$ amorphous alloys at room temperature is shown in Fig. 3. The effect of titanium on the $\lambda_{/\!/}$ value is similar both in as-prepared and in annealed states, that is, the magnitude of $\lambda_{/\!/}$ for Co-Ti binary alloys gradually decreases with increasing titanium content, approaching to the zero value. The $\lambda_{/\!/}$ value around x = 0.2 is small because of its low magnetization and the low Curie temperature. On the other hand, $\lambda_{/\!/}$ takes a small value of

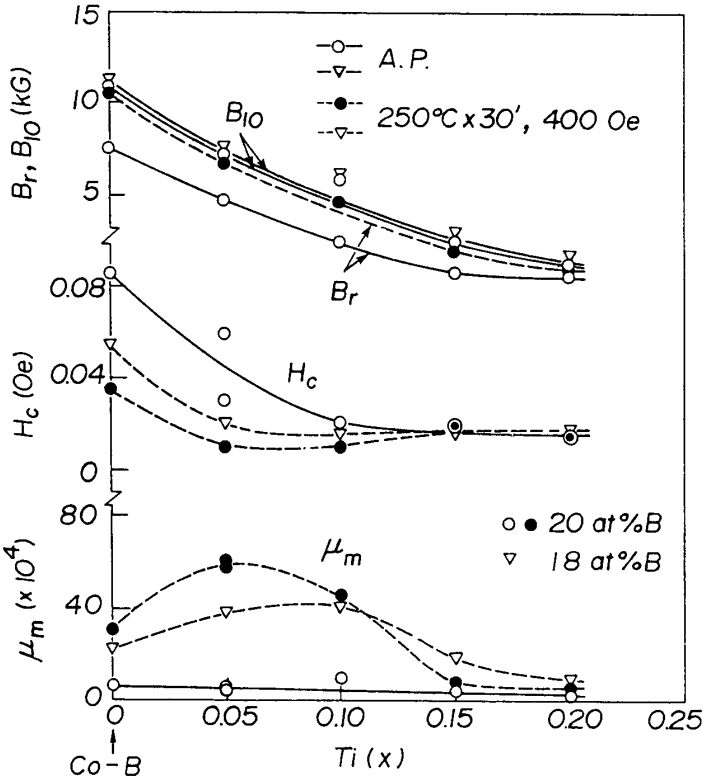

Fig. 2 Concentration dependences of the magnetization at the field of 10 Oe, B_{10}, the residual magnetization B_r, the coercive force H_c and the maximum permeability μ_m of $(Co_{1-x}Ti_x)_{82}B_{18}$ and $(Co_{1-x}Ti_x)_{80}B_{20}$ amorphous alloys. The data were obtained in as-prepared state (solid lines) and annealed state at 250°C for 30 min in the field of 400 Oe (broken lines).

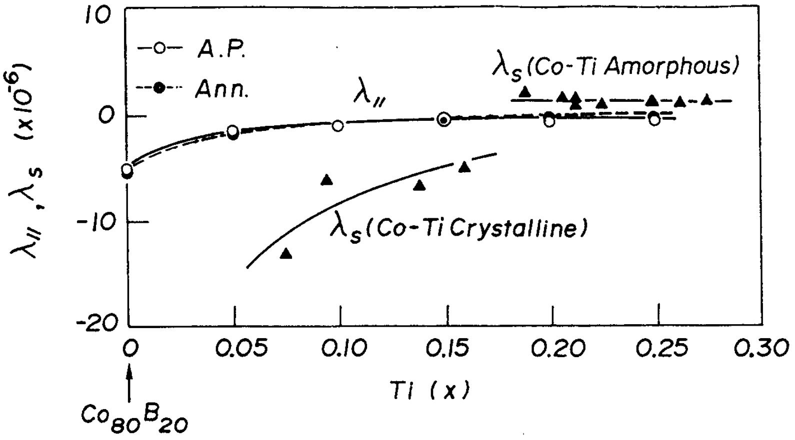

Fig. 3 Longitudinal linear magnetostriction $\lambda_{//}$ of $(Co_{1-x}Ti_x)_{80}B_{20}$ amorphous alloys, in the as-prepared state (-o-) and the annealed state at 200°C for 2 hr.(--o--), and the saturation magnetostriction λ_s of sputtered Co-Ti crystalline and amorphous alloys.

-2.4×10^{-6} at $x = 0.05$ even the high magnetization. The value of $\lambda_{/\!/}$ of $Co_{80}B_{20}$ alloy obtained in the present study substantially agrees with the value of saturation magnetostriction $\lambda_s = -4 \times 10^{-6}$ reported by O'Handley$^{7,11)}$. The values of λ_s of amorphous and crystalline Co-Ti sputtered films$^{5)}$ are also shown in the same figure for comparison. The values of λ_s of Co-Ti alloys take almost zero value regardless of the titanium concentration in the amorphous state, though λ_s of crystalline state is negative and relatively large. It should be noted that the sign of $\lambda_{/\!/}$ is negative for Co-Ti-B ternary amorphous ribbons quenched rapidly from the melts in contrast with that of λ_s for Co-Ti sputtered amorphous films. It is evident that the remarkably large permeability in Fig. 2 is closely related to the very small magnetostriction in the Co-Ti-B amorphous alloys.

The concentration dependence of micro-Vickers hardness H_V of the $(Co_{1-x}Ti_x)_{80}B_{20}$ alloy is given in Fig. 4. As shown in the figure, H_V gradually increases with the titanium content and it is hardly changed by the heat treatment. The titanium is necessary to raise the hardness$^{12)}$, and the H_V value is 700 ∿ 750 in the annealed state for the samples ($x = 0.05$) having the most excellent soft magnetic properties.

Figure 5 shows the titanium concentration dependence of the corrosion rate of the $(Co_{1-x}Ti_x)_{80}B_{20}$ amorphous alloys. The weight loss is remarkably large in $Co_{80}B_{20}$ binary alloy. However by addition of titanium, the corrosion resistance is gradually improved and the corrosion rate shows a low value of 0.21 mg/dm^2/day even at the composition $x = 0.05$. This corrosion behavior is very similar to that of $(Fe_{1-x}Cr_x)_{80}P_{13}C_7$ ($x = 0 \sim 0.725$)$^{13,14)}$ and $(Fe_{1-x}Cr_x)_{85}B_{15}$$^{15)}$ amorphous alloys, and the figure indicates that the corrosion resistance remarkably increases above $x = 0.05$ of $(Co_{1-x}Ti_x)_{80}B_{20}$ amorphous alloys because of the formation of passive film. As is well known, the high corrosion resistance alloys such as stainless steels are corroded locally by pitting in solutions containing Cl^-. In the case of amorphous alloys, however, the pitting corrosion does not occur due to their amorphous structure$^{12)}$. In the present study, the potentiodynamic polarization measurement was carried out in a 3% NaCl solution. The relationship between the critical pitting voltage V_c' and the titanium content is shown in Fig. 6. With increasing titanium content, the value of V_c' increases and shifts to more noble potential side as lowering boron content. The present alloys below $x = 0.09$, which exhibit prominent soft magnetic properties, have the corrosion resistance beyond 2 times in comparison with other amorphous magnetic alloys with low magnetostriction such as $Co_{70.3}Fe_{4.7}Si_{15}B_{10}$ and $Co_{80}Si_5B_{15}$. The crystallization temperatures of Co-Ti-B amorphous

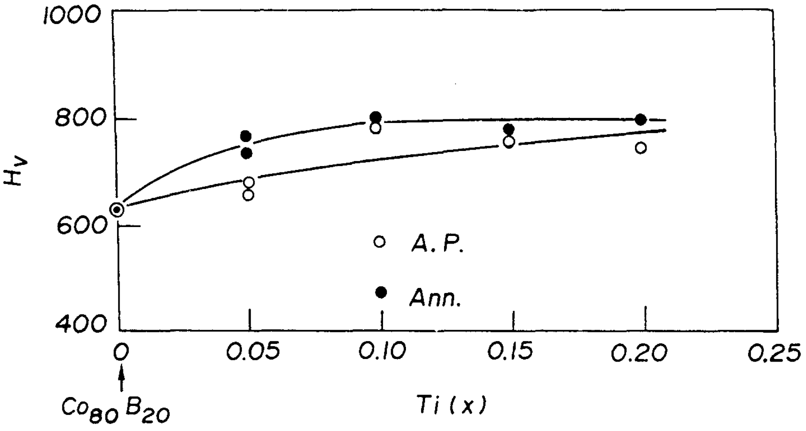

Fig. 4 Micro-Vickers hardness H_V of $(Co_{1-x}Ti_x)_{80}B_{20}$ amorphous samples as-prepared (o) and annealed at 200°C for 2 hr (●).

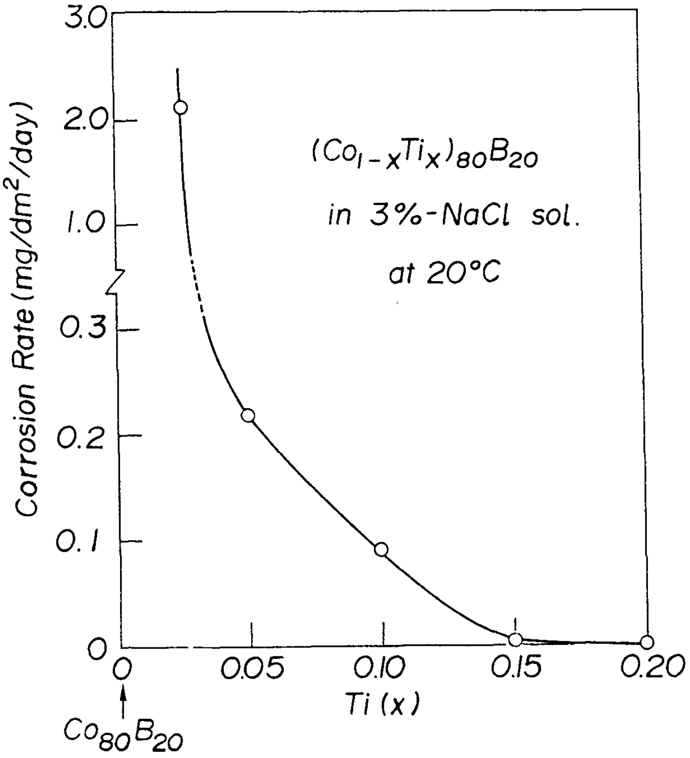

Fig. 5 Concentration dependence of the corrosion rate of $(Co_{1-x}Ti_x)_{80}B_{20}$ amorphous alloys in 3% NaCl solution at 20°C.

alloys are almost the same as those of $Co_{70.3}Fe_{4.7}Si_{15}B_{10}$ and $Co_{80}B_{15}Si_5$ amorphous alloys. In the conventional stainless steels, the addition of titanium elevates their critical pitting potential$^{16 \sim 18)}$. In amorphous alloys, this effect becomes more remarkable because a firm passive film is immediately formed and the pitting corrosion is prevented. Figure 7 shows the relationship between μ_m (solid lines) and V_c' (broken lines) of ternary Co-Ti-B amorphous alloys. The maximum permeability takes high values of $3 \sim 6 \times 10^5$ in the composition range of 18 ∿ 24%B, while the V_c' value gradually increases with increasing both titanium and boron contents. It is clear from the figure that the alloys with a high permeability show a high value of V_c' as -200 ∿ -100mV.

Some magnetic properties and the corrosion rate of melt-quenched $(Co_{0.95}Ti_{0.05})_{80}B_{20}$ amorphous alloy are listed in Table 1, together with those of sputtered Co-Ti film$^{4)}$ for comparison. The magnetostrictions of these both alloys are very small, but the coercive force of the sputtered alloy is not so small for application to soft magnetic devices, and its values are hardly reduced by annealing$^{4)}$. On the other hand, the value of H_c of the melt-quenched alloy is originally small and is reduced remarkably by annealing, showing excellent soft magnetic properties. The corrosion rate of Co-Ti-B amorphous alloy is comparably low. Furthermore, this type of amorphous alloys has a relatively high crystallization temperature (450 ∿ 490°C) and a high hardness.

From the present results, it is concluded that the Co-Ti-B amorphous alloys show excellent soft magnetic properties with a high hardness and an excellent corrosion resistance. It should be noted that the productivity of the melt-quenching method is generally superior to that of the sputtering. Consequently, the Co-Ti-B amorphous alloys produced by melt-quenching are promising as soft magnetic materials for electromagnetic devices such as tape recording heads. Recently, similar excellent properties of Co-Nb-B amorphous alloys have been reported$^{19)}$.

IV. Conclusion

From the practical point of view, the soft magnetic properties, the hardness and the corrosion resistance of Co-Ti-B ternary amorphous alloys obtained by melt-quenching have been investigated. The main results are summarized as follows;

1) Co-Ti-B ternary amorphous alloys have a high crystallization

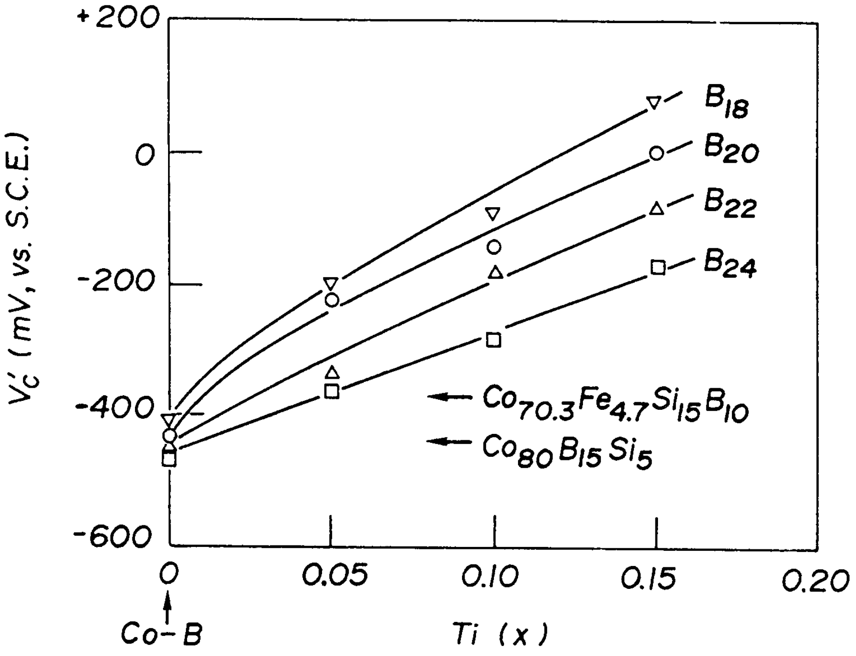

Fig. 6 Critical pitting potential V_c' vs. the standard calomel electrode of Co-Ti-B amorphous alloys as a function of the titanium concentration.

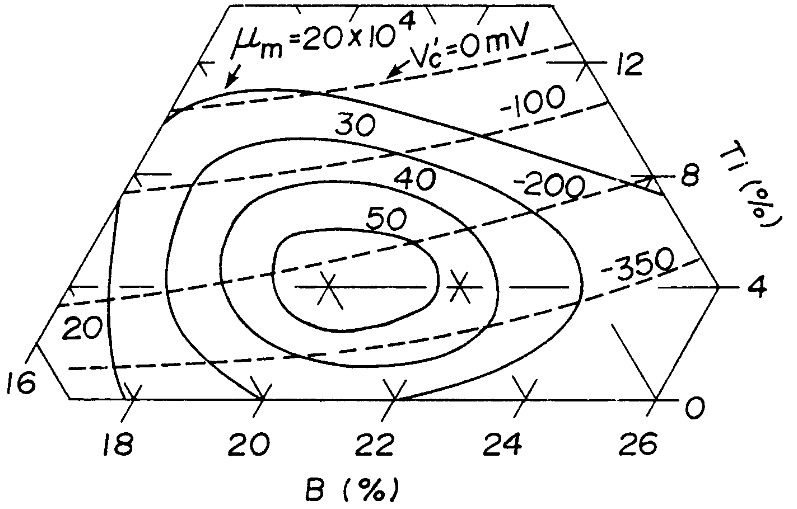

Fig. 7 Critical pitting potential V_c' (broken lines) and the maximum permeability μ_m (solid lines) of Co-Ti-B ternary amorphous alloy system.

Table 1 Magnetic properties and corrosion rate of sputtered Co-Ti[4)] and melt-quenched Co-Ti-B amorphous alloys.

Alloy	Condition	B_{10} (KG)	H_c (Oe)	μ_m ($\times 10^4$)	$\lambda_{/\!/}$, λ_s ($\times 10^{-6}$)	T_x (°C)	T_c (°C)	H_v	Corrosion rate (mg/dm^2/day)
$(Co_{0.95}Ti_{0.05})_{80}B_{20}$	as-prepared	7.2	0.06	5.3	-	490	∿500	700	0.21
	annealed*	7.2	0.01	61.0	-2.5($\lambda_{/\!/}$)	-	-	750	-
$Co_{83}Ti_{17}$	as-deposited	-	0.3	-	-	-	-		-
	annealed**	9∿10†	0.2	-	1.0(λ_s)	-	-		∿0.31

* annealed in the magnetic field at 370 Oe for 30 min at 250°C.

** annealed at 250°C.

† saturated value.

temperature and the Curie temperature decreases with increasing titanium content.

2) The magnetization at the field of 10 Oe and the residual magnetization decrease monotonically with increasing titanium content x. The coercive force vs. titanium content curve has a broad minimum around $x = 0.05$.

3) The magnetostriction exhibits a very small negative value in the wide concentration range in Co-Ti-B ternary system.

4) $(Co_{0.95}Ti_{0.05})_{80}B_{20}$ amorphous alloy has a very low magnetostriction and exhibits excellent soft magnetic properties. The coercive force of 0.01 Oe and the maximum permeability of 6×10^5 are obtained by means of the magnetic field cooling.

5) The hardness of the Co-Ti-B amorphous alloys is very high and it is increased with increasing titanium content.

6) Co-Ti-B ternary amorphous alloys have a high corrosion resistance against the immersion and pitting.

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