Permanent Magnet Properties and their Temperature Dependence in the Fe-Pt-Nb Alloy System*

Kiyoshi Watanabe**

The permanent magnet properties and the temperature dependence of Fe-Pt-Nb ternary alloys were investigated by using a recording fluxmeter, a vibrating sample magnetometer and an X-ray diffractometer.

The excellent permanent magnet properties in the Fe-Pt-Nb system have been obtained by water-quenching from a temperature in the γ phase region and subsequent tempering at about 850–900 K in the γ_1 phase region. A typical Fe-39.5 at%Pt-0.75 at%Nb alloy exhibits the highest value of a maximum energy product of $167 \text{ kJ} \cdot \text{m}^{-3}$, with a residual flux density of 1.05 T and a coercivity of $398 \text{ kA} \cdot \text{m}^{-1}$. These properties are superior to those of the basic binary Fe-Pt alloy. The composition range of the excellent permanent magnet properties of Fe-Pt-Nb ternary alloys spread out wider than that of Fe-Pt magnet alloys, so that the heat-treatments could be controlled easily, and the reproducibility of the magnetic properties would be improved. As a Fe-38Pt-1Nb alloy exhibits the excellent rectangular hysteresis loops at 400 K as well as at 290 K, these magnet alloys have the stable temperature properties and show comparatively high Curie temperature.

It is presumed that the excellent permanent magnet properties of the Fe-Pt-Nb alloys originate from the existence of a constitutionally imperfect γ_1 phase of the initial ordering state which induce the pinning of the magnetic domain wall.

(Received December 4, 1990)

Keywords: iron-platinum alloy, iron-platinum-niobium alloy, permanent magnet, high coercivity, high maximum energy product, order-disorder type magnet, hard magnetic material

I. Introduction

The permanent magnet properties of the equi-atomic FePt alloy have been previously investigated in detail^{(1)–(4)}. The FePt alloy has a maximum energy product $(BH)_{\text{max}}$ of only $24 \text{ kJ} \cdot \text{m}^{-3}$ (3MG·Oe). This alloy is considerably inferior in magnetic properties to CoPt magnets of a similar crystal structure having $(BH)_{\text{max}}$ values as high as $96 \text{ kJ} \cdot \text{m}^{-3}$ ⁽⁵⁾. According to the equilibrium phase diagram of the Fe-Pt alloy⁽⁶⁾ shown in Fig. 1, the Fe-50 at%Pt alloy shows an order-disorder transformation temperature as high as 1573 K. At such a high temperature, the ordering of γ_1 phase (f.c.t., $L1_0$ -type) can occur even when the FePt alloy is quenched rapidly from the disordered γ phase (f.c.c., A1-type) region into stirred ice-water. As a consequence of the fast ordering process, it is difficult, by heat-treatment⁽⁷⁾ to control the transformation in obtaining the desired multiphase structures of the ordered and disordered phases and the excellent permanent magnet properties of the CoPt magnet alloys.

In the study of Fe-Pt permanent magnet alloys, enhancement of the coercivity has been achieved to some extent by forming a disordered phase by means of severe

Fig. 1 Equilibrium phase diagram of Fe-Pt alloys.

* This paper was presented at the 1987 Autumn and 1988 Spring Meeting of the Japan Institute of Metals. It was originally reported in Japanese in J. Japan Inst. Metals, **54** (1990), 1284; 250th report from the Research Institute for Electric and Magnetic Materials.

** The Research Institute for Electric and Magnetic Materials, 2 Yagiyama-minami, Taihaku-ku, Sendai 982, Japan.

mechanical plastic deformation or pulverization⁽⁷⁾⁻⁽⁹⁾ and then applying proper post heat-treatment. Recently, some similar results have been obtained by a special rapid cooling of the molten FePt alloy⁽¹⁰⁾. Although, the FePt permanent magnet is expensive, it has excellent corrosion resistance and workability. It is thus important to demonstrate experimentally that such an alloy with high crystal magnetic anisotropy energy would actually achieve high coercivity.

In order to control order-disorder transformation kinetics during the heat-treatment of Fe-Pt magnetic alloys, we investigated the crystal structures and the possibility of permanent magnet properties of iron-rich alloys instead of equi-atomic FePt because the former have much lower order-disorder transformation temperatures than the latter. As a result, we obtained the maximum energy product value of $159 \text{ kJ} \cdot \text{m}^{-3}$ in the initial ordered state⁽¹²⁾⁽¹³⁾. Later, the effects of some additional elements in the Fe-Pt permanent magnet alloys were studied and it was confirmed that the maximum energy product and coercivity increased with the additions of small amounts of titanium or vanadium⁽¹⁵⁾. However, the control of the heat-treatment of the iron-rich alloys with excellent magnet properties was not easier than that of the general permanent magnet alloys. The ordering process is still very fast and it needs special operations in the melting and quenching. In the present paper, the effects of the addition of Nb on enhanced reproducibility of the permanent magnet properties in the Fe-Pt alloys are investigated.

II. Experimental

Iron and platinum used for alloying were of 99.9 mass% purity, while niobium used was of 99.6 mass% purity. Alloys of the required composition were melted in a sintered alumina crucible under an argon atmosphere using a Tammann furnace. The melt was drawn into in a fused silica tube about 3 mm in diameter. The specimen for the general permanent magnet property measurements was about 20 mm long, and for temperature dependence measurement was about 6 mm long. These specimens were vacuum sealed in quartz ampoules, homogenized at high temperatures of 1273–1623 K (disordered γ phase) in the electric furnace, and then quenched in stirred ice-water. These specimens were tempered at temperatures ranging from 723 to 1023 K for 0.3 ks–1.8 Ms (5 min–500 h).

The permanent magnet properties and their temperature dependences were measured using an automatic recording fluxmeter and a vibrating sample magnetometer. The highest measured field was $1600 \text{ kA} \cdot \text{m}^{-1}$ (about 20 kOe).

III. Results and Discussion

1. Permanent magnet properties

Sixty Fe-Pt-Nb alloys in the composition range of 45–

Fig. 2 Effects of tempering at 773–973 K for 54 ks after water-quenching from 1598 K on the magnetic properties of Fe-39Pt, Fe-39Pt-0.5Nb and Fe-39Pt-1Nb alloys.

65 (at%) iron, 35–50 (at%) platinum and 0–10 (at%) niobium were investigated.

Figure 2 shows the relationships between the permanent magnet properties and the heat-treatment for a Fe-39Pt binary alloy, Fe-39Pt-0.5Nb and Fe-39Pt-1Nb ternary alloys. Here, the specimens were tempered for 54 ks (15 h) at temperatures ranging from 773 to 973 K after water-quenching from a high temperature of 1598 K. As seen in the figure, the Fe-39Pt binary alloy shows a high value of coercive force, $H_c = 320 \text{ kA} \cdot \text{m}^{-1}$, in the as water-quenching state, but the H_c value of the Fe-39Pt-0.5Nb alloy is less than one-half that of the binary alloy. From these results it is considered that a stable γ phase is obtained in the ternary alloy with the addition of Nb resulting in a rapid decrease in H_c . Furthermore, with rising tempering temperature, H_c increases gradually, attains a maximum value higher than that of the binary alloy and then decreases rapidly. Such a tendency is more pronounced in the case of the Fe-39Pt-1Nb alloy. The residual flux density, B_r , shows a virtually similar tendency to H_c . Subsequently, the maximum energy product, $(BH)_{\text{max}}$ shows an almost similar tendency to H_c and attains a value higher than that of the Fe-39Pt binary alloy. A considerably high H_c value of the water-quenched binary alloy decreases reversely with a small addition of Nb, and these alloys show improved permanent magnet properties by the tempering treatment that followed. It is suggested that the homogeneity of the alloy promoted by the solution heat-treatment suppresses

Fig. 3 Effects of isothermal tempering at 848–973 K after water-quenching from 1598 K on the magnetic properties of Fe–39.5Pt–0.75Nb alloy.

the ordered phase γ_1 at high temperatures and retains the single disordered phase. By the tempering treatment, the transformation of the homogeneous γ_1 phase progresses and yields an ideal initial ordering state resulting in excellent permanent magnet properties.

Figure 3 shows the permanent magnet properties of a typical Fe–39.5Pt–0.75Nb alloy isothermally heat-treated at various tempering temperatures from 848–973 K after ice-water quenching at 1598 K. As seen in the figure, for each tempering temperature, the permanent magnet properties have maxima. In the case of low temperature tempering, these maxima are obtained with long heating times, while in the case of high temperature tempering, the maxima are obtained in relatively short times, and have high values. When tempered at 873 K, this alloy shows the highest $(BH)_{\max}$ of $167 \text{ kJ} \cdot \text{m}^{-3}$, B_r of 1.05 T and H_c of $398 \text{ kA} \cdot \text{m}^{-1}$. Figures 4–6 show the composition dependences of the permanent magnet properties corresponding to the highest $(BH)_{\max}$ obtained in each of the alloys.

Fig. 4 Maximum energy product in each of the Fe–Pt–Nb alloys tempered at 773–1023 K after water-quenching from 1598 K.

Fig. 5 Residual flux densities corresponding to the highest maximum energy product in each of Fe–Pt–Nb alloys tempered at 773–1023 K after water-quenching from 1598 K.

The $(BH)_{\max}$ of Fe–39Pt based alloy (Fig. 4) increases with a small addition of Nb and attains the highest value of $167 \text{ kJ} \cdot \text{m}^{-3}$. The extremely narrow composition regions of the excellent permanent magnet properties in the binary alloys are spread over wide composition ranges. Furthermore, alloys with 1.5–3%Nb addition extend the composition region having very large $(BH)_{\max}$ values of over $100 \text{ kJ} \cdot \text{m}^{-3}$ and attain compositionally stable properties.

Figure 5 shows the relationship between the B_r and composition corresponding to the above-mentioned $(BH)_{\max}$ in Fig. 4. As shown in the figure, B_r is composed of equivalent curves parallel to the Pt concentration and decreases gradually with increasing Nb, indicating the favorable effect of Nb additions.

Figure 6 shows the relationship between the H_c and composition in the state having the highest $(BH)_{\max}$. As shown in the figure, first, the H_c increases with the addition of Nb and the region of the composition having a very high H_c of $300 \text{ kA} \cdot \text{m}^{-1}$ is extended in the Fe–Pt–Nb alloys. It is shown that the stable permanent magnet properties are obtained in a very wide range. From these

Fig. 6 Coercivity corresponding to the highest maximum energy product in each of the Fe–Pt–Nb alloys tempered at 773–1023 K after water-quenching from 1598 K.

results, the permanent magnet properties of the Fe-Pt-Nb alloys are superior to those of the Fe-Pt binary alloys. Furthermore, excellent magnetic properties appear in a wider compositional region than the previously reported Fe-Pt-Ti alloys. In addition, the heat-treatments of the Fe-Pt-Nb magnet alloys can be controlled more easily in reproducing the excellent permanent magnet properties than the binary alloys.

2. Temperature dependence of permanent magnet properties

Figure 7 shows the magnetic transformation (Curie temperature), T_c of Fe-Pt binary alloys in water-quenched and tempered states. The water-quenched state consists basically γ of phase, and the tempered state having high coercivity has the ordering state transformed from the γ to the γ_1 phase. As seen in the figure, the T_c of the equivalent FePt alloy is 753 K and is independent of heat-treatment. It is considered that the ordering of the γ_1 phase has progressed even in the water quenched state, but in compositions rich in iron a perfect single γ phase can be obtained by increasing iron content. In general, T_c of the ordered γ_1 phase is higher than that of the disordered γ phase.

Figure 8 shows the results of the thermo-magnetic analyses of the Fe-38Pt-1Nb alloy (1) and Nb-rich Fe-42Pt-10Nb alloy (2). Alloy (1) has a comparatively high H_c and B_r , and alloy (2) has an inferior magnetic property. The applied magnetic fields range from 40 to 800 $\text{kA} \cdot \text{m}^{-1}$. The temperatures at which magnetization disappears rise with increasing applied magnetic fields. In the present work, the T_c of these permanent magnet alloys are determined by measuring magnetic fields near the temperatures at which magnetization disappears. From these measurements T'_c is determined as the square of the magnetization crosses the temperature axis. T_c is then determined by extrapolating $T'_c(H)$ to zero field. As seen in the figure, the temperature curve of the magnetization at the low magnetic field is extremely low in the low tem-

Fig. 7 Comparison of Curie temperatures in each of the Fe-Pt alloys, in both tempering and water-quenching states.

Fig. 8 Thermo-magnetic analyses of the tempered Fe-38Pt-1Nb and Fe-42Pt-10Nb alloys.

perature region, and shows a maximum at the high temperature side. It is considered that this magnet alloy has a large crystal magnetic anisotropy of $5 \times 10^6 \text{ J/m}^3$ ⁽¹⁶⁾⁽¹¹⁾ which cannot be magnetized easily with low magnetic fields at low temperatures. This crystal magnetic anisotropy, however, decreases with increased temperature, and maximum magnetization appears when it becomes easily magnetized with the low magnetic fields. At high magnetic fields, the magnetization of the alloy has nearly the value of the saturation magnetization, and therefore, it shows a monotonous curve without the appearance

Fig. 9 Curie temperatures of the tempered Fe-Pt-Nb alloys having the highest coercivity.

Fig. 10 Temperature dependences of coercivity of Fe-Pt and Fe-Pt-Nb alloys.

Fig. 11 Temperature dependences of residual flux densities of Fe-Pt and Fe-Pt-Nb alloys.

of any maximum. Further, alloy (2) has a low crystal magnetic anisotropy, and shows monotonous curves even with a low magnetic field of $160 \text{ kA} \cdot \text{m}^{-1}$.

Figure 9 shows the relationships between the measured T_c and the compositions of the Fe-Pt-Nb alloys in the high coercivity state. As shown in the figure, the T_c decreases gradually with increasing niobium, and has the good property as hard magnetic material.

Figures 10 and 11 show the temperature dependences of the permanent magnet properties in Fe-40Pt, Fe-38Pt-1Nb, Fe-39Pt-3Nb and Fe-42Pt-3Nb alloys. Figure 10 shows the measured values of H_c at each temperature. H_c decreases linearly with increasing temperature, but the ternary Fe-Pt-Nb alloys show lower rates of decrease than the binary alloys, and thus, higher values are obtained on the high temperature side. Figure 11 shows the temperature dependence of B_r corresponding to H_c in Fig. 10. As seen in the figure, the Fe-Pt-Nb alloys show large B_r values up to the high temperature side with increasing Pt. This tendency is similar to the results of the thermo-magnetic analyses with high magnetic fields shown in Fig. 8.

For reference, Fig. 12 shows the measured hysteresis

Fig. 12 Hysteresis loops of Fe-38Pt-1Nb magnet alloy at 290 and 400 K.

loops of the Fe-38Pt-1Nb alloy at room temperature (290 K) and 400 K the practical upper-limit operating temperature. This alloy shows excellent magnetic properties of rectangularity at room temperature and these remain at 400 K, indicating good thermal stability.

3. X-ray diffraction

The basic crystal structure⁽¹³⁾ of this permanent magnet alloy is the f.c.t. ($L1_0$ -type) of the equivalent FePt alloy, but almost no detailed X-ray diffraction studies available in the literature except for the work of Cabri *et al.*⁽¹⁷⁾ Accordingly, Fig. 13 shows the X-ray powder diffraction pattern and the values of the integral intensity I/I_0 of the ordered FePt alloy annealed at 1023 K for 200 ks, then slowly cooled with $4.2 \times 10^{-3} \text{ K/s}$ (15 K/3.6 ks). Our results agree with previous data regarding the interplanar spacing and integral intensities of the low angle side in the diffraction lines, but differ greatly in intensity at the high angle side; specifically, much higher intensities were reported by Cabri *et al.*

The γ_1 Fe-Pt alloy powders begin sintering by heating at about 1273 K. When the sintered alloys are powdered mechanically, the crystal structures change to the γ

Fig. 13 X-ray diffraction pattern obtained with Co-K α radiation of the ordered γ_1 single phase of Fe-50Pt alloy.

Fig. 14 Permanent magnet properties and X-ray diffraction patterns obtained with Co-K α radiation of the Fe-38Pt-1Nb alloy tempered for 90 ks after water-quenching from 1598 K.

phase. For this reason, plate-specimens of the Fe-Pt-Nb alloy with little preferred orientation can be made for the X-ray diffraction measurement.

Figure 14 shows the X-ray diffraction patterns and coercivity in the plate-specimens of Fe-38Pt-1Nb alloy having comparatively excellent properties and remarkable effects by the heat-treatment. Bragg angle centering indices of (200) and (002) are shown where the γ is replaced by the γ_1 phase. In the figure, (1) shows the case of iced water-quenching after homogenizing at 1598 K. The pattern exhibits the diffraction lines of the disordered γ single phase. The coercivity of the γ phase is less than $2 \text{ kA} \cdot \text{m}^{-1}$, showing soft-magnetic material properties. In the figure, (2) shows the coexistent state of the ordered γ_1 and γ phases when the alloy is tempered at 848 K for 90 ks. The coercivity is $35 \text{ kA} \cdot \text{m}^{-1}$. In the figure, (3) shows the diffraction pattern of a specimen heat-treated at 923 K with the coercivity of $280 \text{ kA} \cdot \text{m}^{-1}$. The (200) γ phase now disappears, and is replaced by the diffraction lines of the γ_1 phase. Furthermore, the diffraction lines become sharper when tempered at temperatures higher than 923 K, and H_c decreases with the progressive order-

ing. From these results, the excellent permanent magnet properties of Fe-Pt-Nb alloys occur directly after transformation to the γ_1 phase. It is considered that the pinning structure of the magnetic domain wall interacting with the microstructure⁽¹⁸⁾⁽¹⁹⁾ of the imperfect γ_1 phase in the initial ordering state results in the high coercivity.

IV. Conclusion

60 kinds of Fe-Pt-Nb alloys were homogenized by heating at high temperatures, quenching in ice-water and then tempering at 723–1023 K. The relationship between the permanent magnet properties and the compositions, the temperature dependences and X-ray diffractions were measured. The results are summarized as follows.

(1) A comparatively stable γ phase was obtained with small niobium additions to Fe-Pt alloys, and then excellent properties were obtained by the tempering. These properties were superior to the values of binary Fe-Pt permanent magnet alloys. The typical Fe-39.5Pt-0.75Nb alloy tempered at 873 K after ice-water quenching exhibits $(BH)_{\text{max}}$ of $167 \text{ kJ} \cdot \text{m}^{-3}$, B_r of 1.05 T and H_c of $398 \text{ kA} \cdot \text{m}^{-1}$.

(2) The compositional regions of the maxima in the Fe-Pt binary alloys were extremely narrow, but the compositional region of the excellent properties in the Fe-Pt-Nb alloy is extended to a wider range. Control of the heat treatment became easy and has used to obtain the stable permanent magnet properties.

(3) The T_c of the ordered γ_1 phases in Fe-Pt alloys were higher than in the disordered γ phase. In the Fe-Pt-Nb alloys of the high coercivity state, T_c decreased gradually with increasing Nb content. Consequently, the permanent magnet alloys exhibited desirable properties. Furthermore, the hysteresis curve of Fe-38Pt-1Nb alloy has excellent rectangularity and stable properties at 400 K as observed at 290 K.

(4) The basic crystal structure of the Fe-Pt permanent magnet alloys is the f.c.t. ($L1_0$ -type) of the ordered FePt. The integral intensities of X-ray diffraction lines of the powder alloy differ remarkably from the known intensities at the high angle side. From the results of X-ray diffraction of the Fe-38Pt-1Nb alloy, the disordered γ phase exhibits soft magnetic properties, but the initial ordered γ_1 state by the tempering shows high coercivity. The coercivity decreases markedly with the advance in ordering of the γ_1 states.

REFERENCES

- (1) L. Graf and A. Kussmann: Phys. Z., **36** (1935), 544.
- (2) M. Fallot: Ann. Physik, **10** (1938), 291.
- (3) H. Lipson, D. Shoenberg and G. V. Stupart: J. Inst. Metals, **67** (1941), 333.
- (4) A. Kussmann and G. Rittberg: Ann. Physik, **7** (1950), 173.
- (5) H. Kaneko, M. Homma and K. Suzuki: Trans. JIM, **9** (1968), 124.
- (6) M. Hansen: *Constitution of Binary Alloys*, McGraw Hill, N.Y., (1958), 698.
- (7) S. Shimizu and K. Watai: J. Japan Inst. Metals, **29** (1965), 822.
- (8) T. Yamamoto and K. Kawamura: Bulletin Japan Inst. Metals, **8** (1969), 412.

- (9) L. M. Magat, G. V. Ivanova, L. V. Solina, N. N. Shchegoleva and Ya. S. Shur: *Phys. Metals Metallog.*, **29** (1970), 175.
- (10) A. Ye. Yermakov and V. V. Maykov: *Phys. Met. Metall.*, **60** (1985), 113.
- (11) O. A. Ivanov, L. V. Solina, V. A. Demshina and L. M. Magat: *Phys. Met. Metall.*, **35** (1973), 81.
- (12) K. Watanabe and H. Masumoto: *J. Japan Inst. Metals*, **47** (1983), 699; *Trans. JIM*, **24** (1983), 627.
- (13) K. Watanabe: *J. Japan Inst. Metals*, **51** (1987), 91; *Trans. JIM*, **29** (1988), 80.
- (14) K. Watanabe and H. Masumoto: *J. Japan Inst. Metals*, **48** (1984), 930; *Trans. JIM*, **26** (1985), 362.
- (15) K. Watanabe: *IEEE Trans. Magnetics*, **MAG-23** (1987), 3196.
- (16) T. Nakamichi, K. Watanabe and H. Masumoto: *Collected Abstracts of the Spring Meeting of Japan Inst. Metals* (Apr. 1985), 348; T. Endo: *Treatise of Master in Tohoku Univ.* (1987).
- (17) L. J. Cabri, D. R. Owens and J. H. G. Laflamme: *Can. Mineral.*, **12** (1973), 21.
- (18) K. Watanabe and K. Hiraga: *MRS Intern. Meet. Adv. Mater.*, **11** (1989), 161.
- (19) K. Watanabe, K. Hiraga and M. Hirabayashi: *Collected Abstracts of the Autumn Meeting of Japan Inst. Metals*, (Oct. 1983), 549.