

Effect of Magnetic Field on Ordering of FePd

Katsushi Tanaka, Tetsu Ichitsubo, Masahiro Koiwa and Kazuo Watanabe*

Department of Materials Science and Engineering, Kyoto University, Kyoto 606-8501, Japan.

Fax: +81-75-753-4861, e-mail: katsu@mtl.kyoto-u.ac.jp

*Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan.

Effect of magnetic field on ordering of FePd was examined. The following two types of ordering treatments were adopted under the magnetic fields up to 10 T; (i) isothermal annealing at 673 K, and (ii) annealing near the magnetic transition temperature of 763 K. In the specimen subjected to treatment (i), the energetically favorable variant has been formed predominantly but with a substantial amount of the other two variants; the volume fraction of the favored one is about 50 %. The rate of ordering increases with increasing the strength of the applied magnetic field. In contrast, treatment (ii) with the magnetic field of 10 T has yielded a fully ordered structure with only one type of variant of the favored orientation. The results can be well explained by the change in nucleation probability of each variant caused by the magnetic and the elastic strain energies.

Key words: Order-disorder, Magnetic field, Magnetocrystalline anisotropy, $L1_0$ mono variant, nucleation rate

1. INTRODUCTION

Phase transformations in solids are affected by the application of external magnetic fields. Since the magnetic interaction energies are generally small in comparison with the chemical energies, very strong magnetic fields are required to affect the phase stability significantly. In the case of martensitic transformations, the process proceeds very fast so that a short duration of the magnetic field is sufficient to examine the effect, if any, of the field. In fact, Kakeshita *et al.* have observed the effect by using a pulse magnetic fields up to 40 T [1]. For most of the other phase transformations, the time required to complete the process is usually very much longer. Recent developments of superconducting magnets have made it possible to provide a stationary magnetic field of considerable strength. Watanabe *et al.* have constructed a furnace which can be operated under a magnetic field up to 11 T [2] or 15 T [3], using a liquid helium-free superconducting magnet. The effects of the magnetic field on the formation of the microstructures have been investigated for spinodal decomposition [4-6], recrystallization [7, 8] and ordering process [9].

The ferromagnetic $L1_0$ ordered alloys, FePd, FePt and CoPt exhibit high uniaxial magnetocrystalline anisotropy [10]. In these alloys, three kinds of $L1_0$ variants are formed in the ordering process, and each variant possesses the c-axis along either of $\langle 100 \rangle$ directions of the fcc disordered matrix. In the absence of any external fields, these variants are formed with an equal probability and hence the ordered bulk material as a whole would lose a uniaxial magnetocrystalline anisotropy.

Ichitsubo *et al.* have reported that the relative population of variant is significantly modified when compressive stresses are applied along the $\langle 100 \rangle$ direction of the single crystal of FePd [11, 12]. This stress effect can be explained as the change in the nucleation rates of different variants caused by the stress.

Since the $L1_0$ ordered phase has a magnetocrystalline anisotropy with the easy axis parallel to the c-axis, the magnetic field is expected to have an effect similar to the compressive stress. Such an

observation has been reported by Oshima *et al.* on an Fe-55at%Pd alloy [13].

This paper reports a quantitative investigation of the effect of the magnetic field on the ordering of the equiatomic FePd alloy, by measuring the volume fraction of the three variants after various treatments.

2. EXPERIMENTAL PROCEDURES

2.1 Sample preparation

Alloy ingot of the equiatomic FePd was prepared by arc-melting of an appropriate mixture of 99.9% Fe and 99.95% Pd in an argon atmosphere. Single crystals were grown from the melt by the Bridgman method. The composition of grown single crystal was determined to be Fe-49.8at%Pd by chemical analysis. After determination of crystallographic orientation of the single crystals by the back Laue method, specimens of near cube shape were cut from the single crystal rods. The dimension is about 2-4 mm in each edge length, and all the surfaces are parallel to the $\{100\}$ crystallographic planes within the accuracy of 0.5° .

2.2 Heat treatments

All the specimens were annealed at 1073 K (the order-disorder transition temperature T_t is about 923 K) for 18 ks in an evacuated quartz tube, and quenched into iced brine so as to attain the disordered state. In reference to the result of the stress effect experiment, we adopted the following two types of ordering treatments as shown in Fig. 1. The magnetic fields up to 10 T were applied along the $[001]$ direction throughout the ordering process. This direction is denoted as the z-direction in the following sections.

(i) The specimen was heated up to 673 K, held there for 3.6 ks or 7.2 ks and furnace-cooled.

(ii) The specimen was heated up to 793 K (the magnetic transition temperature of the ordered phase is 763 K) and cooled down at a rate of $1/60 \text{ Ks}^{-1}$ to 673 K and then furnace-cooled to room temperature.

In treatment (i), the ordering is considered to proceed by a spinodal ordering; ordering proceeds spatially

homogeneously. In contrast, the ordering proceeds through nucleation and growth in treatment (ii).

2.3 Determination of volume fractions of three variants

After the heat treatments, specimens were sliced into thin foils with the thickness of about 50 μm. The volume fraction of the ordered phase can be determined from the intensities of the superlattice reflections of the X-ray diffraction. Furthermore, by noting the fact that the superlattice reflections, 100, 101 and 001, for example, come from the three variants with the c-axis parallel to the x, y and z directions, respectively, the volume fractions of the three variants are determined from the following equation:

$$V = k \frac{1}{\eta^2} \frac{I_s}{I_f} \tag{1}$$

where I_s and I_f are observed intensities of the super and fundamental reflections, k is a constant consisting of the atomic scattering, absorption and temperature factors and η is the long range order parameter of the ordered phase which is assumed to be unity in this analysis. Strictly speaking, this assumption is not valid for the specimen subjected to treatment (i), because the spinodal ordering occurs in the treatment.

3. EXPERIMENTAL RESULTS

Figure 2 shows the volume fractions of the three variants after treatment (i). The height of columns in this figure represents the total amount of the ordered phase, and differently hatched regions correspond to the three types of variants. Note that the variant with the c-axis parallel to the z-direction is energetically more stable under the external magnetic field.

In the absence of the magnetic field (0 T), three types of variants were formed almost in equal proportions, as naturally expected. Total amount of the ordered phase increases with increase in the strength of the magnetic field. This means that the ordering is enhanced by the application of magnetic field. In the specimen ordered under external magnetic field, the volume fraction of the favorable variant is

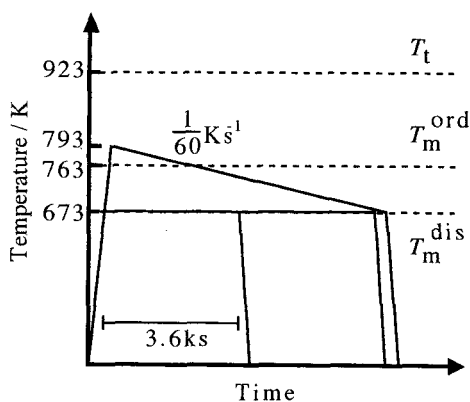


Fig. 1. Heat treatment diagram. The magnetic field was applied throughout the process. The temperatures indicated as T_t , T_m^{ord} and T_m^{dis} are the order-disorder transition temperature, and the magnetic transition temperatures of ordered and disordered phases, respectively.

larger than the other two; it increases from about 33 % for 0 T to about 50 % under the fields. The duration of aging time, 3.6 ks or 7.2 ks, does not lead to any significant change.

Figure 3 shows the volume fractions of the three variants after treatment (ii). When the specimen is ordered under the magnetic field of 4 T, the relative population of the favored variant is about 50 %. A very significant magnetic field effect was observed for the specimen ordered under the magnetic field of 10 T. The ordering is fully completed, with the formation of only one type of variant.

4. DISCUSSION

4.1 Estimation of free energies under magnetic field

The free energy of ferromagnetic substance depends on the strength and the direction of the external magnetic field. The field dependent terms of

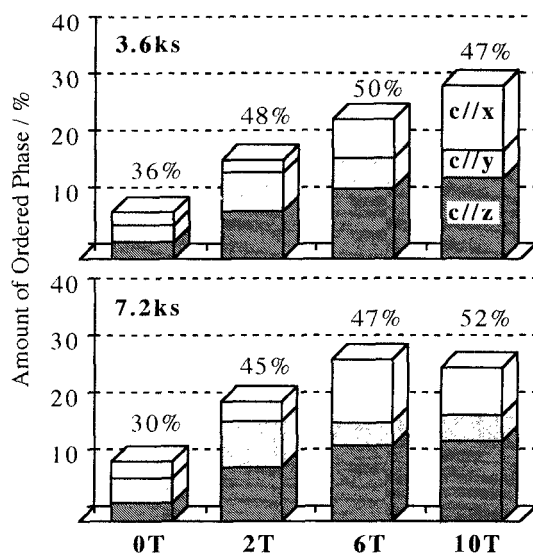


Fig. 2. Volume fractions of the three variants after isothermal annealing at 673K for 3.6ks and 7.2ks under the magnetic fields along the z-direction.

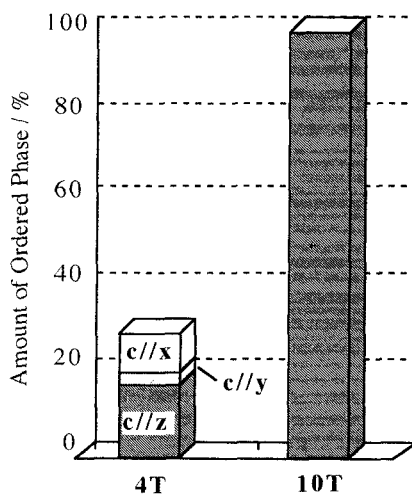


Fig. 3. Volume fractions of the three variants after isothermal annealing near the magnetic transition temperature under the magnetic fields along the z-direction.

the free energy may be written as

$$G_{\text{magnetic}} = -HM \cos\theta + \int_{M(0)}^{M(H)} H dM + K_1 \sin^2\phi \quad (2),$$

where H and M are the strength of the magnetic field and magnetization. θ and ϕ are the angles between the direction of the magnetization and the directions of the external field and the easy-axis of magnetization. The magnetocrystalline anisotropy coefficient is denoted as K_1 .

The magnetization, M , of FePd has been measured as a function of temperature by Yermakov and Maykov [14]; it follows the Curie-Weiss law. Thus, we use the law for calculating the magnetization under the magnetic field. The followings are the values adopted in the numerical calculation:

Atomic magnetic moment: $1.6\mu_B$ [15]

Magnetic transition temperature: [16]

673 K for disordered phase

763 K for ordered phase

Magnetization at room temperature: [14,16]

1.32 T for disordered phase

1.38 T for ordered phase

Figure 4 shows the calculated magnetizations for different magnetic fields as a function of temperature.

The magnetocrystalline anisotropy coefficient, K_1 , can be calculated as a function of the magnitude of magnetization. Since the ordered FePd has a uniaxial anisotropy, the value of magnetocrystalline anisotropy coefficient, K_1 , is expressed as,

$$\frac{K_1}{K_1^0} = \left(\frac{M}{M^0}\right)^3, \quad (3)$$

where the superscript 0 means the value at 0 K. The value of K_1^0 has been reported as 2.2 MJ/m^3 [14]. In this calculation, the magnetocrystalline anisotropy coefficient of disordered FePd was set to be zero, because the value is considered to be small.

Figure 5 shows the field dependence of the free energy, G_{magnetic} (eq. 2). Owing to the Zeeman effect, the free energy difference between ordered and disordered phases becomes large with increasing the field; the magnetization of disordered phase is small in comparison with the ordered one (see Fig. 4). Thus, the $L1_0$ ordered phase is stabilized under the magnetic field, and as a result, the ordering is enhanced.

4.2 Change in relative population of three kinds of

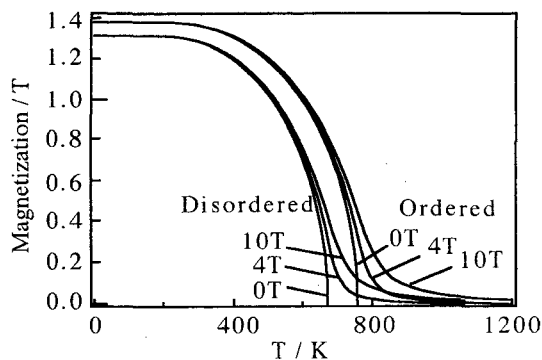


Fig. 4. Temperature dependence of magnetization of ordered and disordered FePd under magnetic fields.

variants.

The effect of the magnetic field on the formation of microstructure is very similar to that of the stress reported in a previous paper [11]. The effect of the stress can be understood in terms of the nucleation rates of different variants, as discussed in Ref. [12]. Here we will discuss the effect of the magnetic field in a similar way to the case of the external stress. From the classical nucleation theory, the nucleation rate, P , is expressed as,

$$P \propto \exp\left(-\frac{W^*}{kT}\right) \quad (4)$$

where W^* is the critical energy for nucleation. If we assume that the shape of ordered phase particle is ellipsoidal with the aspect ratio of 0.3, the critical energy W^* is expressed as

$$W^* \approx 40.2 \frac{\gamma^3}{\Delta G^2} \quad (5)$$

where γ and ΔG are the surface energy and the free energy change, respectively. The free energy change, ΔG , is expressed as,

$$\Delta G = \Delta G_{\text{chemical}} + \Delta G_{\text{elastic}} + \Delta G_{\text{magnetic}} + \Delta G_{\text{demagnetization}} \quad (6)$$

The magnetic term is given in eq. 2. In order to evaluate the effect of the magnetic field on the microstructure, the absolute values of the nucleation rate are not required; the ratio of nucleation rates for favorable (the c -axis parallel to the external magnetic field, H), $P_{//}$, and unfavorable (the c -axis perpendicular to the external magnetic field, H), P_{\perp} , variants is the quantity of interest. Since the magnitude of the surface energy, γ , is not known definitely, the ratio is calculated for various values of γ , as an example the result for $T = 793 \text{ K}$ is shown in Fig. 6; details of the calculation will be reported elsewhere [17].

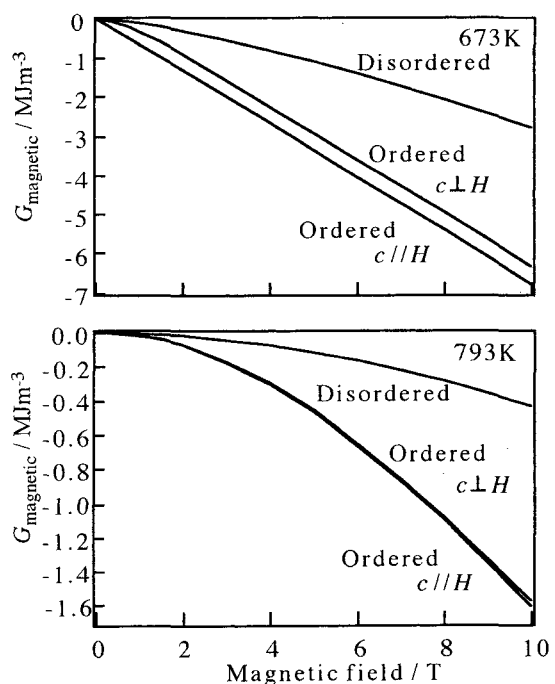


Fig. 5. Free energy changes of ordered and disordered FePd under magnetic fields parallel and perpendicular to the easy axis.

When the surface energy is larger than 50 mJm^{-2} , the ratio calculated for 10 T becomes significantly large. When the preferential nucleation of one type of variant occurs at an early stage of ordering, the same type of variants form cooperatively [18], and as a result, the specimen becomes mono-variant $L1_0$ ordered phase.

5. CONCLUSION

The effect of magnetic field on ordering of FePd is examined with various annealing temperatures and strength of the magnetic fields. The energetically favorable variant is formed preferentially for all the cases of ordering treatments with the application of magnetic fields. The effect is significant when specimens are ordered near the magnetic transition temperature where the ordering proceeds by nucleation-growth process. The specimen becomes mono-variant $L1_0$ ordered phase, which has never been achieved without the application of the external fields. The results are well explained by considering free energy changes under the magnetic field.

ACKNOWLEDGMENT

This work is partly supported by Grant-in-aid for Scientific Research on Priority Area on "Phase Transformation" from Ministry of Education, Science, Sports and Culture of Japan. The heat treatments were performed at High Field Laboratory for Superconducting Materials, Institute for Materials Research, Tohoku University.

REFERENCES

1. T. Kakeshita, T. Saburi, K. Kindo and S. Endo, *Jpn. J. Appl. Phys.* **36**, 7083 (1997).
2. K. Watanabe, S. Awaji, J. Sakuraba, K. Watazawa, T. Hasebe, K. Jikihara, Y. Yamada and M. Ishihara, *Cryogenics*, **36**, 1019 (1996).
3. K. Watanabe and M. Homma, *Jpn. J. Appl. Phys.*, **37**, L1148 (1998).
4. Y. Iwama and M. Takeuchi, *Trans. JIM*, **15**, 371 (1974).
5. Y. Belli and R. K. Mishra, *Mater. Sci. Eng.*, **47**, 69 (1981).
6. J. W. Cahn, *J. Appl. Phys.*, **34**, 3591 (1963).
7. T. Watanabe, Y. Suzuki, S. Tani and H. Oikawa, *Phil. Mag. Lett.*, **62**, 9 (1990).
8. N. Masahashi, M. Matsuo and K. Watanabe, *J. Mater. Res.*, **13**, 457 (1998).
9. T. Ichitsubo, M. Nakamoto, K. Tanaka and M. Koiwa, *Proceeding of The Third Pacific Rim International Conference on Advanced Materials and Processing*, The Minerals, Metals & Materials Society (1998), p. 1369.
10. B. Zhang and W. A. Soffa, *Scr. Met. Mater.*, **30**, 683 (1994).
11. T. Ichitsubo, K. Tanaka, M. Nakamoto, T. Miyoshi and M. Koiwa, *Proceedings of the International Conference on Solid-Solid Phase Transformations '99*, Japan Institute of Metals (1999), p.385.
12. T. Ichitsubo, K. Tanaka, M. Nakamoto and M. Koiwa, *Proceedings of the International Conference on Solid-Solid Phase Transformations '99*, Japan Institute of Metals (1999), p.389.
13. R. Ohsima and H. Tokoro, *J. Jpn. Inst. Metals*, **62**, 317 (1998).
14. A.Ye.Yermakov and V.V.Maykov, *Phys. Met. Metall.*, **69**, 198 (1990).
15. M. Matsui and K. Adachi, *Physica B*, **161**, 53 (1989).
16. S. Shimizu and E. Hashimoto, *J. Jpn. Inst. Metals* **35**, 902 (1971).
17. K. Tanaka, T. Ichitsubo, M. Amano, M. Koiwa and K. Watanabe, in preparation.
18. T. Ichitsubo, K. Tanaka, M. Koiwa and Y. Yamazaki, in preparation.

(Received January 17, 1999; accepted January 24, 2000)

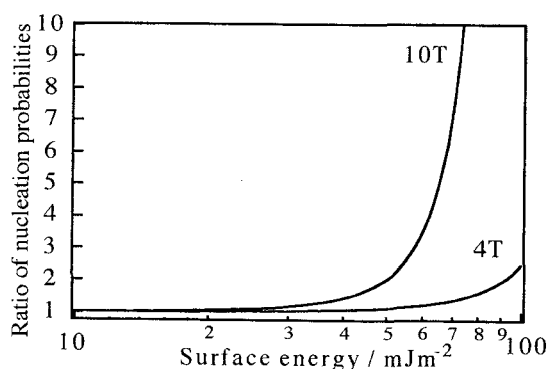


Fig. 6. Ratio of nucleation rate of ordered variants with the easy-axis parallel and perpendicular to the external magnetic field at 793 K as a function of surface energy. The shape of ordered phase particle is assumed as ellipsoidal with the axial ratio to be 0.3.