Ordering Process and Variant Selection under Magnetic Field in L1₀-type Co–50Pt and Fe–55Pd Alloys

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Selected formation of variants under magnetic field in a diffusional process has been investigated by using Co–50Pt (at%) and Fe–55Pd (at%) alloys exhibiting A1 (disorder)–L1₀ (order) transformations. A single variant of the ordered phase is obtained in these alloys by applying a magnetic field during the early stage of ordering. The lowest magnetic field required for obtaining the single variant is about 0.5 T for the Co–50Pt alloy, and 4 T for the Fe–55Pd alloy in the present heat-treatment conditions. Such a difference could be due to the relation between nucleation barrier for the formation of the ordered phase and magnetocrystalline anisotropy at the nucleation stage.

KEY WORDS: cobalt–platinum alloy; iron–palladium alloy; Curie temperature; single variant; magnetocrystalline anisotropy.

1. Introduction

Recently, structural and functional control of materials under magnetic field has attracted much attention partly because magnetic field is found to be effective for controlling the microstructure formed by solid–solid phase transformations and partly because of progress in superconducting magnet technology. An alloy exhibiting a solid–solid phase transformation usually forms several crystallographic domains (variants) in its low temperature phase. All the variants have the same free energy with one another unless external fields, such as stress and magnetic field, are applied. Under a magnetic field, however, there arises some difference in magnetic energy among different variants. If the magnetic anisotropy is high, we can expect selected formation of the specific variant with the lowest magnetic energy. In fact such a selection of variants was reported in some ferromagnetic shape memory alloys. In these alloys, the rearrangement of martensite variants occurs under a magnetic field, resulting in a large magnetic field induced-strain of several percent. It is now well understood that magnetocrystalline anisotropy is high, we can expect selected formation of the specific variant with the lowest magnetic energy.

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In the present paper, we will describe in detail such experimental results as well as the ordering process at each step and the relation between magnetic properties and variant selection.

2. Experimental Procedure

Ingots of Co–50Pt (at%) and Fe–55Pd (at%) were prepared by arc melting using high purity degassed electrolytic cobalt, iron, platinum and palladium plates as starting materials. These alloys are abbreviated as Co–50Pt and Fe–55Pd alloys here. The ingots were grown into a single crystal by a floating zone method. The single crystalline rods were homogenized at 1 273 K for 168 h followed by ice-water quenching. After determining their orientation by a Laue camera, they were heat-treated at 1 273 K (Co–50Pt) and 1 173 K (Fe–55Pd) for 1 h and then quenched in ice-water to obtain the disordered (A1-type) phase. Two types of specimens were prepared.

One is a rectangular parallelepiped which is used to examine the ordering process under zero magnetic field and Curie temperature by electrical resistivity measurement. Electrical resistivity was measured by a direct current four-probe method with a current density of 100 mA.

The other is a cubic specimen (1.6×1.6×1.6 mm³), which is used to examine selected formation of a variant during the ordering process under a magnetic field. Every edge of the cubic specimen is parallel to one of {100}ₐ₁ planes (the suffix A₁ stands for the A1-type structure). In the ordering process, a magnetic field was applied along one of the three equivalent {100}ₐ₁ directions. We call this direction as Z-direction and remaining two {100}ₐ₁ directions as X- and Y-directions. We term the variant whose easy axis (c-axis) lies in the X-, Y-, and Z-directions as X-, Y- and Z-variance, respectively.
Y-, Z-variants, respectively, and these fractions as \( f_x, f_y, \) and \( f_z \). The fraction of each variant was determined by magnetization measurements using a SQUID magnetometer. When the specimen is highly ordered, the fraction will be obtained by using the relation \( f_x = M^0_x / M_s, \ f_y = M^0_y / M_s, \ f_z = M^0_z / M_s; \) where \( M_s \) is the spontaneous magnetization; \( M^0_x, M^0_y, M^0_z \) are the magnetization at zero field extrapolated from the high field region measured along the \( X-, Y-, Z \)-directions, respectively.

3. Results
3.1. Disorder–Order Transformation under Zero Magnetic Field and Magnetic Properties

In this section, we will show the ordering process in Co–50Pt and Fe–55Pd alloys in the absence of magnetic field and determine the Curie temperatures of their disorder and order phases.

First, time evolution of disorder–order transformation has been examined by measuring electrical resistivity at 273 K after performing an isothermal heat-treatment at different ordering temperatures followed by quenching into ice-water. The result is shown in Fig. 1, where the resistivity is normalized by the value of the as-quenched specimen, \( \rho_{\text{A.Q.}} \) at 273 K. In the case of the Co–50Pt alloy, the resistivity saturates within 3 h by the heat-treatment at 1 023 K, while not within 200 h by the heat-treatment at 973 K, 873 K, and 773 K. These results imply that the ordering process is the fastest at 1 023 K and slowest at 773 K in the examined temperature range. Similar results were reported by Newkirk et al.\(^{10}\) in a Co–48Pt (at\%) alloy. In the case of Fe–55Pd alloy, the resistivity saturates within 3 h by the heat-treatment at 873 K, within 21 h at 773 K, while not within 163 h by heat-treatment at 673 K.

Second, we examined the Curie temperature of the disordered phase by electrical resistivity measurement. The measurements were made by heating the disordered specimen from room temperature with a heating rate of 100 K/min, and the result is shown in Fig. 2 by solid curves. In the case of the Co–50Pt alloy (a), the resistivity heating curve exhibits a bending as indicated by an arrow at about 850 K. We can interpret this temperature as the Curie temperature of the disordered phase, \( T_c^{(d)} \), considering the same bending appears at Curie temperature of iron and nickel alloys.\(^{11,12}\) The heating curve of the Fe–55Pd alloy also shows the bending at 740 K, corresponding to \( T_c^{(d)} \).

Third, we determined the Curie temperature of the ordered phase by resistivity measurement. Before the measurements, the Co–50Pt alloy was heat-treated at 1 023 K for 3 h, and the Fe–55Pd alloy at 773 K for 24 h to obtain a highly ordered state (see Fig. 1). Then, the resistivity was measured with a heating rate of 1 K/min, and the result is shown by open marks in Fig. 2. In the case of the Co–50Pt alloy, the slope changes at 730 K, and in the case of the Fe–55Pd alloy, the slope changes at 670 K. These temperatures should be the Curie temperature of the ordered phase, \( T_c^{(o)} \). The same Curie temperature was obtained in the cooling process (solid marks in Fig. 2) after heating up to 1 200 K. By comparing \( T_c^{(o)} \) with \( T_c^{(d)} \), we notice that \( T_c^{(o)} \) is lower than \( T_c^{(d)} \) for both the Co–50Pt and Fe–55Pd alloys, and the difference is larger in the Co–50Pt alloy.

The resistivity curves shown in Fig. 2 also include the information of the order–disorder transformation temperature, \( T_{(o-d)} \), and the disorder–order transformation temperature, \( T_{(d-o)} \). In the case of the Co–50Pt alloy, \( T_{(o-d)} \) is

![Fig. 1. Ordering time dependence of the electrical resistivity of (a) Co–50Pt and (b) Fe–55Pd through isothermal annealing. The value of resistivity is normalized by resistivity of the as-quenched specimen (\( \rho_{\text{A.Q.}} \)) at 273 K.](image)

![Fig. 2. Temperature dependence of the electrical resistivity of (a) Co–50Pt and (b) Fe–55Pd.](image)
1 095 K, being consistent with 1 100 K reported by Leroux et al.,\textsuperscript{13} and \( T^{(d-o)} \) is 1 045 K. In the case of the Fe–55Pd alloy, \( T^{(o-d)} \) is 1 025 K and \( T^{(d-o)} \) is 955 K. The difference between \( T^{(o-d)} \) and \( T^{(d-o)} \) for the Fe–55Pd alloy (70 K) is larger than that for the Co–50Pt alloy (50 K), meaning that nucleation of the ordered \( L1_0 \)-phase requires larger supercooling in the Fe–55Pd alloy compared with the Co–50Pt alloy.

Incidentally, we notice in Fig. 2(a) that the resistivity of the disordered phase (solid curve) coincides with the resistivity of the ordered phase (open marks) at about 1 000 K and higher. This means that ordering of the Co–50Pt alloy cannot be avoided in the heating process of 100 K/min. On the other hand, in the case of the Fe–55Pd alloy (Fig. 2(b)), the solid curve keeps the value of the disordered phase, meaning that ordering of the Fe–55Pd alloy is suppressed in the heating process of 100 K/min.

3.2. Ordering under a Magnetic Field

Considering the results of Fig. 1 and the Curie temperatures, we determined the ordering temperature under magnetic field for the selected formation of variants. Expecting that the magnetic field is especially effective at the nucleation stage of ordering, we employed a two-step ordering heat-treatment. The first step is made below \( T_c(d) \), where the progress of ordering is slow, under a magnetic field, \( H_1 \). The second step is made near \( T^{(d-o)} \), where the progress of ordering is fast, to complete ordering.

The two-step heat-treatment is schematically shown in Fig. 3. In the first step, the specimen of the Co–50Pt (Fe–55Pd) alloy was heated up to 773 K (673 K) under \( H_1 \) applied in the Z-direction with a heating rate of 5 K/min, which is the fastest rate of the furnace used in the present study. Then the specimen of the Co–50Pt (Fe–55Pd) alloy was kept at 773 K for 0.5 h (673 K for 1 h) followed by cooling down to room temperature with a cooling rate of 5 K/min under \( H_1 \). In the second step, the specimen of the Co–50Pt (Fe–55Pd) alloy was heated up to 1 023 K (773 K) with a heating rate of about 100 K/min and kept at 1 023 K for 3 h (773 K for 24 h) under no magnetic field.

The magnetization curves of the Co–50Pt alloy measured at 300 K in the \( X \), \( Y \), and \( Z \)-directions after the first step of ordering are shown in Figs. 4(a)–4(d) and those after the second step of ordering are shown in Figs. 4(a′)–4(d′). It should be noted in Figs. 4(a), 4(b) that when \( H_1 \) is 10 T and 0.5 T, the magnetization curve of the \( Z \)-direction is obviously easy to magnetize compared to the \( X \) and \( Y \)-directions after the first step. Once such a difference is achieved, the magnetization curve measured in the \( Z \)-direction after the second step shows that of the easy axis, and the magnetization curve measured in the \( X \) and \( Y \)-directions shows that of the hard axis as seen in Figs. 4(a′), 4(b′). This means that a single variant state is realized when \( H_1 \) is 10 T and 0.5 T. On the other hand, when \( H_1 \) is 0.1 T and 0 T, no significant difference is observed in the magnetization curve after the first step as seen in Figs. 4(c), 4(d). In this case, the magnetization curves after the second step of ordering shows that of the mixture of easy and hard axes for all the \( X \), \( Y \), and \( Z \)-directions as seen in Figs. 4(c′), 4(d′).

Similar results were obtained in the Fe–55Pd alloy. That
is, the magnetization curves of the Fe–55Pd alloy measured in the \( X \), \( Y \), and \( Z \)-directions after the first step are shown in Figs. 5(a)–5(d), and those after the second step are shown in Figs. 5(a’)/H_{11032} –5(d’)/H_{11032}. As in the Co–50Pt alloy, the \( Z \)-direction after the first step is slightly easy to magnetize compared to the \( X \)- and \( Y \)-directions when \( H_1 \) is 10 T and 4 T. In addition, single variant is obtained after the second step when \( H_1 \) is 10 T and 4 T. On the other hand, when \( H_1 \) is 2.5 T and 0 T, the difference in magnetization curves becomes less significant after the first step as seen in Figs. 5(c), 5(d), and single variant state is not obtained after the second step as seen in Figs. 5(c’)/H_{11032}, 5(d’)/H_{11032}.

Considering the results described in Figs. 4 and 5, we calculated the fraction of the \( Z \)-variant \( f_z \) (the preferable variant under magnetic field) after the second step of ordering heat-treatment, and the result for Co–50Pt and Fe–55Pd alloys is summarized in Fig. 6. For both the Co–50Pt and Fe–55Pd alloys, the value of \( f_z \) is about one-third when \( H_1 \) is 0 T, and it increases with increasing \( H_1 \). We notice that there is a jump in \( f_z \) near \( H_1=0.3 \) T in the case of the Co–50Pt alloy, and near \( H_1=3 \) T in the case of the Fe–55Pd alloy. This result suggests that there is a critical condition for the selected formation of variants although the detail is not known yet.

Furthermore we notice in Fig. 6 that the lowest value of \( H_1 \) for obtaining the single variant state of Fe–55Pd is higher than that of Co–50Pt alloy. In the following we will discuss the reason for such difference.

4. Discussion

First, we discuss the reason why the preferential formation of the \( Z \)-variant occurs under a magnetic field. Since the disorder–order transformation of the present alloys are first order, occurring by the nucleation and growth of the ordered L1\(_0\) domains in the A1 matrix,\(^{4,15}\) there should be a nucleation barrier, \( \Delta \), for the formation of the ordered phase. As described above, the \( Z \)-direction is slightly easy to magnetize compared with the \( X \)- and \( Y \)-directions after the first step. This means that the fraction of the \( Z \)-variant is higher than that of the \( X \)- and \( Y \)-variants after the first step. Thus, it is most likely that the nucleation barrier for the formation of the \( Z \)-variant, \( \Delta_Z \), is lower than that of the \( X \)- and \( Y \)-variants (\( \Delta_X, \Delta_Y \)) under a magnetic field.

Such a change in the nucleation barrier by the application of magnetic field was discussed in the martensitic transformation in some ferrous alloys.\(^{16}\) If we use the model for the nucleation proposed in the paper,\(^{16}\) the probability for the formation of each variant will be proportional to \( \exp(-\Delta/k_BT) \) at the set temperature of the first step. Then the nucleation ratio of the \( Z \)-variant to that of the \( Y \)-variant (or \( X \)-variant), \( P_Z/P_Y \), comes to be given by \( \exp(-\Delta_Z/\Delta_Y)/k_BT) \). Considering the present result, we can speculate that the ratio \( P_Z/P_Y=\exp(-\Delta_z/\Delta_Y)/k_BT) \) should be larger than a critical value to obtain a single variant state after the second step. This critical value will be...
reached by the application of magnetic field of 0.5 T in the Co–50Pt alloy and of 4 T in the Fe–55Pd alloy in the present study, and under this condition, a single variant will be obtained in the growth process by elastic interactions, such as dipole–dipole interaction.

Next, we consider the factors affecting the nucleation barrier, $D$. The magnetocrystalline anisotropy will be one of the factors. In order to obtain such anisotropy in the present alloys, we measure magnetization curves in the $a$- and $c$-axes of the ordered phase at the holding temperature of the first step, and the result is shown in Fig. 7. For both alloys, the $c$-axis is easier to magnetize compared to the $a$-axis. From the difference in magnetization curves between the $c$- and $a$-axes, the induced magnetic anisotropy energy at 1 T is obtained to be 4.1 kJ/m$^3$ for the Co–50Pt alloy at 773 K and 45.3 kJ/m$^3$ for the Fe–55Pd alloy at 673 K. Obviously, the magnetic anisotropy in the Co–50Pt alloy is lower than that of the Fe–55Pd alloy at the holding temperature of the first step. If the change in $\Delta$ by the application of magnetic field is simply an increasing function of magnetic anisotropy common to the two alloys, then the result of magnetic anisotropy seen in Fig. 7 contradicts the result seen in Fig. 6 (that the lowest field for the formation of single variant is lower for the Co–50Pt alloy compared to the Fe–55Pd alloy). Thus we should consider other factors affecting nucleation barrier $D$, and it is a problem in the future.

4. Conclusions

Effect of magnetic field on selected formation of a specific variant has been investigated in Co–50Pt and Fe–55Pd exhibiting a disorder-order transformation from A1 type structure to L1$_0$-type structure. Single variant of ordered phase is obtained by applying a magnetic field of 0.5 T and higher in Co–50Pt alloy, and 4 T and higher in Fe–55Pd alloy. The difference in the field strength could be due to the relation between nucleation barrier for the formation of the ordered phase and the magnetic anisotropy of the ordered phase at the nucleation stage.

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