Shape Memory Effect and Magnetostriction in Rapidly Solidified Fe-29.6 at%Pd Alloy

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Rapidly solidified ferromagnetic shape memory Fe-29.6 at% Pd alloy was fabricated to develop a new type of actuator material responded to magnetic field. The thin ribbon samples which were made by the originally designed electromagnetically controlled nozzleless melt-spinning method showed stronger crystal anisotropy and larger shape memory effect. Magnetostriction increased with increasing magnetic field and its value changed with increasing temperature up to about 1800 microstrain at an applied magnetic field, $H = 8.0 \times 10^5$ A/m ($= 10$ kOe), at just below the inverse phase transformation temperature (A_s). This phenomenon may be caused by the re-arrangements of the activated martensitic twin variants due to applying magnetic field. The dependencies of shape memory effect and giant magnetostriction on metallurgical microstructures are discussed from the viewpoint of the crystal anisotropy and the grain boundary character distribution.

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I. Introduction

Recently, the demand for development of higher performance solid-state actuator materials having large strain, rapid response time and long durability has been increasing for fabricating the advanced mechatronics system such as micromachine and intelligent/smart structures. The rare-earth alloy, Terfenol-D ($\text{Tb}_{0.27}\text{Dy}_{0.73}\text{Fe}_2$) is a commercially available magnetostrictive material with a strain of 0.17% ($\epsilon = 1,700 \times 10^{-6}$) in the field of $H = 8.0 \times 10^5$ A/m ($= 10$ kOe).⁽¹⁾ In ordinary magnetostrictive materials, the lattice is strained when the magnetic moments in the unit cells (*i.e.*, domains) turn in the direction of the external magnetic field (H). Magnetostrictive materials can provide much higher operating frequencies than the conventional thermoelastic shape memory alloy (SMA) as described later, but their strains are very small in comparison to SMAs. On the other hand, SMA can exhibit a few percent recoverable strain by thermoelastic phase transformation.⁽²⁾ The shape memory effect is based on the reorientation of the twin variants of the martensite phase after the martensitic transformation. However, a disadvantage of SMA actuators is their slow response due to thermal control, especially, in cooling process and its poor thermal energy conversion. These factors have been suppressing the applicability of SMA actuators.

In very recent years, magnetic field control of shape memory effect was suggested as a principle to operate a new

type of actuator material where the re-arrangements of the activated martensite twins due to applied magnetic field causes the shape change just like a magnetostrictive material. Interesting studies on the magnetostriction of martensite have been recently reported in the Heusler type alloy, Ni_2MnGa by MIT group⁽³⁾, etc. However, this alloy is too brittle to be worked into thin plate or wire etc. at the present. Magnetic-field-induced shape changes associated with the reorientation of the twin structure are expected in several kinds of ferromagnetic materials whose twin boundaries or martensite interfaces have high mobility as recently demonstrated in ferromagnetic SMA, Fe-33.5Ni alloy⁽⁴⁾. It has been well known that Fe-Pd system alloy can also show shape memory effect and this is ferromagnetic material. Moreover, the crystal anisotropy also has an essential role in enhancing the martensite twin movements instead of both magnetic domain movements and following rotations due to a high magnetocrystalline anisotropy energy. Therefore, in the present study, the thin plate of Fe-29.6 at%Pd alloy was prepared by the originally designed, "electromagnetic nozzleless melt-spinning method"⁽⁵⁾ for enhancing crystal anisotropy due to the formation of fine columnar grains structure as pointed out previously⁽⁶⁾. The shape memory effect and the possibility of magnetic-field-induced type striction are discussed from the viewpoint of metallurgical microstructures, especially, crystal anisotropy and grain boundary character distribution.

II. Mechanism of Magnetostriction by Martensitic Transformation

When a kind of ferromagnetic shape memory alloy having the activated martensite twin variants is subjected to an external magnetic field, the twins are apt to grow along a favorable orientation relative to the externally applied magnetic field (H) by spreading over other twins of different directions, and finally, the martensite phase in the material would be composed of almost only one type of twin variant. **Figure 1** is the schematic figure showing the differences of mechanisms that cause the striction in (a) ordinary magnetostriction, (b) shape memory, and (c) new magnetically actuated shape memory materials investigated in this study. **Figure 2** shows the macroscopically schematic figure of the growth of twin variants which are re-arranged magnetically along the favorable orientation to the external magnetic field ($H_1 < H_2$), and this can cause the shape change of the materials by externally applied magnetic field (H) as similar as the thermoelastically re-arranged martensite variants in SMA.

It has been discussed by Ullakko⁽³⁾ that shape changes due to applied magnetic field will become more effective in such materials that have large magnetocrystalline anisotropy energy (U_k) comparable or greater than the driving energy to rearrange the twin variants, namely twin boundary motion energy (E_t), to reach a certain strain of the material. If U_k is high and E_t is low, it might become difficult for the magnetic moment in the unit cell of one twin variant to turn into another by the external field (H). This phenomena essentially differs from ordi-

nary magnetostriction phenomena in which magnetic moment rotates to the external magnetic field direction without changing the unit cell orientations. Magnetic-field-induced turning of the unit cells of one twin into another results in a strain of the actuator material becomes and it possible if the following appropriate energetic condition (E) is satisfied.

$$U_k > E > E_t + W,$$

where U_k is the anisotropy energy, E_t is the energy for twin boundary motion including mechanical work factor done in the matrix and W is the the work done by actuator material.

III. Experiments

1. Sample preparation

The test samples of thin ribbon were prepared by originally designed "electromagnetic nozzleless melt-spinning method"⁽⁵⁾ for controlling the metallurgical microstructures and enhancing the material properties by rapid solidification. The schematic figure of the system of the apparatus to produce continuously the thin ribbon samples by combining the electro-magnetic float-melting with rotating twin rolls for rapid-solidification is shown in **Fig. 3**. The apparatus and detailed production procedures of test samples are described in the previous paper⁽⁵⁾⁽⁷⁾. After cutting the arc-melted button of Fe-29.6 at%Pd alloy into the shape of rectangular block, the raw Fe-Pd alloy block was chucked at the tip of the rotating rod attached with the upper motor on the vacuum chamber. By moving the rectangular shape of block of raw Fe-

Fig. 1 Schematic figures of the shape changes that cause the strokes in (a) conventional magnetostrictive, (b) shape memory effect and (c) new magnetically driven shape memory actuator materials⁽³⁾.

Fig. 2 Magnetically induced growth of the twin variants which is in favorable orientation to the external magnetic field ($H_1 < H_2$)⁽³⁾.

Fig. 3 Schematic figure of the system of the proposed electro-magnetically controlled nozzleless rapid solidification method⁽⁵⁾.

Fig. 4 The conventionally hot-roll processed polycrystalline Fe-29.6 at%Pd block with many cracks ((a) upper photograph) and rapid-solidified melt-spun thin plate with ductility of complete bending ((b) lower photograph).

Pd alloy downward continuously into the high frequency current Cu spiral coil for float-melting (*i.e.* levitation), the melt finally flows down within the coil after the balance between the weight of melt and electromagnetic Lorenz force for floating the melt is broken. Changing the shape of spiral coil to make the flow of melt more slender and as fine as possible, it became possible to produce the continuous thin plate of Fe-Pd alloy 60–120 μm thick, 10–20 mm wide and 200–300 mm long. An example of the produced Fe-29.6 at%Pd thin plate by twin roll whose rotating speed was 28 m/s (*i.e.* 3600 rpm) in Ar atmosphere are shown in Fig. 4. It was so ductile that the sample can be bent completely although the arc-melted alloy block was broken by the formation of cracks after several passes of hot-rolling at 1373 K as shown in the upper part of Fig. 4. Some of the produced samples were annealed at 1173 K for X ($X=0, 1$ h) hours in vacuum atmosphere ($=1.33 \times 10^{-2}$ Pa $=1 \times 10^{-4}$ Torr) to verify the effect of heat treatments on shape memory effect and magnetostriction.

2. Material evaluation

The grain orientation and grain boundary character distribution (GBCD)⁽⁸⁾ were determined by using the SEM-EBSP (electro-backscatter pattern) to investigate the effect of crystal arrangements as well as grain boundary structures on the performance of this sensor/actuator material. The thermoelastic transformation temperatures relating shape memory effect were measured by differential scanning microscopy (DSC) from 273 to 673 K. The shape memory effect was evaluated from the changes of shape recovery of the curled Fe-Pd thin plate in the furnace with increasing temperature by the continuous observation using a video camera, and the magnetostriction was measured by non-magnetic electric strain-

gage attached on the sample (size: 60 μm thick, 16 mm wide and 50 mm long) which was set between the electromagnetic coils. In some cases, the chucked thin plate samples were loaded by the dead-weight (W) at the under side of the specimen to investigate the pre-stressed (σ) effect on magnetostriction. The magnetic field (H) was generated from $H = -8.0 \times 10^5$ A/m ($= -10$ kOe) to $H = +8.0 \times 10^5$ A/m ($= +10$ kOe) in one triangular-waved cycle at 0.005 Hz by using digitally controlled direct-current power supply.

Striction by the magnetic shape memory effect in Fe-Pd alloy depends on the environmental temperatures because this alloy also shows innate thermoelastic phase transformation. Therefore, the magnetostriction measurements were also conducted in a constant-temperature, controllable, cylindrical electric furnace which was set between the two concentric coils for magnetization. The magnetostrictive strain was measured parallel to the rolling direction of the produced thin plate specimen because the magnetostriction perpendicular to rolling direction was one order of magnitude smaller than in the parallel direction.

IV. Results and Discussion

The samples of rapid-solidified Fe-29.6 at%Pd ribbon by this method were produced by different cooling rates, 28.3 m/s and 37.7 m/s, and the following annealing time from 0 to 1 h at 1173 K. Metallurgical microstructures, shape memory effect and magnetostriction of this ferromagnetic shape memory alloy are studied by correlating these factors to each other.

1. Grain boundary character distribution (GBCD)

The melt-spun ribbon samples have the columnar

Fig. 5 Grain structure mapped by OIM/SEM/EBSP at the surface of rapid-solidified Fe-29.6%Pd thin plate (roll speed = 28.3 m/s, 1173 K, 1 h annealed).

Fig. 6 Grain size distribution in Fe-29.6 at% thin ribbon in rapidly solidified and annealed at 1173 K for 1 h (roll speed: 28.3 m/s).

Fig. 7 Grain size distribution in Fe-29.6 at% thin ribbon in rapidly solidified and annealed at 1173 K for 1 h (roll speed: 37.7 m/s).

grains along the thickness direction. A photograph of grains is shown in Fig. 5. The grains orientation are characterized by OIM/SEM/EBSP at the electropolished surface of the rapidly solidified thin plate which was produced at the roll speed of 28.3 m/sec and annealed at 1173 K, 1 h. The average grain size is 2.9 μm in the as-spun sample produced at the roll speed of 28.3 m/s and grain growths occurred by recrystallization during annealing heat treatments as shown from the grain size distributions in Figs. 6 and 7. Four typical examples of GBGD, (*i.e.* (a) the relationship between grain boundary existence frequency (F) and coincidence boundary (Σ), and (b) the crystal anisotropy of orientation distribution in the pole figure) for 28.3 m/s rolling speed and 37.7 m/s are shown in Figs. 8, 9, respectively. Black solid bars represent experimentally obtained frequency of occurrence of specific boundaries (F) and white open bars indicate the theoretically predicted frequency F for ideally random-oriented polycrystal like powders. From the data in the as-spun (Fig. 8(a)), 1 h annealed (Fig. 8(b)) sample of 28.3 m/s rolling speed and as-spun sample (Fig. 9(a)) of 37.7 m/s, the frequency (F) of low Σ coincidence boundaries which may have low energy boundary increased extraordinarily although a slight drop of F at low Σ values seems to occur after 1 h annealing. On the other hand, Fig. 9(b) shows the sample of 37.7 m/s speed, 1 h anneal treatment. The value of F for low Σ

Fig. 8 Grain boundary character distributions (GBGD) and pole figures in the rapidly solidified Fe-29.6 at%Pd alloy thin ribbons, (a) as-spun at roll speed=28.3 m/s, (b) the heat-treated at 1173 K, 1 h annealing after melt-spinning at roll speed=28.3 m/s.

Fig. 9 Grain boundary character distributions (GBGD) and inverse pole figures in the rapidly solidified Fe-29.6 at%Pd alloy thin ribbons, (a) as-spun at roll speed=37.7 m/s, (b) the heat-treated at 1173 K, 1 h annealing after melt-spinning at roll speed=37.7 m/s.

coincidence boundaries decreases and the distribution of F spreads into the x axis in a similar manner with random-oriented polycrystalline material except that the anomalous increase of $\Sigma 3$ boundary due to the emergencies of twin boundaries with annealing in the crystals

with high energy (*i.e.* high Σ) grain boundary. The distributions of each crystal orientation (100), (110) and (111) are shown in the lower part of each figure. The case of roll speed = 28.3 m/s, 1173 K 1 h annealed sample (Fig. 8(b)) shows the most intense density at the central point of the pole figure (100) among three samples, and it is followed by roll speed = 28.3 m/s, as-spun sample in Fig. 8(a). The case of roll speed = 37.7 m/s, 1173 K, 1 h annealed sample did not show the concentration of any planes and the points from crystal planes were randomly oriented in the pole figure as shown in Fig. 9(b).

Accordingly, it can be confirmed that the rapid-solidification by rotating high-speed rolls enhances the formation of fine columnar grains, and its solidification results in the strong crystal anisotropy. Rapid-solidification increases the frequency of low Σ ($\Sigma 1$, $\Sigma 3$) boundaries provably having lower energy and (100) plane concentration occurs more intensively by annealing heat treatment of short time. Striations by twins formed within the grains with high energy (*i.e.* high Σ value) boundary are recognized very often after annealing in these tested samples.

2. Shape memory effect

The inverse transformation temperatures (A_s and A_f) in Fe-Pd alloy whose composition of Pd is near 30 at% was investigated by using DSC. From DSC curve during heating, the transformation temperatures, $A_s = 447$ K, $A_f = 493$ K, were obtained in the roll-speed = 28.3 m/s, as-spun sample and, similarly, $A_s = 445$ K, $A_f = 491$ K in roll-speed = 28.3 m/s, 1173 K, 1 h annealed sample. From the relationships between shape memory parameter $\Phi = \Phi_i / \Phi_o$ (*i.e.* the normalized shape change of the diameter of the curled thin plate sample) and temperature (T), it was recognized that the shape recovery changes started from 330 K and continued up to 500 K, nevertheless, the latent heat due to the reverse transformation was recognized to begin from 445 K by the DSC measurement. **Figure 10** shows the comparison of shape memory effect among the Fe-Pd samples with different material processings and heat treatments. Shape recovery effect is stronger in the cases of roll-speed = 28.3 m/s, as-spun sample and the strongest in the 1173 K, 1 h annealed sample. The most weak recovery is recognized in the roll-speed = 37.7 m/s, 1173 K 1 h annealed sample in which distinct concentration of (100) direction of the crystals was not observed as shown in Fig. 9(b).

3. Magnetostriction by martensite phase transformation

The unique mechanism of the magnetostriction by the martensitic phase transformation will also depend on the metallurgical microstructures although the mechanism may be different from the ordinary magnetostriction caused mainly by the rotations of magnetic domains during magnetization process of ferromagnetic materials. **Figure 11** shows the relationships between magnetostriction (ϵ) and applied magnetic field intensity (H) measured at room temperature for three types of samples. The

Fig. 10 Comparison of shape memory effect among the Fe-29.6 at%Pd samples with different material processings and heat treatments (roll speed = 28.3 ~ 37.7 m/s, 1173 K, 0 ~ 1 h annealed).

Fig. 11 Changes of hysteresis curves of magnetostriction vs magnetic field at room temperature ($T = 293$ K) in rapid-solidified, melt-spun Fe-29.6%Pd thin ribbon (roll speed = 28.3 m/s, 1173 K, 1 h annealed).

external magnetic field was applied perpendicular to the specimen plate and strain changes were measured along the rolling direction. Among the samples, the largest striction was obtained in the roll-speed = 28.3 m/s, 1173 K, 1 h annealed sample. The next largest was in the as-spun

sample. On the other hand, the smallest striction was obtained in the roll-speed=37.7 m/s, 1173 K 1 h annealed sample.

We can notify that the magnitude of the magnetostrictive effect for each sample is similar to that of the case of shape memory effect in the paragraph 4-2. The existence frequency of low energy boundary (*i.e.* small Σ value=1~29) is very similar between the two 28.3 m/s roll-speed samples, but, the density of grains with surface orientation (100) becomes more distinct in the roll-speed=28.3 m/s, 1173 K, 1 h annealed sample and this sample could show the highest shape recovery striction. On the other hand, it is completely indistinct due to the random-oriented crystals in the roll-speed=37.7 m/s, 1173 K, 1 h annealed sample and this sample showed the smallest striction. Taking account of the correlation between the magnitude of magnetostrictive strain and GBCD of the melt-spun Fe-Pd thin ribbon samples, we conclude that crystal anisotropy control is more effective to enhance the magnetostriction of this alloy.

Fig. 12 Dependencies of hysteresis curves of magnetostriction on testing temperature in melt-spun Fe-29.6 at%Pd alloy thin ribbon (roll speed=28.3 m/s, 1173 K, 1 h annealed, $A_s=436$ K).

Fig. 13 Changes of magnetostriction vs magnetic field curves with increasing temperature in melt-spun Fe-29.6 at%Pd alloy thin ribbon (roll speed=28.3 m/s, 1173 K, 1 h annealed, $A_s=436$ K).

Finally, the possibility of the very large magnetostrictive strain which is correlated with phase transformation in this melt-spun shape memory Fe-Pd alloy was investigated based on the mechanism discussed in Sec. 2. **Figures 12 and 13** show the temperature dependencies of magnetostrictions in the roll-speed=28.3 m/s, 1173 K, 1 h annealed sample which showed the largest magnetostriction in this test. Magnetostriction was measured under a constant tensile stress $\sigma=10$ MPa because the stress (*i.e.* external mechanical energy supply) will work on activating the twin boundary motion as well as arrangements of twin orientation along the external magnetic field just like a training effect in shape memory alloy. Magnetostriction increases with increasing temperature and its value is 1800 microstrain at $H=8.0 \times 10^5$ A/m (=10 kOe) at 423 K just below the inverse phase transformation temperature ($A_s=445$ K, DSC test). At the temperature above A_s , magnetostriction remarkably decreased about 300 microstrain at 8.0×10^5 A/m (=10 kOe) as shown in Fig. 12. This value is nearly the same as that in the ordinary ferromagnetic iron-based rapid-solidified thin plate sample⁽⁹⁾; therefore, the obtained maximum strain value at 423 K in this study is about six times as large as the conventional iron-based polycrystalline magnetostrictive material, and almost equal to the magnetostriction of Tarfenol-D.

Based on these experimental facts, we conclude that this remarkable giant magnetostrictive phenomenon was caused by the mechanism of re-arrangements of the activated martensitic twin variants responded to external magnetic field in the melt-spun Fe-Pd thin ribbon which has a strong crystal anisotropy as well as low energy grain boundary. These unique crystalline features are expected to result from the columnar fine grains formed by rapid solidification process. More detailed studies on the giant magnetostriction phenomena in this kind of ferromagnetic shape memory alloys will have to be done to develop further higher performance magnetostrictive actuators. Of course, it is also necessary to investigate the basic properties such as (1) the response speed against cyclic applied magnetic field (H), (2) the strain vs H hysteresis curve and (3) the degradation of the magnetostriction of this rapidly solidified Fe-Pd system alloy for engineering usage in intelligent/smart material systems⁽¹⁰⁾.

V. Conclusions

The rapid-solidified, melt-spun Fe-29.6 at%Pd alloy ribbons were fabricated to develop a new type of actuator material responded to magnetic field with larger and faster actuation for designing the intelligent material systems. The samples made by originally designed electromagnetically controlled nozzleless melt-spinning method have fine columnar grains with low Σ grain boundary and an intense crystal anisotropy. They show larger shape memory effect than those of the conventionally processed, randomly oriented sample having its same origin. Magnetostriction changed with increasing temperature and its value is about 1800 microstrain at

$H=8.0 \times 10^5$ A/m ($=10$ kOe) just below the inverse phase transformation temperature (A_s). The shape memory effect and magnetostriction are more strongly affected by crystal anisotropy. From these experimental facts, it can be concluded that this remarkable giant magnetostrictive phenomena might be caused by the mechanism of re-arrangements of the activated martensitic twin variants responded to external magnetic field.

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