Effect of rapid solidification on giant magnetostriction in ferromagnetic shape memory iron-based alloys

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Abstract

Ferromagnetic shape memory Fe–29.6 at.% Pd alloy ribbons prepared by the rapid solidification, melt-spinning method, showed a giant magnetostriction of 830 microstrain when an external magnetic field of 7 kOe was applied nearly normal to the ribbon surface at room temperature. This ribbon’s magnetostriction was several times as large as conventional polycrystalline bulk’s one before rapid solidification. The magnetostriction in the rolling direction depended strongly on a direction of applied magnetic field. We considered that this phenomenon is caused by a rearrangement of activated martensite twin variants just below the austenite phase transformation temperature. We investigated their basic material properties, i.e. the dependencies of magnetostriction on temperature as well as on magnetic angular orientation to the surface, magnetic properties, crystal structure, surface texture morphology and shape memory effect of Fe–29.6 at.% Pd ribbon samples by comparing with conventional bulk sample. It can be concluded that the remarkable anisotropy of giant magnetostriction of ribbon sample is caused by the unique uniaxial-oriented fine grain structure formed by the melt-spinning method. In addition, we confirmed the possibility of rapidly solidified Fe–Pt ribbon as a new kind of iron-based ferromagnetic shape memory alloys for magnetostrictive material. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Ferromagnetic shape memory alloys (FSMA) are expected to be useful as a sensor/actuator material for a micro-machine and intelligent/smart material system driven by a magnetic field. Martensite twin’s initiation and the following their movement depending on magnetic field are thought to be closely related to a new type of magnetostriction [1]. In several single crystal FSMA, the studies of this magnetostrictive phenomenon have been carried out [2–5] up to the present. In particular, Murray et al. [2] reported that the recoverable magnetostrictive strain of 6% (60,000 microstrain) obtained in Ni\textsubscript{2}MnGa single crystal with a weak compressive stress. However, these are researches for single crystals, and it seems to be unsuitable for the industrial material because of expensive cost and difficulty for production. From such background, the studies of polycrystalline FSMA have been carried out in recent time, but there are problems for their industrial application. For instance, polycrystalline Ni\textsubscript{2}MnGa is too brittle to be produced. In addition, even in iron-based FSMA (ex. Fe–Pd, Fe–Pt, etc.) with ductility, a large magnetostriction comparable to that of Terfenol-D have not been reported.

Our previous studies [6,7] showed that the rapidly solidified Fe–29.6 at.% Pd alloy ribbons reveal strong crystal anisotropy, a giant magnetostriction as well as a thermal shape memory effect. The magnetostriction changed with temperature and had a maximum of 1800 microstrain at an external magnetic field of 10 kOe just below Af point under a tensile stress of 10 MPa. However, the mechanism of this magnetically induced strain has not yet been discussed in detail. We considered that the dependence of magnetostriction on the direction of magnetic field is probably caused by fine columnar grains uniquely formed by the rapid solidification method [8,9]. To confirm this hypothesis, in the present study, we analyze several material

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properties, i.e. magnetostriction, magnetic property, crystal structure, surface texture and shape memory effect of Fe–29.6 at.% Pd ribbon samples and compare these properties with those of the conventional polycrystalline bulk samples before rapid solidification. Moreover, we tried to confirm the possibility of rapid solidified Fe–22.7 at.% Pt alloy as a kind of iron-based FSMA to investigate whether the rapid solidification, melt-spinning method is effective for the other FSMA.

2. Experimental details

The rapidly solidified Fe–29.6 at.% Pd and Fe–22.7 at.% Pt ribbon samples 60 μm in thickness, were prepared by originally designed electro-magnetic melt-spinning single-or twin-roll method from bulk alloys [8]. The samples were annealed at 1173 K for 0–6.0 h in vacuum atmosphere to study the effect of heat treatment on magnetostriction. The magnetization (M) versus applied external magnetic field (H) loop was measured by a vibrating sample magnetometer (VSM) method. The magnetostriction (ε) was measured by a strain-gauge attached on the sample which was set in a furnace between the electromagnets. The sample can be rotated in the magnetic field, and the rotation axis is set up against the rolling direction (RD). The magnetic field was applied perpendicular to RD and strain changes were measured along RD with increasing measurement direction (θ) from 0 to 90°, where θ is the rotation angle between the transverse direction of ribbon and magnetic field (see Fig. 1). The X-ray diffraction (XRD) profiles for the sample surface were obtained with Cu Kα line for ribbon and bulk samples. The appearance and disappearance of thermoelastic martensite twin boundaries were observed by using the laser microscope in a heat furnace. The shape memory effect was evaluated from the changes of shape recovery of the curled ribbon with increasing temperature in silicone oil. The shape change was monitored by a digital camera.

3. Results and discussion

3.1. Magnetostriction in rapidly solidified Fe–29.6 at.% Pd ribbon

Fig. 2(b) shows the M versus H loops of the melt-spun ribbon sample prepared by the single-roll method (S-0h ribbon). Fig. 2(a) shows that of the bulk sample before rapid solidification. In Fig. 2(b), the magnetization for θ = 0° was saturated at H < 2 kOe showing small coercive force (Hc) of ~35 Oe. Then, a saturation magnetization at H = 5 kOe was 150 emu/g, its value was nearly equal to that of bulk as shown in Fig. 2(a). It was proven that the rapidly solidified ribbon sample is the ferromagnet with magnetization ability equivalent to bulk sample before rapid solidification. On the other hand, M–H loop of both samples for θ = 90° was not saturated even at H = 5 kOe because of a large demagnetizing field due to the very thin shape of ribbon sample. But the ribbon sample revealed large Hc of ~65 Oe compared with that of the ribbon at θ = 0°. In contrast, the bulk sample, which is annealed for 0.5 h at
1173 K in order to remove residual strain caused by cutting and have the ability of shape memory, also showed the similar magnetization at $H = 5$ kOe, but its coercive force decreases to smaller values in almost directions. Fig. 3 shows a comparison of direction dependency of coercive force ($H_c$) between the ribbon and bulk samples. The coercive force of the ribbon depended remarkably on $\theta$ and had a maximum of 98 Oe at $\theta = 85^\circ$ and, in contrast, that of the bulk depended scarcely on $\theta$. The coercive force of the ribbon generally decreases with long heat treatment time. Then, a lowered coercive force of the ribbon almost corresponded to that of the bulk at $\theta = 0$–45°. However, in the sample thickness direction, the tendency of showing stronger coercive force did not change. These results suggest that the coercive force of the melt-spun Fe–29.6 at.% Pd thin ribbon sample was generally larger than that of the bulk, and this phenomenon might be originated from a thermal stress induced during rapid solidification. Moreover, the ribbon samples have the crystal magnetic anisotropy as large coercive force appears at the direction of $\theta = 85^\circ$. This anisotropy probably results from the strong texture that consists of columnar crystals developed by the rapid solidification. On the other hand, the coercive force of the bulk depends scarcely on $\theta$, which means that the bulk has magnetically isotropic texture.

Fig. 4(a) shows the dependence of magnetostriction of S-0h ribbon on the direction ($\theta$) of magnetic field. The magnetostriction depended remarkably on $\theta$ and had a maximum value of $-830$ microstrain at $\theta = 85^\circ$. Fig. 4(b) shows the dependence of magnetostriction of bulk sample on $\theta$. The magnetostriction had a maximum value of $-28$ microstrain at $0^\circ$ and $-18$ microstrain at $\theta = 90^\circ$, respectively. The magnetostriction of bulk sample at $\theta = 0^\circ$ was saturated nearly at $H = 2$ kOe as ordinary expected in a conventional polycrystal. These results show that the magnetostriction of ribbon sample becomes larger than that of conventional polycrystals. Beside, it can be noticed that the magnetostriction of ribbon and bulk samples showed a directional dependency that is similar to the change of coercive force as shown in Fig. 3. The large value of magnetostriction in the ribbon gradually decreased with heat treatment time, however, the tendency of showing largest magnetostriction at $\theta = 85^\circ$ did not change and its tendency also preserved in the coercive force of ribbon. The formed martensite twin variants act as an obstacle to a magnetic domain wall movement in the magnetization process, therefore, the large coercive force revealed in that direction in which large magnetostriction appeared. From the results of magnetic properties and magnetostriction as shown earlier, it is considered that martensite twin variants which caused the rearrangement of the twin mainly exist at $\theta = 85^\circ$ for the ribbon sample.

Fig. 5 shows XRD profiles obtained on the surface of ribbon and bulk samples. In the bulk, the face-centered cubic (f.c.c.) structure and the body-centered cubic (b.c.c.) structure equally existed, on the other hand, in rapidly solidified ribbon, the b.c.c. phase scarcely existed, but martensite phase with the face-centered tetragonal (f.c.t.) and austenite phase with f.c.c. appeared clearly. This result shows that the ribbon had a more effective and better texture.
for the appearance of a large magnetostriction further than the bulk, because f.c.t. phase seems to be more effective for martensite twin variant movement. Consequently, the (200) peaks at 293 K consist of three structures: f.c.t. (200), f.c.c. (200) and f.c.t. (002), and the orientation of [200] peaks of ribbon to near the sample surface direction was stronger than that of bulk. In Fe–Pd alloy, the f.c.t. martensite phase consist of expansion a-axes of (100) direction which is known as the direction of easy magnetization as well as shrinkage c-axes of (001) direction [4]. Therefore, it is proven that the sample surface direction of the ribbon has oriented texture to (100) direction that is favorable for the rearrangement of martensite twin variants by the applied magnetic field, and the ribbon shows larger magnetostriction as the texture becomes stronger. These results are consistent with our previous study [6]. So, we consider that the ribbon consists of the fine columnar grains that grows along the heat flow direction, i.e. sample thickness direction, and conclude that the giant magnetostriction appears by the peculiar microstructure that shows uniaxial anisotropic property probably resulting from rapid solidification.

3.2. Phase transformation behavior in rapidly solidified Fe–29.6 at.% Pd ribbon

Fig. 6 shows the photographs of S-0h ribbon surface in heating process, which taken by the laser microscope. In the largest grains, about 30 μm in diameter, the martensite twin stripe-pattern observed at 303 K almost disappeared at 307 K. In addition, in cooling process from 333 K, the twin appeared again at 298 K. Therefore, this martensite phase is thermoelastic and is not stress-induced type. This result shows that the reverse phase transformation from martensite to austenite occurs at nearly room temperature. This phase transformation temperature is almost consistent with the previous study by Sugiyama et al. [10]. Fig. 7 shows temperature dependence of XRD profiles of the ribbon which was prepared by the twin-roll method and then annealed at 1173 K for 0.5 h (T-0.5h ribbon). In this profile, a peak at diffraction angle (2θ) of 44.8° is attributed to an instrumental artifact. The f.c.t. martensite phase formed at 293 K decreases in heating process and disappears at 333 K and above, while the f.c.c. austenite phase grows. This result shows that the austenite phase transformation finishing temperature (Af) is about 333 K, which approximately corresponds to the result of Af point from disappearance of twins by the surface observation.

Here, when the general concept of grain size dependence of the phase transformation temperature is taken into consideration, it seems to be phenomenologically reasonable that the phase transformation temperatures of Fe–Pd single crystal [10] and the rapidly solidified sample are very different to each other, since the rapid solidified ribbon consists of very fine micrometer-sized grains. From these experimental results, however, the Af determined from the analysis of the crystal structure and the surface observation, is approximately consistent with that of single crystal. We will discuss about this contradiction as following. Fig. 8 shows the annealing time dependence of XRD profiles of the twin-roll ribbon. XRD profiles of the Fe–Pd ribbon with an appropriate heat treatment temperature show an increase.
of the intensity of the f.c.c peaks from austenite phase with increasing annealing time. This result suggests that the transformation temperature of the ribbon decreases by the stress relaxation after the heat treatment, in other words, the transformation temperature might be elevated by a complicated thermal stress induced during rapid solidification. Therefore, the transformation temperature determined by the XRD analysis and the laser microscope is regarded as being reasonable, because the increase of the transformation temperature was caused by the induced residual stress.

Fig. 9 shows temperature dependence of the magnetostriction for T-0.5h ribbon and S-0h ribbon at $\theta = 80$ and 85°, respectively, where the largest magnetostriction appeared in both samples. A jump discrepancy between process (1) and (1') was caused by the experimental discontinuity of annealing process. Absolute value of the magnetostriction first decreased with increasing temperature from $-630$ to $520$ microstrain and then increased to a maximum value of $-680$ microstrain at 400 K, and it suddenly decreased with increasing temperature to 140 microstrain at 440 K. Thereafter, we let the temperature down (see process (2)). The magnetostriction recovered again to $-350$ microstrain at 400 K and decreased to $-160$ microstrain at 190 K. We elevated the temperature again (see process (3)). The magnetostriction increased and moved approximately back over its way as shown as shadowed open circles in Fig. 9. It is known that the magnetostriction caused by the rearrangement of martensite twin variants in FSMAs shows a maximum state at nearly temperature changing from martensite phase to austenite phase [6]. We consider that this phenomenon is closely related with changes of twin’s property, i.e. the increase of the mobility of activated martensite twin variants by the heating, so that, the magnetostriction increased with increasing temperature, and the magnetostriction starts to decrease since martensite twin variants disappears by their transforming into austenite phase in higher temperature region. From this reason, it can be understood that the magnetostriction showed maximum value at 400 K just near the austenite phase transformation starting temperature, As point. Here, we discuss about the reason that magnetostriction at 400 K decreased during the thermal heating and cooling cycles. It is thought that this phenomenon would originate from the residual strain which cannot return to initial state, even if a magnetic field is removed. From this idea, the value of magnetostriction decreases by thermal cycles because rearranged martensite twins continue to be accumulated toward the direction of magnetic field. Nevertheless, the peaks of the magnetostriction always appeared at 400 K, i.e. As points of T-0.5h and S-0h ribbons are about 400 and 376 K, respectively.

Next, we note a discrepancy between the measured temperatures of the phase transformation, that is to say, this $Af$ from XRD disagrees with $Af$ estimated from the relationship between $\epsilon$ versus $T$ curve. To clear the reason of this discrepancy, we investigated the shape memory effect for the whole geometry of S-0h (○) and T-0.5 h (△) ribbons, as seen in Fig. 10(a), where the shape recovery ratio, $\Phi_{T_f}/\Phi_{T_i}$ is shown. $\Phi_{T_i}$ and $\Phi_{T_f}$ are the diameters defined in Fig. 10(b) at $T = T_1$ and $T = T_2$, respectively. The ratios for both ribbons increase with increasing temperature. In particular, the ratio rises sharply as temperature increases in the temperature ranges of 300–330 K and 380–420 K, which correspond to the As point determined by the XRD profiles of the ribbon and $\epsilon$ versus $T$ measurements, respectively. These results imply that the ribbon might have mechanically (two-step phase) transformation temperature, i.e. the phase transformation temperature estimated from the magnetostriction is different from that of the analysis of crystal structure and the surface observation. Following subject will become one reason for explaining this gap of transformation temperature. The $Af$ point determined from the XRD profiles which correspond to the previous study [10], is obtained from only the surface

Fig. 8. The annealing time dependence of XRD profiles of the T-roll ribbon, (a) 200 peaks, (b) 220 peaks (WQ = water quench).

Fig. 9. Maximum magnetostriction versus temperature curves for two different ribbons.
structure about 10 μm in depth because of the mass absorption coefficient of Fe and Pd are large for the Cu Kα line. Beside the texture as seen in Fig. 6, is also observed from the surface of the ribbon sample. From these viewpoints, this difference of metallic microstructure between surface and inner part result in the different transformation temperature in microstructural view point, and this difference might cause the two-step transformation as shown in Figs. 7, 9 and 10.

3.3. Properties of rapid solidified Fe–22.7 at.% Pt alloy ribbon

Fe–X at.% Pt (X ≈ 25) alloy is also known as a kind of iron-based FSMA, then, we tried to study the possibility of rapidly solidified Fe–Pt alloy as one new magnetostrictive material just like a Fe–Pd alloy. We examined several material properties of the bulk and the rapidly solidified ribbon (as melt-spun) of Fe–22.7 at.% Pt alloy as in the case of Fe–29.6 at.% Pd alloy. This alloy composition was examined by the analysis using a scanning electron microscope-energy dispersive analysis of X-ray (SEM-EDAX).

The experimental results of Fe–22.7 at.% Pt alloy are shown in Table 1. The ribbons were rapidly solidified by the single-roll and melt-spinning method. Since the saturation magnetization of Fe–22.7 at.% Pt ribbon is as large as Fe–29.6 at.% Pd ribbons, it is a good ferromagnet without showing the magnetization loss by rapid solidification. This ribbon shows crystal magnetic anisotropy similar to Fe–Pd ribbon, and a giant magnetostriction of −420 microstrain, which appears nearly in the sample thickness direction at \( H = 7 \) kOe. The maximum magnetostriction of this ribbon is over eight times larger than that of the bulk sample. At 293 K, the ribbon has two phase structure of the f.c.c. and the f.c.t. which are oriented (100) direction almost parallel to the sample thickness direction. The temperature dependence of XRD profiles of the ribbon implies that \( A_f \) is 313 K. Though the clear peak to estimate \( A_s \) point did not appear in the temperature dependence of the magnetostriction, the magnetostriction implied \( A_s \) exists further than \( A_f \) in the high temperature region. The characteristics of transformation behavior in Fe–Pt ribbon is similar to that of Fe–Pd ribbon, and it is considered that the disagreement of the phase transformation temperatures of \( A_s \) estimated from the magnetostriction peak and \( A_f \) determined from the XRD profiles, is caused by the complicated thermal stress induced in the rapid solidification process as in the case of Fe–Pd ribbon. From these results, Fe–22.7 at.% Pt ribbon shows the similar behavior to that of Fe–29.6 at.% Pd ribbon, and it is proven that a giant magnetostriction was also obtained in Fe–Pt ribbon.

Here, it is known that quenched material of Fe–22.7 at.% Pt alloy at room temperature has the b.c.c. structure [11]. Muto et al. reported that only the f.c.c.–b.c.c. phase transformation occurs in disordered Fe–Pt alloy at Pt composition below 25.5 at.%. In contrast, rapidly solidified Fe–22.7 at.% Pt ribbon sample measured in this study is composed of the f.c.c. and the f.c.t. phase. The produced various ribbon samples consist of the mixed phase of the f.c.c. and the b.c.c. phases or the b.c.c. single, although it has been verified that the Pt composition was kept constant to approximately 22.7% in all these samples by SEM-EDAX. Therefore, it is considered that the origin of the variation of the structure results from the difference of the producing condition, i.e. changes of melting temperature and roll rotational speed in rapid solidification process. But, the details of the appearance of the f.c.t. phase that mainly causes the shape memory effect at room temperature region is unknown, and it is to be investigated in the next study.

4. Conclusions

In this study, we carried out various experiments to investigate effects of rapid solidification on the giant
magnetostriction in iron-based FSMAs, and got following conclusions.

1. Both Fe–Pd and Fe–Pt ribbons consist of fine grain structure with (100) columnar texture by rapid solidification, which show unique uniaxial anisotropy. By this texture, rapidly solidified ribbons yielded larger magnetostriction in the ferromagnetic shape memory effect further than the bulk samples with the isotropic property, and the magnetostrictions are over 800 microstrain in Fe–29.6 at.% Pd, over 400 microstrain in Fe–22.7 at.% Pt, respectively.

2. Two-step phase transformation behavior was observed in the ribbon samples. This originates from the complicated thermal stresses within rapidly solidified samples. Therefore, the surface and the inner part of the ribbon are considered to consist of different texture. This feature in rapid-solidified ribbon sample is experimentally discussed from the observation of XRD profile for crystal microstructure on the surface and shape recovery behavior of total sample.

3. Considering both of the maintenance of functional properties and strength improvement by the grain size refinement in the material with the crystal anisotropy, rapid solidification method can be regarded as an effective method.

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