Magnetic and magnetostrictive properties in heat-treated Fe-Co wire for smart material/ device

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Received: 1 November 2017; Revised: 18 December 2017; Accepted: 29 March 2018

Abstract
The use of inverse magnetostriction effect is a possible approach for the applications of actuator, sensor and energy harvester. A strong textured Fe_{100-x}Co_x (x = 70 mol%) magnetostrictive alloys have been studies as a new smart material. The design of microstructure plays important roles in performance enhancement of power generation by heat-treatment at several temperatures from 420°C to 850°C. Experimentally, the effect of heat-treatment on their microstructures was evaluated by laser microscope and X-ray diffraction and orientation analysis. Furthermore, the magnetic, magnetostrictive and electric power generation characteristics were investigated by vibrating sample magnetometer (VSM), single-axis strain gauge and drop impact test, respectively. These results indicated the lattice strain in the crystal grain was related to the coercivity resulting from the domain wall mobility in the materials. Moreover, the orientation aligned by the drawing process was related to the magnetostriction. Also, the large grain width, that is, low grain boundary density was strongly attributed to enhance the magnetostrictive susceptibility. The output power calculated from the output waveform was reached up to 91 mJ/s for 820°C-WQ (water quenching) resulting from the high magnetostrictive susceptibility as well as the quenching effect from the temperature near the (bcc + fcc)/bcc interface. These results indicated that it is important to control not only the annealing conditions for improving magnetostrictive susceptibility but also the control of residual stress or grain boundary density for developing higher performance of output characteristics.

Keywords: Inverse magnetostriction effect, Fe-Co magnetostrictive alloy, Heat-treatment, Microstructure, Crystalline texture, Energy harvester

1. Introduction
Magnetostriuctive materials play an increasingly important role in applications ranging from actuators (Baras and Tan, 2004), damping devices (Davino, et al., 2011), energy harvesters (Wang and Yuan, 2008) to stress and torque sensors (Furuya, et al., 2010). Energy harvesting is an emerging technology that has been recently attracting great interest as an alternative method to wireless battery-free devices for the arrival of Internet of Things (IoT) society. There have been many studies conducted on energy harvesters from sources such as vibrations and dynamics stress resulting from mechanical loads (Vullers, et al., 2009).

One of the promising approaches for energy harvesting is utilizing inverse magnetostriective (Villari) effect, which is described most generally as the change of magnetic flux density of ferromagnetic materials when subjected to the alternative mechanical stresses. It is essential to design a magnetostrictive material having the higher magnetostriction, mechanical strength, and a low cost by mass production. Terfenol-D (Tb-Dy-Fe alloy) has been investigated because of the giant magnetostriction (800–1600 ppm) and low magnetic anisotropy (Clark, et al., 1965) as a traditional
magnetostrictive material. However, the fatally brittleness and high-cost resulting from composing a single crystal and including rare earth elements, Terfenol-D might be difficult not only to be more weight reduction or miniaturization for integrating with microelectromechanical system (MEMS) as sensors, but also to secure robust stability from large dynamical stress such as unexpected loads or mechanical vibrations.

Galfenol (Fe-Ga alloy) also exhibits large magnetostriction (~400 ppm) under very low magnetic field of 100 Oe (8 kA/m) reported by Clark, et al. (2003). Previous investigations have proved that the structure of single crystal Fe-Ga alloys is sensitive to heat treatment. Xing, et al. (2008) demonstrated that the interplay of hetero-phase interphases, especially, metastable DO₃ and the stable L1₂ phases in as-cast Fe-Ga alloys plays a crucial role for the formation of functional properties such as magnetostriction and coercivity of Galfenol. However, they also have some difficulty in the low mechanical strength, the product cost and the mass productivity.

More recently, Fe-Co with high Co content alloy (> 50 mol%) (Mashiyama, et al., 1932) is also emerging as one of the prospective magnetostrictive materials for energy harvesting applications owing to their great workability and lower cost compared with Terfenol-D and Galfenol. Yamaura, et al (2015) prepared polycrystal FeₓCoₓ (x = 50-90 mol%) alloy by forging and subsequent cold-rolling (rolling rate: ~97%) and reported the large magnetostriction of 128 ppm along rolling direction using as-rolled FeₓCoₓ alloys. Also, the high textured structures are considered to suppress the generation of fcc-Fe phase having negative magnetostriction. In addition, Hunter, et al. (2011) developed Fe-Co binary alloy thin films using a co-sputtering technique, and they found significant magnetostriction enhancement at the (bcc+fcc)/bcc phase boundary. The effective magnetostriction was 260 ppm for an FeₓCoₙOₙ thin film quenched from 1073 K, and the intrinsic magnetostriction λ₁₀₀ was estimated to be more than 1000 ppm. It had been proposed that magnetic domain rotation model as a mechanism of magnetostriction enhancement at the (bcc+fcc)/bcc interface (Yamaura, et al., 2014).

As above described, we developed the new wire-drawn FeₓCoₙ alloys for expecting higher magnetostrictive characteristics which are related to their microstructures. However, the contributions of crystallographic controls in polycrystal magnetostrictive materials to the high magnetostrictive properties have not been elucidated very well.

Therefore, the aim in this study is to clarify the relationship between magnetic and magnetostrictive properties, and the microstructural factors in FeₓCoₙ alloy wires for designing practical energy harvesters. The effective heat-treatment conditions for enhancing magnetostrictive characteristics were determined by phase diagram of binary Fe-Co alloy. Furthermore, the influence of the microstructural morphology on each property was evaluated by microstructure analysis using laser microscope. Finally, for investigating the usefulness of these materials as a micro power generator, output characteristics were evaluated by the drop impact test for the heat-treated samples.

2. Experimental

Feₓ₀₅Co₅ (x = 70 mol%) wires having a diameter of 1 mm as specimens were used in this study. For investigating the microstructure dependence of magnetic and magnetostrictive characteristics, several heat treatments were performed with the reference of Fe-Co phase diagram as shown in Fig. 1. Annealing at 420°C for 24 hours and furnace cooling (hereinafter, 420°C-FC) were conducted for removing residual stress and internal strain. Also, annealing at 750°C, 780°C, 800°C, 820°C and 850°C for 5 hours and water quenching (WQ) were conducted for modifying the coarsened microstructures and freezing a coexistence of two phase, which is the (bcc-Fe+fcc-Co)/bcc-Fe interface as a morphotropic phase boundary (MPB). Each heat-treatment was conducted in vacuum-sealed quartz tube with Ar. These wires were cut into a predetermined length as follows, Microstructural observation: 30 mm, X-ray diffraction measurement: 30 mm, VSM measurement: 10 mm, and drop impact test: 10 mm of length.

The microstructure observation such as grain’s width dₓ, the shape of aspect ratio Rₓ of drawing direction (D.D.) to the transverse direction (T.D.) and we evaluated the intensity of orientation from the inverse pole figure (IPF) by Electron backscatter diffraction (EBSD; JEOL Ltd.) analysis. The crystallographic phases of the Fe-Co alloy wire were characterized by X-ray diffraction (XRD; Ultima-IV, Rigaku Co.) analysis using Cu Kα radiation with a monochromator at the range of 30 to 90 degrees.

Magnetization hysteresis was evaluated using a vibrating sample magnetometer (VSM; VSM-5, Toei Kogyo Co., Ltd.). The maximum value of applied magnetic field was 0 to ± 796 kA/m (± 10 kOe) at room temperature and the magnetization was applied along the drawing direction (D.D.). From the magnetization curves, we evaluated saturated magnetization Mₛ and coercivity Hₓ. Under above conditions, the magnetostriction was measured by using single-axis strain gauge attached to the surface of each specimen along the longitudinal direction. From the magnetostriction
curves, we evaluated saturated magnetostriction $\lambda_S$ and the magnetostrictive susceptibility $d_m$ for as-drawn sample and the other heat-treated samples.

For evaluating the performance of power generation, vibration energy harvesting test was conducted for as-drawn sample, 420°C-FC and 820°C-WQ. Figure 2 shows the schematic illustrates of the impact loading device which was designed by aluminum frame and several equipment. Output voltage generated by impacting steel ball on the surface of each sample was measured by oscilloscope connected to the pick-up coil (Turn number: 1750 turns, Electric resistance: 140.5 Ω) around the sample. A neodymium was put under the specimen as a bias magnet for enhancing inverse magnetostriction effect. A steel ball (0.89 g in weight) was dropped from the height of 30 cm, and the number of sample inside the pick-up coil was 1. The number of trial of calculating average was 10 times for each sample.

In this test, the average value of the peak to peak voltage, $V_{\text{P-P}}$ [V] and the output power, $W$ [J/s] was calculated the following Eq. (1),

$$W = \int |V(t)|^2 / R \cdot t \, dt$$

where, $V(t)$ [V] is output voltage change with time, $R$ [Ω] is electric resistance of pick-up coil and $t$ [s] is measurement time. We evaluated the comparison of the output power for each specimen and discussed the influence of microstructural factors of Fe-Co alloy wire.

Fig. 1 Fe-Co phase diagram. The red line shows a morphotropic phase boundary (MPB) in Fe-Co alloy system. The (bcc-Fe+fcc-Co)/bcc-Fe interface is a MPB at temperature of around 800°C of Fe$_{100-x}$Co$_x$ ($x = 70$ mol%) alloys.

Fig. 2 Photograph (a) and schematic (b) of experimental energy harvesting set-up by drop impact test. The peak to peak voltage and the output power was measured by search coil around Fe-Co alloy wire using oscilloscope when steel ball (0.89 g) was dropped at the height of 30 cm.
3. Results and discussions

3.1 Annealing effect on the microstructure

Figure 3 shows the results of microstructure observation and orientation analysis for as-drawn sample, 420°C-FC (furnace cooling) sample and 820°C-WQ (water quenching) sample along to the drawn direction (D.D.). The color mapping indicated the intensity gradient of orientation of crystal texture of Fe-Co alloy wires. As a result, as-drawn wire has very small columnar crystal toward elongation direction. The grain width was about 13 μm and the aspect ratio was about 8.4. Similarly, as-annealed sample at the temperature of 420°C has the same shape grain as large as as-drawn sample. While, 820°C-WQ sample has recrystallized grain whose width was 25 μm and the shape of aspect ratio was close to 1. From the IPF, each sample has strong orientation to {110} <100> direction resulting from the wire drawing process. Also, we investigated the XRD patterns for above three kinds of specimens as shown in Fig. 4(a). From these peaks, there was no impurities (phases), and all samples have a single-phase bcc structure were confirmed. The enlarged figure in Fig. 4(b) shows the normalized intensity obtained from bcc (110) peaks for each sample.

Figure 5 shows the annealing temperature dependence of microstructural factors such as grain width $d_g$, shape aspect ratio $R_a$, intensity of <110> orientation calculated from the IPF and full width at half maximum (FWHM) values of Fe-Co alloy wire. By annealing at 420°C, $d_g$, $R_a$ and the intensity of IPF were kept almost constant, but the FWHM was decreased. On the other hand, by annealing at 820°C and quenching just after that, $d_g$ was increased up to 2 times as large as that of as-drawn sample, and $R_a$ and FWHM were significantly decreased. The FWHM values of peaks were decreased as the annealing temperature was increased. It is seen that the decrease of FWHM is owing to the release of internal strain inside the crystal lattice and the decrease of grain boundary density by annealing. The orientation evaluated from intensity of IPF was decreased slightly after annealing at 820°C.

3.2 Microstructural effect on the magnetic and magnetostrictive characteristics

Figure 6 shows the annealing temperature dependence of the coercive force and saturation magnetization evaluated from the magnetization curves for as-drawn sample, 420°C/24h annealed sample and several quenched samples in the range of 750-850°C/24h. From these results, saturation magnetization was almost constant compared with each sample. The results indicate that the amount of magnetization is independent of the microstructural factors. On the other hand, the coercive was decreased significantly with the increase of the temperature of heat-treatment and it was increased again as the temperature was increased. The coercivity of the quenched sample at 820°C was changed up to 0.22 times as compared with that of as-drawn sample. The improvement of coercivity which is contributing to reduce the energy barrier of domain wall mobility was due to the release of internal strain and dislocation by annealing.
Fig. 4 X-ray diffraction patterns for as-drawn (R.T.), 420°C-FC (furnace cooling) and 820°C-WQ (water quenching) (a) radiating to the angle of drawing direction (D.D.) and the enlarged pattern of the bcc (110) reflection peaks (b) for each specimen showing full width of half maximum (FWHM). The FWHM indicates the internal strain of the crystal lattice or the dislocation density. The values were decreased as the annealing temperature was increased. It is seen that the decrease of FWHM is due to the release of lattice strain and the decrease of grain boundary density by heat treatment.

Next, Fig. 7(a) shows Temperature dependence of the value of saturation magnetostriction, $\lambda_S$ and magnetostrictive susceptibility, $d_m (= d\lambda/dH)$ for each sample. Also, Fig. 7(b) shows the magnetostriction curve for as-drawn sample and heat-treated samples at 420°C/24h, 820°C/5h. From the results, the $\lambda_S$ was decreased with increasing of the temperature of heat treatment. On the other hand, the $d_m$ m was increased significantly due to the quenching at the (bcc+fcc)/bcc phase boundary as a MPB region. In addition, the $d_m$ of the quenched sample at 820°C was 3.5 times as large as that of as-drawn sample. These results indicate that the value of $\lambda_S$ was slightly decreased against the annealing temperature, which is depending on the orientation of the textures of Fe-Co alloys. The $d_m$ is considered to be significantly increased depending on the grain width or the shape of grain boundary which might be a factor in hindering domain wall movement (Panina, et al., 1992).

Fig. 5 Temperature dependence of grain width $d_g$, shape aspect ratio of drawn direction (D.D.) to transverse direction (T.D.) $R_a$, intensity of {110} $<100>$ orientation calculated from inverse pole figure (IPF) and the full width of half maximum, FWHM of Fe-Co alloy wire. By annealing low temperature, $d_g$, $R_a$ and IPF kept almost constant, but the FWHM was decreased. On the other hand, by annealing high temperature and quenching, $d_g$ was increased up to 2 times as large as that of as-drawn sample, and $R_a$ and FWHM were significantly decreased. The intensity of IPF was slightly decreased after annealing at 820°C.
Fig. 6 Temperature dependence of the value of coercive force and saturation magnetization. From these results, saturation magnetization was almost constant compared with each sample. On the other hand, coercive force was decreased significantly with the increase of the temperature of heat-treatment and it was increased again as the temperature was increased. For further understanding of the relationship between microstructure and the magnetic and magnetostrictive properties, we replotted these results quoting the previous data of the as-melt and as-rolled samples in Fe$_{30}$Co$_{70}$ alloys. Figure 8 shows the plots of magnetostriction, $\lambda_s$ against magnetostrictive susceptibility, $d_m$ considering the microstructural factors for the Fe-Co alloy wire. It is seen that the rolling process made their magnetostriction drastically higher due to the strong orientation of crystal texture $\{110\} <100>$ and internal strains. By annealing at 420°C, magnetostriction was greatly decreased because of the release of internal strain caused by restoration of crystal grain. The decrease of magnetostriction and the increase of magnetostrictive susceptibility by as the quenching effect were induced by the decrease of grain boundary density resulting from recrystallization. Regarding to the magnetostrictive properties of 820°C-WQ sample, the increase of magnetostriction might be caused by the quenching at the (bcc+fcc)/bcc phase boundary.

The enhancement of the magnetostrictive characteristics by heat treatment near a MPB and the microstructure effect are unknown well. Therefore, it will become necessary to perform quantitative evaluation by controlling microstructures. Our findings of magnetostriction and the magnetostrictive susceptibility increased not only due to the quenching at the (bcc+fcc)/bcc phase boundary, but also due to effects of lattice strains, orientation and grain boundary density, support the understanding of the magnetic domain mobility contribute to the enhancement of power generation for the Fe-Co alloy system.

Fig. 7 Temperature dependence (a) of the value of saturation magnetostriction and magnetostrictive susceptibility for each sample. And the magnetostriction curve (b) for as-drawn (R.T.), 420°C-FC and 820°C-WQ. From the results, magnetostriction was decreased with increasing of the temperature of heat treatment. On the other hand, the magnetostrictive susceptibility was increased significantly due to the quenching at the (bcc+fcc)/bcc phase boundary as a MPB region.
3.3 Power generation characteristics by drop impact test

For demonstrating the performance of power generation as energy harvesters, we evaluated the power generation characteristics by drop impact test for as-drawn (R.T), 420°C-FC and 820°C-WQ samples of Fe-Co alloys wire.

Figure 9(a) shows an example of output profile with time when a steel ball was dropped on the surface of as-drawn sample. In the figure, the first large waveform has the frequency of about 15 kHz. So, the output voltage might be due to the strain by steel impact. On the other hand, the small waveform in the latter half might be the output voltage generated by the natural vibration after the steel ball was separated from the sample’s surface. At that time, the oscillation frequency was about 140 kHz which is almost same frequency of the natural oscillation. Also, the period of impulsive vibration of 420°C-FC sample was shorter than that of 820°C-WQ sample.

Furthermore, Fig. 9(b) shows the comparison of average value of output power for each specimen calculated from the area of the waveform. At that time, Table 1 shows the value of power generation characteristics such as peak-to-peak voltage, \( V_{p-p} \) and output power \( W \), and the standard deviation of them. From these results, 820°C-WQ sample was the highest value and 420°C-FC sample was the lowest value of output power among them. These differences might be caused not only by the magnetostrictive susceptibility and the quenching effect at the temperature near the (bcc + fcc)/bcc interface, but also the mechanical properties such as Young’s modulus, residual stress.

Narita (2016) elucidated the stress-rate dependence of the output voltage and the effect of the pre-stress by resin embedding for Fe-Co alloy fibers/polymer composites. Also, Hauser, et al. (2004) also proposed that the output voltage characteristics resulting from the local magnetic induction change is induced by a large domain wall jumping. This dynamic behavior of domain walls should be considered to further understand the mechanism of inverse magnetostriction effect.

4. Conclusions

In this study, we evaluated the heat-treatment effect on the wire-drawn Fe_{30}Co_{70} (mol%) sample, and investigated the magnetic, magnetostrictive and power generation characteristics to clarify the relationship between magnetic and magnetostrictive properties, and the microstructural factors such as lattice strain, orientation and grain width.

By annealing at 420°C for 24 h, the internal strain of a crystal lattice was released and by high temperature annealing at 820°C/5h, the average grain width was increased to about 2 times larger than that of as-drawn specimen and the shape aspect ratio got 1.4. The orientation \{110\} <100> of each specimen was decreased slightly.

Regarding to magnetic and magnetostrictive properties, the magnetization and magnetostriction were decreased slightly according to the increase of heat-treatment temperature. While, the magnetostrictive susceptibility of 820°C-WQ sample was 3.5 times larger than that of as-drawn sample.

These results indicate the lattice strain in the crystal grain is related to the coercivity resulting from the domain
wall mobility in the materials. Next, the orientation aligned by the drawing process is related to the magnetostriction. Finally, the grain width, that is, grain boundary density is mainly related to the magnetostrictive susceptibility which might be the important parameter for estimating the power generation performance.

The output power evaluated by drop impact test was reached up to 91 mJ/s for 820°C-WQ sample owing to the high magnetostrictive susceptibility and quenching at the temperature near the (bcc + fcc)/bcc interface. However, it might be important to consider not only the magnetostrictive susceptibility, but also the residual stress because the amount of output voltage of as-drawn sample having much internal strains was higher than that of 420°C-FC sample regardless of magnetostrictive susceptibility.

However, it is still difficult to identify the critical factors related to the enhancement of inverse magnetostriction effect, because these parameters were nothing more than the static or quasi-static properties. Therefore, it is necessary to quantitatively evaluate the dynamics behavior of domain wall or its pinning phenomenon generated at microstructures in detail.

In conclusion, the newly developed Co-rich Fe-Co magnetostrictive alloy wire has a great expectation as energy harvesters or stress sensors by controlling their microstructures.

Fig. 9 An example of output waveform (a) when a steel ball was dropped on the surface of as-drawn sample. From the profiles, the peak to peak voltage and the output power were measured. Comparison of the output power (b) calculated from the area of the waveform for each sample. From these results, 820°C-WQ sample was the highest value and 420°C-FC sample was the lowest value of output power. These differences might be caused not only by the magnetostrictive susceptibility and the quenching effect at the temperature near the (bcc + fcc)/bcc interface, but also the mechanical properties such as Young’s modulus and residual stress.

Table 1 The mean value and standard deviation (SD) of peak to peak voltage and output power calculated from the output profiles for each specimen.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak-peak voltage [V]</th>
<th>Output power [mJ/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>SD</td>
</tr>
<tr>
<td>as-drawn</td>
<td>43.3</td>
<td>1.62</td>
</tr>
<tr>
<td>420°C-FC</td>
<td>35.7</td>
<td>1.61</td>
</tr>
<tr>
<td>820°C-WQ</td>
<td>47.6</td>
<td>2.09</td>
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References


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