Micostructure and Magnetic Properties in Nanostructured Fe and Fe-Based Intermetallics Produced by High-Pressure Torsion

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The microstructure and magnetic properties of nanostructured pure iron, FeCo and FeNi₃ produced by high-pressure torsion (HPT) were investigated. Electron backscattered diffraction (EBSD) technique was used to study the evolutions in microstructure and crystallographic texture during HPT, revealing that a weak deformation texture with an orientation of (110)_{hpc} being parallel to the disc normal for pure iron and FeCo while (110)_{hpc} was found to be parallel to the hoop direction of the HPT disc in FeNi₃. The grain size of the HPTed materials was characterized by means of EBSD and transmission electron microscopy (TEM), and its influence on the coercivity was investigated. The other highlight of this paper is the use of a focused ion beam (FIB)-SEM dual beam instrument. This enabled us to obtain quite high image quality (IQ) values for the EBSD measurements even for the highly deformed microstructure in the current ferromagnetic intermetallics. [doi:10.2320/matertrans.M2014119]

(Received April 3, 2014; Accepted May 29, 2014; Published July 18, 2014)

Keywords: bulk nanostructured metals, severe plastic deformation, electron backscattered diffraction (EBSD), magnetic materials, coercivity, focused ion beam-scanning electron microscope (FIB-SEM)

1. Introduction

It is widely known that coercivity $H_c$ of ferromagnetic materials is highly dependent on material’s microstructure. The coercivity $H_c$ of a material is known to be proportional to $D^{-1}$ when the grain size $D$ exceeds some critical value $l_c$ (referred to as ferromagnetic exchange length $= 35$ nm), while $H_c$ becomes proportional to $D^2$ when $D$ is smaller than the critical grain size. This phenomenon is supported both by theory and experiments. Due to this mechanism, it has been reported that a nanocrystalline Fe-based melt-spun ribbon exhibit an excellent soft magnetic properties.

By the way, severe plastic deformation (SPD) as represented by high-pressure torsion (HPT) has been recognized as a promising method to produce fine grained materials. A tremendous amount of papers have been published on grain refinement by HPT. However, most of those papers have been focusing on the microstructural development and its influence on mechanical properties as expected from the Hall–Petch equation. A question that arises here is whether it is possible to produce soft magnetic materials by cold working such as HPT. Few investigators have studied the influence of the grain refinement by HPT on magnetic properties, except for the work by Scheriau et al. Although, the grain refinements for various metallic materials by HPT have been extensively reported by numerous authors, it has been reported that there is an ultimate minimum grain size that can be achieved for pure metals by HPT. Edalati and Horita stated that HPT deformation at room temperature cannot refine the grain size of most of pure metals below 200 nm. Clearly, this grain size is far above the aforementioned ferromagnetic exchange length $l_c$. Therefore, it seems impossible to produce a good soft magnetic materials from pure ferromagnetic metals.

Alloying might be a possible approach to obtain further refined grain structure. However, the results by Scheriau and his co-workers showed that the HPT deformation of Fe–Co, Fe–Ni solid solution alloys at room temperature did not reach the ferromagnetic exchange length $l_c$.

Meanwhile, it has been reported that several intermetallic compounds reach below 100 nm by HPT. To the best knowledge of the authors, no one has reported on the microstructural development of ferromagnetic intermetallic compounds by HPT deformation and its influence on magnetic properties. We thus have decided to focus on fully ordered ferromagnetic intermetallic compounds.

We narrowed down the candidate materials to FeCo and FeNi₃ since these intermetallic compounds have quite high magnetic saturation moments and thus are considered as good candidates for soft magnetic materials if the grain refinement is successful. Pure iron is also chosen, which is known to exhibit high magnetic moment, which is potentially beneficial to obtain soft magnetic properties.

The purpose of this paper is to present the microstructural developments of FeCo, FeNi₃, Fe, as well as their influence of coercivity. Based on the results, the possibility of tailoring the magnetic properties by HPT deformation is discussed.

2. Experimental

Pure iron (12 ppm C), FeCo and FeNi₃ were arc melted under argon atmosphere, then casted into a cylindrical rod with a diameter of 10 mm. The pure iron ingot was heat treated at 1173 K for 1 h. The homogenization was performed for the FeCo ingot at 1173 K for 3 days, and also for the FeNi₃ ingot at 1273 K for 3 days. The ingots were then sliced by wire electro-discharge machining (EDM) to prepare HPT discs (10 mm in diameter, 0.85 mm in thickness). The final thickness of the HPT discs was controlled by handy-lapping. The discs were then subjected to HPT deformation with a rotation speed of 0.2 rpm. The number of HPT turns $N$ ranged from a half to ten.
The deformed discs were cut into half circular, and then embedded within resins for cross-sectional metallography (OM and SEM/EBSD) and microhardness testing. SEM/EBSD was performed using the orthogonally arranged FIB-SEM instrument. The data collection and the orientation analyses of individual grains during EBSD measurements were conducted using the TSL OIM software. The surface was finished by FIB inside the vacuum chamber of FIB-SEM. It has recently been reported that the surface finished by FIB yields a better image quality (IQ) in EBSD measurements. Microvickers hardness was also measured from the well polished cross sections, whereby the radial position of the individual indentations were measured to quantify the local strain. Magnetization curves were measured using vibrating sample magnetometer (VSM) and partially using superconducting quantum interference device (SQUID). The specimens with a diameter of 1 mm and a thickness of 0.5 mm for VSM and SQUID were cut out from the region at \( r = 3 \) mm of the HPTed discs. The maximum magnetic field applied was 5 T.

Transmission electron microscopy (TEM) was performed using the JEOL-2010F TEM equipped with a field-emission gun operated at 200 kV. In preparing the TEM foils, circular discs with a diameter of 2 mm were cut out of the HPTed discs. The thickness of those discs were then reduced to 0.1 mm by mechanical grinding the outer regions from both the sides so that the discs are taken out from the central region along the thickness direction. Each disc was then glued on a Pt grid. The inner diameter of a grid was 0.5 mm while the outer diameter was 3 mm. Afterward, twin-jet electropolishing was performed to prepare TEM foils using an electrolyte composed of 10% HCl\(_4\) and 90% ethanol at 243 K.

3. Results and Discussions

3.1 Optical microscopy and XRD

The development in microstructure by HPT deformation was first examined by optical microscopy. The typical results are shown in Fig. 1. The grain sizes for all the pre-deformation materials were found to be large enough to visualize by optical microscopy. Those initially coarse grain structures for all the materials seem to be significantly refined by HPT deformation, and the morphology of individual grains is no longer observable with those optical micrographs. The development of the microstructures during HPT deformations will be further demonstrated with electron microscopy as will be shown later in detail.

Figure 2 shows the results of X-ray diffractometry with Co target that was measured for both FeCo and FeNi\(_3\). In this figure, only the certain regions of diffraction angles are shown, thereby showing the superlattice reflections of \( \{100\}\)\(_{\text{BZ}}\) (Fig. 2(a)) and \( \{100\}\)\(_{\text{L1}}\) (Fig. 2(b)). These results together with the selected area diffraction patterns (SADPs) of the as-aged samples (will be shown later) guaranteed that the FeCo and FeNi\(_3\) were well ordered.

3.2 Vickers hardness

The results of the Vickers microhardness testing also indicated that the hardness increased by HPT, being clear evidences of a significant grain refinement. The evolutions of the Vickers microhardness \( H_V \) with the increasing equivalent plastic strains \( \varepsilon_{V,M} \) are shown in Fig. 3. The strain introduced by HPT deformation is quantified as follows. The shear strain, \( \gamma \), is given by the equation:

\[
\gamma = \frac{2\pi rN}{t}
\]  

(1)

where \( r \) is the distance from the center along the radial direction, \( N \) the number of turns, and \( t \) is the thickness of the disc. The equivalent strain \( h_{eq} \) is obtained by substituting \( \gamma \) into the following equation:

\[
h_{eq} = \frac{1}{\sqrt{3}} \ln \left( \frac{2 + \gamma^2 + \gamma \sqrt{4 + \gamma^2}}{2} \right)
\]  

(2)

It is widely known that the strain of an HPTed disc is uniquely determined on the basis of both the increasing distance from the center \( r \) and the number of turns \( N \). As long as the \( r \) and \( N \) for individual indents created by Vickers hardness testing are known, the relation between the hardness. The flow stress \( \sigma \) was obtained using the relation \( \sigma = 3.33H_V \) being used as secondary \( \gamma \)-axis in the figure. The corresponding values of \( r \) and \( N \) to the equivalent strain (or von Mises strain) can be seen at the secondary \( x \)-axis of Fig. 3. The error bars in this figure were calculated from the three different “scans” along the radial direction (i.e., three different sets of hardness measurements were performed
along the radial direction, and a simple arithmetic mean and a standard deviation were estimated for each strain value). The pure iron and FeCo, both are BCC based crystal structure, seem to keep work hardening up to a quite large strain while the work hardening of FeNi₃ appears to cease at a quite early stage of the deformation. Nevertheless, the hardness values of all the materials after reasonable amount of HPT deformation were found to be significantly larger in comparison with the virgin materials, presumably because of the formation of highly refined grains.

3.3 TEM and SEM/EBSD

Electron microscopy (including TEM and SEM/EBSD) is a powerful tool to investigate the microstructure containing very fine grains. As was mentioned, superlattice reflections for FeCo (B2) and FeNi₃ (L₁₂) were observed not only in XRD patterns but also in SADPs as shown in the insets of Figs. 4(a) and 4(b), respectively. This results confirmed more strongly that the FeCo and FeNi₃ prior to deformation were well ordered.

The developments of the microstructures at a much finer scale were investigated by TEM and partially SEM/EBSD for all the materials as shown in Fig. 5. All the TEM specimens were taken from the region where \( r = 3 \text{ mm} \) of an HPTed disc. The minimum grain sizes attained by HPT deformation were 265 nm for pure iron, 152 nm for FeCo and
207 nm for FeNi₃, respectively. The values of the grain size attained after HPT deformations are summarized in Table 1. Furthermore, it was found that the superlattice reflections of FeCo and FeNi₃ that were observed in the as-aged TEM samples disappear after HPT deformation with larger N. It is interesting to note that the ordered structure is lost after N = 1/2 in FeNi₃ while the order remains even after N = 1 in FeCo.

3.4 Deformation texture

Deformation textures formed by HPT deformation for individual materials were investigated by EBSD. The crystallographic orientation is represented based on a cylindrical coordinate (Thickness, Radial, and Hoop directions) instead of the ordinary Cartesian coordinate (i.e., ND, TD, RD) for EBSD analyses. Thickness direction represents a direction parallel to the HPT disc thickness, Radial direction represents the direction parallel to the radius, and Hoop direction represents the direction parallel to the hoop (or circumferential) direction of the HPT discs. The IPF maps and the grain boundary maps were superposed as shown in Fig. 6. The observed region is r = 4 mm of HPTed discs after 10 turns whereby the plastic strain is as high as 6.92. It is found from the grain boundary maps that the majority (~70%) of the grain boundaries are composed from the high angle grain boundaries (HAGBs) at this strain level. It was found that the values of IQs in these EBSD measurements are quite good as shown in Fig. 6, validating the quality of the current EBSD measurements. In fact, when we first attempted an EBSD measurement for the HPTed FeCo it was not successful and thus the IQ value for this case could not be obtained. At that time, the sample surface was finished by mechanical polishing using colloidal silica (0.05 µm) and the EBSD measurement was performed with an SEM equipped

<table>
<thead>
<tr>
<th>N = 1/2</th>
<th>N = 1</th>
<th>N = 10</th>
<th>N = 100</th>
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<tbody>
<tr>
<td>FeCo</td>
<td>319 ± 114 nm</td>
<td>252 ± 147 nm</td>
<td>152 ± 52 nm</td>
</tr>
<tr>
<td>FeNi₃</td>
<td>220–330 nm&lt;sup&gt;1&lt;/sup&gt;</td>
<td>192 ± 92 nm</td>
<td>207 ± 121 nm&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>Fe</td>
<td>394 ± 236 nm</td>
<td>320 ± 236 nm</td>
<td>265 ± 155 nm</td>
</tr>
</tbody>
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<sup>1</sup>The error bar was not estimated.
<sup>2</sup>Measured by EBSD.
with field emission gun (FEG-SEM). The orientations of the HPTed FeCo samples could not be determined within most of the region by the combination of the mechanical polishing and FEG-SEM, while the EBSD scan using the FIB-SEM machine enabled us to index majority of the region of interest with quite high confidence index and the image quality. Although the IQ values obtained by mechanical polishing and FEG-SEM for FeCo and FeNi$_3$ are not available for comparison, it is at least qualitatively clear that the IQ values obtained by the FIB-SEM machine for these two intermetallic compounds become higher.

The IPFs measured by this set of high-quality EBSD measurements are shown in Fig. 7. Our previous work reported that a weak deformation texture is formed by HPT for pure iron, whereby $h110$ becomes parallel to the disc normal. It is interesting to note that FeCo (B2) also resulted in a similar deformation texture. By contrast, the deformation texture observed in HPTed FeNi$_3$ was different from those bcc-based materials. A remarkable feature in FeNi$_3$ is that $h110$ axis is pointing the hoop direction (i.e., the direction of the shear). Languillaume and his co-workers$^{12}$ reported a torsion texture in Ni$_3$Al (which is also L1$_2$) with the $h110$ component being parallel to the shear direction, which is consistent with our EBSD results.

### 3.5 VSM and SQUID

Figure 8 shows the magnetization curves for individual materials. The specimens for VSM and SQUID, with the diameters and the height being 1 mm typically, were all taken from the region $r = 3$ mm of the HPTed discs. This region is essentially the same as the region observed in TEM regarding the equivalent strain introduced.

Two sets of the magnetization curves were measured by applying the magnetic field along the radial and the hoop directions to observe the anisotropy in magnetic properties. Nevertheless, the difference between the magnetization curves along the radial direction and that along the hoop direction was not remarkable. Therefore, only the results for the radial direction is shown in Fig. 8. As was expected from the Slater-Pauling curve,$^{13}$ it was indicated that the saturation magnetizations for pure iron (239 to 249 emu/g) and FeCo (249 to 261 emu/g) are approximately the same while that for FeNi$_3$ is lower. The scatter of the values in magnetization could be due to the machine capability and could also be by the readability of the electric balance that was used to measure the sample weight. Coercivity of materials was measured from the width of the hysteresis loops. Although the width of the hysteresis loop may appear too small to measure the coercivity at the first glance, this becomes possible by magnifying these magnetization curves.

One may notice that the permeability appears to become higher for FeCo after HPT of $N = 100$ as shown in Fig. 8, but this is not really the case. In fact, the specimens used for these magnetic measurements are not the same. Especially, the specimen of FeCo ($N = 100$) is quite thinner than those for as-aged FeCo and $N = 10$ samples. To compensate for this effect, demagnetization correction must be performed to compare these data from the samples with different shapes. However, the specimens used in this study were actually notched along the radial direction so that the shear deformation direction can be recognized. This notch made difficult to estimate the demagnetization factor for these samples. We therefore gave up discussing the difference in permeability which would be strongly affected by the shape of specimens. Instead, we focus on discussion on coercivity that is considered to be independent of the shape of specimens.

The relation between the coercivity and the grain size can now be plotted as shown in Fig. 9. The data obtained by Herzer$^{1}$ and by Scheriau and his co-workers$^{3}$ are plotted together. It seems that the coercivity of both pure iron and FeCo increases with the decreasing grain size in accord with the $D^{-1}$ law. Our results show reasonable agreement with the data reported by Scheriau et al.$^3$ Curiously, the coercivity for FeNi$_3$ did not change with the significant decrease in grain size. Careful observation allows us to notice that the extended
trend line of the coercivity for the HPTed FeNi3 almost coincides with the data of Permalloy that was reported by Herzer.\textsuperscript{1)} The chemical composition of Permalloy, which is a fully solid solution, is in fact very similar to FeNi3. On the other hand, the SADPs of the FeNi3 even after the HPT deformation of a half turn in Fig. 5 indicates that the HPTed FeNi3 is disordered. Therefore, it is not surprising that the trends of the HPTed FeNi3 and cold-rolled Permalloy are similar. After all, it seems conclusive that the minimum grain size attained by HPT deformation in pure iron, FeCo, and FeNi3 can never be below 100 nm and thus the coercivity follows the $D^{-1}$ law.

It might be interesting to apply aging treatment for the HPTed intermetallic compounds. Mangler \textit{et al.}\textsuperscript{14,15)} demonstrated that the post-HPT aging treatment in FeAl B2 intermetallics yields a fairly refined microstructure with a grain size of about 5 nm, which is way too small compared to the grain size after the HPT deformation. They concluded that this grain refinement during heating is due to the recurrence of the chemical long-range order that is ruined by the HPT deformation. It would be expected that the further extraordinary grain refinement occurs by post-deformation aging treatment in our materials as well.

4. Conclusions

The influences of HPT deformation on microstructure and crystallographic texture as well as on magnetic properties of magnetic intermetallics were investigated. The following conclusions were obtained. The grain size attained by HPT deformation can not be smaller than 100 nm. Hence, the coercivity obtained by HPT deformation was found to be limited by the intersection of $D^6$ law and $D^{-1}$ law. It seems difficult to obtain soft magnetic properties by HPT deformation only.

The deformation texture formed by HPT deformation in FeCo and pure iron consists of the (110) component being parallel to the disc normal, while the texture formed in FeNi3 was found to consist of the (110) axis being parallel to the hoop (i.e., shear) direction.

\textbf{Acknowledgment}

This work is supported by a Grant-in-Aid for Scientific Research from the MEXT, Japan, in Innovative Areas “Bulk Nanostructured Metals”.

\textbf{REFERENCES}