The Effect of Cold Working on the Precipitation of Co-Fe-Nb Semihard Magnetic Alloys

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The effect of cold working on the magnetic properties and the precipitation morphology of Co-Fe-Nb alloys has been investigated by means of hysteresis loop measurements and transmission electron microscopy.

The results obtained are summarized as follows:

(1) The solution treated and 50% cold rolled specimens show a peak value of coercive force when they are annealed at 800°C for 1 h. While, this peak occurs when the specimen heavily cold worked by 97.8% is annealed at 700°C for 1 h. The squareness ratio and the rectangularity increase as the cold working rate increases.

(2) In the solution treated and 50% cold rolled specimens, the precipitates are in the form of a thin platelet, while in the alloy is cold worked heavily by 97.8%, the precipitates become spherical. The structure of the precipitates is confirmed to be a hexagonal Laves phase Co_3Nb .

(3) Magnetic hardening of the heavily cold worked alloy is attributed to the precipitation of spherical Co_3Nb .

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I. Introduction

We have developed semihard magnetic alloys of the Co-Fe-Nb system for remanent reed contact applications⁽¹⁾⁽²⁾.

Previous studies have revealed that the magnetic hardening of those alloys is attributed to the precipitation of intermetallic compounds containing Nb from the matrix during annealing.

In the sheet specimens which were cold rolled lightly by 10% reduction in area, we have already reported that the precipitate is a hexagonal Laves phase Co_3Nb in the form of platelets and the plane of these platelets in laminar form are oriented parallel to the (111) plane of the *fcc* matrix⁽³⁾.

The Co-Fe-Nb alloys exhibit high squareness ratios and rectangularity of hysteresis loops on annealing after cold working by more than 90% reduction in area. For this reason, these alloys are used practically after heavy cold working and annealing.

In this paper, we have investigated the morphology of the precipitates of heavily cold

rolled Co-Fe-Nb alloy sheets together with the solution treated and 50% cold-rolled ones.

II. Experimental Procedure

Chemical composition of the alloy used in the present investigation is shown in Table 1.

As shown in Fig. 1, the vacuum-melted alloy was processed to sheet specimens of 100 μm thickness in a series of hot working and cold rolling operations with several intermediate annealings at 1150°C. The final cold reduction rate in area was selected at three levels, 0% (as solution treated), 50% and 97.8%. Then these specimens were annealed at various temperatures from 600 to 900°C in vacuum.

For the magnetic measurements, Cioffi type recording fluxmeter was used for the tapes of 0.2 m length in the direction parallel to the rolling direction.

For the observation by transmission electron

Table 1 Chemical composition of the specimen investigated. (wt%)

Nb	Ta	C	Si	Fe	Co
2.98	0.16	0.012	0.07	11.96	Bal.

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Fig. 1 Process of Co-Fe-Nb alloy sheets.

microscope, the heat treated sheets were electrolytically polished in a solution of 23% $\text{HClO}_4\text{-C}_2\text{H}_5\text{OH}$ and the thinned specimens were examined in Hitachi HU-11A and JEOL JSEM-200B electron microscopes operating at 100 and 200 kV, respectively.

III. Results

Figure 2 shows the variation in coercive force as a function of annealing temperature for the specimens subjected to various amounts of cold working.

The broadened peak of coercive force is observed at an annealing temperature of about 700°C in a 97.8% cold rolled specimen. The peak temperature of coercive force rises to about 800°C for the solution treated and 50% cold rolled specimens. It is concluded that the precipitation temperature is mainly determined by the amount of prior cold working, that is,

Fig. 2 Effect of annealing temperature on the coercive force of Co-Fe-Nb alloy sheets. The magnetization direction is parallel to the rolling direction.

R.A.: Reduction rate in area

the lesser the degree of cold working, the higher the precipitation temperature, as the increase in coercive force is directly explained by the onset of the precipitation.

Examples of hysteresis loops taken for the specimens which are annealed at the temperatures for the maximum coercive force are shown in Fig. 3.

As shown in Fig. 3, the squareness ratio (Br/B_{100}) and rectangularity ($\sqrt{(BH)_{\max}}/BrH_c$) are relatively poor for the solution treated and 50% cold rolled specimens because of their weakness of the rolling texture. However, the squareness ratios of more than 0.9 are obtained for the 97.8% cold rolled specimen, because the amount of the (110), $[1\bar{1}2]$ rolling texture is considerably increased in this specimen⁽⁴⁾.

Photograph 1(a) and (b) show the electron micrographs for the solution treated and 50% cold rolled specimens annealed at 800°C for 1 h, respectively. Plate-like precipitates can be observed in both specimens and the precipitates

Fig. 3 Effect of cold working on the hysteresis loops of Co-Fe-Nb alloy sheets. The magnetization direction is parallel to the rolling direction.

R.A.: Reduction rate in area

Photo. 1 Electron micrographs of Co-Fe-Nb alloy annealed at 800°C for 1 h.

- (a) Reduction rate in area: 0%
(b) Reduction rate in area: 50%

are identified to be a hexagonal Laves phase $\text{Co}_3\text{Nb}^{(3)}$. Also, the direction of the orientation of Co_3Nb precipitates in the matrix is confirmed to be

$$(111)_{\text{matrix}} // (0001)_{\text{Co}_3\text{Nb}}, \\ [11\bar{2}]_{\text{matrix}} // [10\bar{1}0]_{\text{Co}_3\text{Nb}}.$$

This form of precipitation is characteristic of the moderately cold rolled or solution treated specimens. In other words, the growth of the precipitate parallel to the c-axis of hexagonal Co_3Nb is suppressed and only the growth within a basal plane is promoted.

The deformation-induced substructure of the 97.8% cold rolled specimen is shown in Photo. 2(a). The contribution of such a deformation-induced substructure is not very effective in the increase of the coercive force, because the coercive force of this specimen is mostly about 477 A/m. Photograph 2(b) shows the microstructure of the 97.8% cold rolled specimen annealed at 700°C for 1 h. By this heat treatment, spherical shaped precipitates appeared

Photo. 2 Electron micrographs of 97.8% cold rolled Co-Fe-Nb alloy.

- (a) As rolled.
(b) Annealed at 700°C for 1 h.

in a deformation-induced substructure and the coercive force of this specimen increased to 1830 A/m. The precipitates range from 0.04 to 0.25 μm in size and are located about 0.05 ~ 0.30 μm apart.

We tried to identify these precipitates by the selected area electron diffraction method, but it was difficult to determine the structure because of the very weak intensity of the diffracted beams. So, we tried to prepare overaged specimens in order to grow the precipitates large enough for the identification. Three different annealing conditions were selected; 700°C for 30 h and 800 and 900°C for 1 h.

Figure 4 shows the hysteresis loops of each specimen. The coercive force is decreased by overaging, but the squareness ratio shows a high value due to the presence of the (110), $[1\bar{1}2]$ rolling texture⁽⁴⁾.

The electron micrograph of each specimen is shown in Photo. 3(a), (b) and (c). It is observed that the recrystallized region coexists with the deformation-induced substructure in

Fig. 4 Hysteresis loops of overaged Co-Fe-Nb alloy sheets. The magnetization direction is parallel to the rolling direction.

Reduction rate in area: 97.8%

the matrix of the specimens annealed at 700°C for 30 h and 800°C for 1 h. For the specimen annealed at 900°C for 1 h, the deformation-induced substructure is not observed in the matrix. Spherical precipitates are observed in all the specimens.

As stated already, the contribution of the deformation-induced substructure to the increase of coercive force is relatively small, it is reasonable to say that the coercive force of these specimens depends mainly on the morphology of the spherical precipitates.

Photograph 4(a) shows an electron micrograph of the specimen annealed at 700°C for 30 h and Photo. 4(b) shows a selected area electron diffraction pattern from the precipitates which sticks out at the edge of the hole of the specimen. This pattern is well accounted for by assuming that the direction of the incident electron beam is parallel to the $[11\bar{2}1]$ direction of the hexagonal Laves phase Co_3Nb . Therefore, the precipitates appeared in the heavily

Photo. 3 Electron micrographs of 97.8% cold rolled Co-Fe-Nb alloy.

- (a) Annealed at 700°C for 30 h.
- (b) Annealed at 800°C for 1 h.
- (c) Annealed at 900°C for 1 h.

cold rolled specimen are identified to be the hexagonal Co_3Nb , regardless of a considerable difference in the precipitation morphology of the plate-like Co_3Nb .

The matrix of this alloy consists of mostly of the *fcc* phase, but the spots from the *bcc* phase are also observed as shown in Photo. 4(c). This may possibly be due to a small quantity of the Fe-rich *bcc* phase which is formed in the vicinity of the cobalt-rich precipitate Co_3Nb .

Photograph 5 shows an X-ray spectrum taken

Photo. 4 (a) Electron micrograph of Co-Fe-Nb alloy annealed at 700°C for 30 h.
(b) Electron diffraction pattern of the alloy.
(c) Key diagram of (b). ● Co₃Nb ▲ fcc ■ bcc

for precipitate (A) and matrix (B) of the specimen annealed at 800°C for 1 h using an energy dispersion analysis system. It is observed that the niobium content in the precipitate is much greater than in the matrix. Therefore, it may be considered that the greater part of niobium exists in the precipitate phase Co_3Nb .

IV. Discussion

We have found that there exist two types of morphology in the precipitation of the intermetallic compound Co_3Nb in the Co-Fe-Nb system.

One type is thin platelets formed in the specimens which are solution treated or cold rolled by less than 50% reduction in area, and the other is spherical particles in the 97.8% cold rolled specimen. As pointed out by Kelly and Nicholson⁽⁵⁾, in most cases the precipitates take the form of thin platelets when the atomic misfit between matrix and precipitate is larger than 5% to release the strain energy. In the Co-Fe-Nb system, however, this phenomenon

is observed only in the solution treated or moderately cold rolled specimens of which lattice distortion of the matrix due to cold working is relatively small. It is considered that the strain in the matrix caused by precipitation does not have any dominant effect on the growth direction of the precipitates when the alloy is cold worked by more than 90% reduction in area, because a large amount of the lattice strain is already introduced into the matrix. We suppose that this is a reason why the shape of the precipitate Co_3Nb becomes spherical.

When a cold-worked supersaturated solid solution is annealed, the recovery rate of the deformation-induced substructure and the precipitation rate are both dependent on temperature and the amount of prior cold working, and are closely related to each other. Photograph 3(a), (b) and (c) show that the shape of the precipitates in the region which has already recovered is spherical. This indicates that the precipitation precedes the recovery of the deformation-induced substructure even in the

Photo. 5 X-ray spectrum obtained from precipitate (A) and matrix (B) of Co-Fe-Nb alloy using an energy dispersion analysis system. (97.8% cold rolled; 800°C, 1 h)

97.8% cold rolled specimen. If the recovery of the matrix could precede the precipitation of Co_3Nb , the precipitates may have a platelet shape as observed for the specimens which are solution treated or moderately cold worked (Photo. 1). Photograph 3(a) and (b) are regarded as the typical examples, showing that the recrystallization front plane⁽⁶⁾ is moving through the matrix being intersected by the spherical precipitates of Co_3Nb .

V. Summary

(1) The solution treated and 50% cold rolled specimens show a peak value of coercive force when they are annealed at 800°C for 1 h. This peak occurs on annealing at 700°C for 1 h in the alloy cold worked by 97.8%. The squareness ratio and the rectangularity increase as the cold working rate increases.

(2) In the solution treated and 50% cold rolled specimens, the precipitates have the form of thin platelets, while in the alloy cold worked

by 97.8%, the form of precipitates becomes spherical. The structure of the precipitates is confirmed to be a hexagonal Laves phase Co_3Nb .

(3) Magnetic hardening of the heavily cold worked alloy is attributed to the precipitation of spherical Co_3Nb .

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