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Citation: *Applied Physics Letters* **94**, 153105 (2009); doi: 10.1063/1.3119663

View online: <http://dx.doi.org/10.1063/1.3119663>

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Coercivity of nanoporous Ni produced by dealloying

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(Received 27 February 2009; accepted 26 March 2009; published online 14 April 2009)

Nanoporous Ni specimens with the ligament lengths of 10–210 nm were produced by the dealloying of Ni_{0.25}Mn_{0.75} alloy and annealing at 473–873 K. The coercivity (H_c) increased with increasing ligament length (L) up to 50 nm, and decreased with increasing L above 50 nm. At $L < 50$ nm, the size dependence of H_c for nanoporous Ni is lower than that for nanocrystalline Ni. The low size dependence of H_c is discussed on basis of a random anisotropy model. © 2009 American Institute of Physics. [DOI: 10.1063/1.3119663]

Recently, many research studies on the preparation, characterization, properties, and applications of nanosized materials in various fields have been performed because of the unique electronic, optical, magnetic, and chemical properties of nanosized materials that are greatly different from those of bulk materials.^{1–7} For example, nanosized materials exhibit unique magnetic properties, namely, magnetic nanoparticles exhibit superparamagnetism,^{5–8} and also ferromagnetic nanocrystalline metals have a very low coercivity.^{9,10}

Nanoporous metals have been developed by the selective electrochemical dealloying of more active components in homogeneous alloys.^{11–15} Sun *et al.*¹⁶ showed that nanoporous Ni exhibits a higher coercivity and a lower saturation magnetization than bulk Ni. However, the magnetic properties of the nanoporous metals have not been understood sufficiently. The ligament lengths or pore sizes of the nanoporous metals can be varied by postprocessing treatments, such as annealing and immersion in an acid solution.^{12,13} In this study, nanoporous Ni specimens with the ligament lengths of 10–210 nm are produced by the dealloying of Ni_{0.25}Mn_{0.75} alloy and annealing, and the relationship between coercivity and ligament length is investigated.

Commercially available Ni (>99.9%) and Mn (>99.9%) ingots were melted together by arc melting under Ar atmosphere to prepare a precursor Ni_{0.25}Mn_{0.75} alloy ingot. Subsequently, the alloy ingot was annealed at 1173 K for 24 h, quenched in water, and ground to remove surface oxides. After cold rolling of the alloy, nanoporous Ni was produced by the selective electrochemical dealloying. A three-electrode electrochemical cell controlled by a potentiostat (HZ-5000 by Hokuto Denko) was used. Dealloying was carried out at room temperature using a platinum electrode as a counter electrode and 1 mol/l (NH₄)₂SO₄ as an electrolyte. The alloy was held at an applied electrochemical potential of –650 mV (versus a saturated calomel electrode) for 24 h until no current was detected.

Figure 1 shows a scanning electron micrograph (a) and the ligament length distribution (b) of an as-processed nanoporous Ni specimen. The average ligament length and standard deviation of this specimen were 10 and 3.0 nm, respectively. The x-ray diffraction (XRD) measurement on the as-

processed specimen revealed that the specimen is fcc nickel. XRD patterns of the samples indicated crystal face orientation due to the cold rolling prior to dealloying;¹³ thus the samples were mechanically pulverized to powdery form for randomization of the orientation before the magnetization hysteresis measurement. To vary the ligament length, annealing was carried at 473, 573, 673, 773, and 873 K for 15 min in an inert gas. The ligament length was determined to be 11 nm for the specimen annealed at 473 K, 18 nm for the specimen annealed at 573 K, 33 nm for the specimen annealed at 673 K, 79 nm for the specimen annealed at 773 K, and 210 nm for the specimen annealed at 873 K, where more than 100 ligaments are measured by scanning electron microscopy observations.

Magnetization hysteresis loops were recorded at room temperature using a vibrating sample magnetometer, and the coercivity of nanoporous Ni was investigated, as exemplified in Fig. 2(a). Figure 2(b) shows the relationship between the coercivity and ligament length of the nanoporous Ni. Note that the coercivity (H_c) increases with increasing ligament length (L) up to 50 nm, and decreases with increasing L above 50 nm. This size dependence of coercivity for the nanoporous Ni agrees with those for the nanoparticle⁷ and nanocrystalline Ni.¹⁰ The energy of a magnetic particle is proportional to its size or volume via the number of magnetic molecules in a single magnetic domain. When the energy is comparable to the thermal energy, thermal fluctuations significantly reduce the total magnetic moment. This is responsible for the low coercivity of nanoparticles because the di-

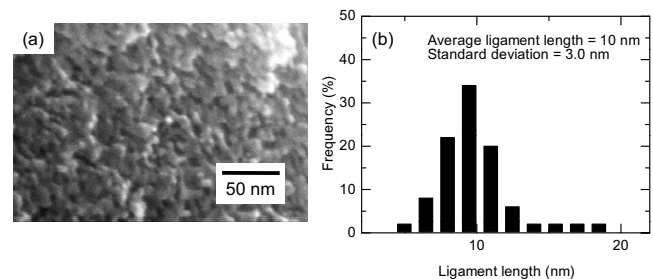


FIG. 1. Scanning electron micrograph (a) and ligament length distribution (b) of as-processed nanoporous Ni. The nanoporous Ni is produced by the dealloying of Ni_{0.25}Mn_{0.75} alloy. The average ligament length of the as-processed nanoporous Ni is 10 nm.

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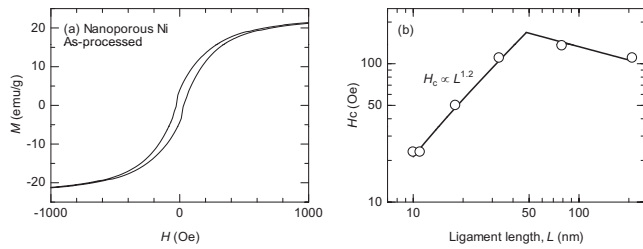


FIG. 2. (a) Magnetization hysteresis loop for as-processed nanoporous Ni. (b) Relationship between coercivity (H_c) and ligament length (L) for nanoporous Ni. H_c increased with increasing L up to 50 nm, and decreases with increasing L above 50 nm. In a range below the critical size, H_c was proportional to $L^{1.2}$.

ameters of nanoparticles are very small.^{5–8} However, the nanoporous Ni has a large volume, compared with the nanoparticles. Therefore, a decrease in coercivity with decreasing ligament length for the nanoporous Ni is unlikely to be attributed to the thermal fluctuations.

It is known that for ferromagnetic nanocrystallines, a decrease in coercivity depends on D^6 , where D is the grain size.^{9,10} According to a random anisotropy model,⁹ the effective local magnetic anisotropy $\langle K_1 \rangle$ can be given by¹⁷

$$\langle K_1 \rangle \approx K_1 \left(\frac{D}{\varphi \sqrt{A/K_1}} \right)^{2n/(4-n)}, \quad (1)$$

where K_1 is the local magnetic anisotropy, φ is a constant, A is the exchange stiffness, and n is the dimension of exchange length. In the case of nanocrystalline metals, n is 3, and therefore, the coercivity of nanocrystallines is expected to depend on D^6 . However, it is of interest to note that a decrease in coercivity for the nanoporous Ni proportionally depends on $L^{1.2}$, where L is the ligament length, as shown in Fig. 2.

A transmission electron micrograph of the as-processed nanoporous Ni specimen is shown in Fig. 3. It can be seen from the electron diffraction pattern that the grain size of the

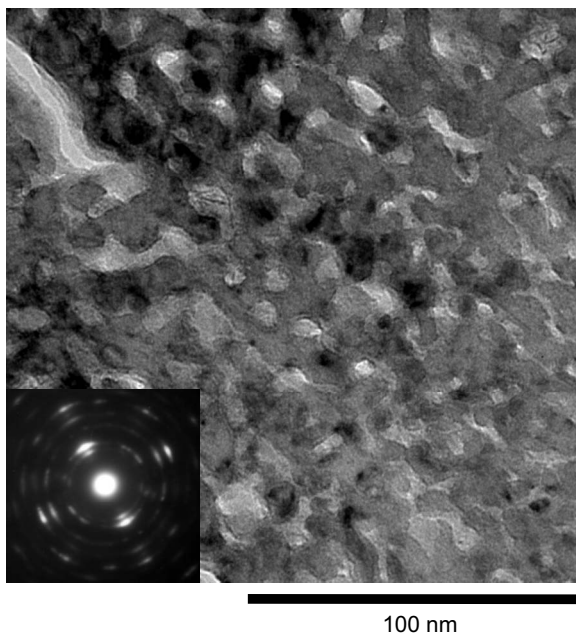


FIG. 3. Transmission electron micrograph and electron diffraction pattern of as-processed nanoporous Ni. The electron diffraction pattern shows that the grain size of the nanoporous Ni is not of the nanometer order.

nanoporous Ni is not of the nanometer order. Note that, for the nanoporous Ni, grain size is much larger than exchange length; however, ligament length is comparable to exchange length.

Considering ligament configurations where needlelike and filmlike ligaments exist, it is reasonable to consider that n is 1–2 for the nanoporous Ni. Assuming that n is 1.5, the size dependence of coercivity is 1.2 from Eq. (1). This value is in agreement with the experimental result in Fig. 2. Therefore, it is suggested that the minimum unit related to the local magnetic anisotropy is the ligament and the dimension of exchange length in the ligament is 1–2, resulting in the low size dependence of coercivity for the nanoporous Ni.

The critical size, below which coercivity decreased with decreasing ligament length, was about 50 nm for the nanoporous Ni, as shown in Fig. 2. This value is much larger than the critical grain size for the nanocrystalline Ni (13 nm).¹⁰ In addition, the coercivity of nanoporous Ni at a ligament length of 79 nm is about twice larger than that of the nanocrystalline Ni at the critical grain size.¹⁰ Previous studies^{18,19} also showed that a ferromagnetic nanostructured network with hundreds of nanometers gives rise to an increase in coercivity. It has been shown that the enhancement of the local magnetic anisotropy is responsible for an increase in coercivity in the nanocrystalline Ni, whose coercivity is five times as large as that of the bulk Ni.¹⁰ However, the coercivity increased by a factor of 10 in the nanoporous Ni, compared with the bulk Ni. Such a large increase in coercivity cannot be explained only by the enhancement of the local magnetic anisotropy. The noncollinear magnetic order at the surfaces strongly affects the magnetization of nanoparticles.^{7,20,21} Similarly, the surface effect due to noncollinear magnetism plays an important role in the magnetization of the nanoporous Ni. This reduces the exchange stiffness, resulting in an increase in the coercivity of the nanoporous Ni. Recently, it has been reported that a significant degree of shrinking occurs during dealloying,²² indicating the presence of a large residual stress in the nanoporous Ni specimens. The residual stress,²³ which is not completely relaxed by annealing, may also give rise to the increase in coercivity in the nanoporous Ni.

In conclusion, the coercivity of nanoporous Ni decreased with decreasing ligament length in a range below the critical size of about 50 nm. This trend for the nanoporous Ni is the same as those for the nanoparticles and nanocrystallines. However, the size dependence of coercivity for the nanoporous Ni is lower than those for the other materials. It is suggested that the dimension of exchange length in the ligament is 1–2 for the nanoporous Ni, resulting in the low size dependence of coercivity.

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