

Structure and magnetic properties of FePt and FePt–Ag nanostructured magnets by cyclic cold rolling

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This paper reports phase components, nanostructure, coercivity mechanism, and hard magnetic properties of FePt and FePt–Ag bulk nanostructured magnets prepared by cyclic cold rolling and subsequent annealing. Annealing temperature of 500 °C or higher and annealing time of 120 min or longer are necessary for the as-rolled nanolaminate foils to complete the diffusion and ordering phase transformation. The addition of a small amount of Ag to the as-rolled Fe/Pt foils results in an increase of both the ordering temperature and relative volume fractions of Fe₃Pt and FePt₃ phases. The diffusion and phase formation mechanism linked to the specific nanostructures of the cold-rolled foils are discussed. The coercivity mechanism of FePt and FePt–Ag nanostructured magnets is analyzed by Gaunt's domain-wall pinning model. © 2006 American Institute of Physics. [DOI: 10.1063/1.2169545]

Cyclic cold rolling is expected to get uniform and highly textured nanostructure, which is essential in attainment of record-high $(BH)_{\max}$ in either FePt/Fe nanocomposites or FePt single-phase nanostructured magnets.^{1–3} On the other hand, the addition of a small amount of Ag results in obviously reducing the ordering temperature of forming face-centered-tetragonal (FCT) FePt phase and further increasing the magnetic properties in the self-assembled FePt–Ag nanoparticles and sputtered FePt–Ag thin films.^{4,5} This paper reports phase components, nanostructure, coercivity mechanism, and hard magnetic properties of FePt and FePt–Ag bulk nanostructured magnets prepared by cyclic cold rolling and subsequent annealing.

For the preparation of equiatomic FePt, the cyclic sheath cold rolling of a composite stack of 12 bilayers of Fe and Pt foils {Fe(75 μm)/Pt(100 μm)}₁₂ was used to create a nanolaminate Fe/Pt foil. The Ag-added samples were prepared with starting architecture of 12 quadrilayers of Fe, Pt, and Ag foils {Fe(50 μm)/Ag(20 μm)/Fe(25 μm)/Pt(100 μm)}₁₂, in which Ag is 7.1 wt %. In a given rolling cycle of about 100 passes, the total thickness was reduced by a factor of 10. The sample was submitted to four such rolling cycles without intermediate heat treatment. The details about preparation of the as-rolled foils are given in the Ref. 6. The as-rolled foils were about 20 × 12 × 0.1 mm³ in size. Samples of 4 × 3 × 0.1 mm³ were cut from the central part of the foils and then annealed at temperatures ranging from 455 to 1010 °C for 20–210 min with a 19 T out-of-plane magnetic field. The annealed samples from the as-rolled Fe/Pt and Fe/Pt–Ag foils are noted as FePt and FePt–Ag, respectively. Magnetic annealing with a 19 T out-of-plane field was per-

formed for all the samples, as it resulted in an improvement in the magnetic properties of FePt nanostructured magnets due to a magnetic-field-induced enhancement of (001) out-of-plane texture of the FePt hard phase and promotion of the solid-state phase transformation.^{3,7} Phase components of the samples were identified by x-ray diffraction (XRD). The average grain sizes of the fct FePt phase were calculated from the (200) diffraction peak using the Scherrer formula. The lattice parameters of the fct phase were deduced from its XRD data and the absolute error was less than 0.002 Å. The magnetic properties were measured using a superconducting quantum interference device (SQUID) magnetometer in fields up to 6.5 T.

Scanning electron microscopy images of the as-rolled Fe/Pt and Fe/Pt–Ag nanolaminate foils showed that the individual layer thickness after four deformation cycles was of the order of several tens of nanometers, in agreement with the bulk reduction factor ($\approx 10^4$).⁶ In the as-rolled samples, the main XRD peaks are characteristic of Pt; the reflections from both Fe and Ag are very weak due to the fact that their atomic weights are much less than that of Pt and the top layer is Pt which is more chemically stable in the air.

Annealing the as-rolled Fe/Pt foils at temperatures ranging from 455 to 555 °C leads to a formation of nanostructured fct FePt phase, accompanied by a small amount of FePt₃ phase (see Fig. 1). The FePt₃ phase obviously decreases after annealed at 500 °C for 210 min or 555 °C for 120 min. Similarly, for the Ag-added samples, annealing at 455 °C or above leads to the formation of a mixture of nanostructured fct FePt and FePt₃ phases. However, the relatively strong intensities of the (111) and (220) diffractions peaks of the FePt₃ indicate a great relative volume fraction of FePt₃ phase in the FePt–Ag sample annealed at 450 °C for 20 min (see Fig. 2). Both high anneal temperature and long anneal

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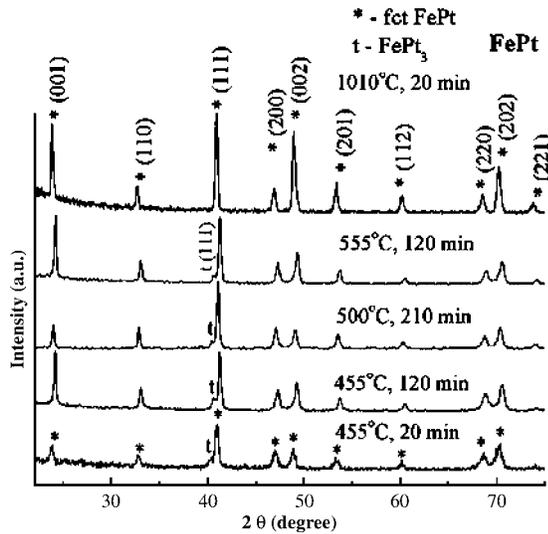


FIG. 1. XRD patterns of the FePt samples annealed with a 19 T out-of-plane field at (a) 455 °C for 20 min, (b) 455 °C for 120 min, (c) 500 °C for 210 min, (d) 555 °C for 120 min, and (e) 1010 °C for 20 min.

time benefit completion of the diffusion of Fe and Pt atoms and the ordering phase transformation to completely form fct FePt for both as-rolled Fe/Pt and Fe/Pt–Ag foils. Especially, a single fct FePt phase was obtained in the FePt sample annealed at 1010 °C for 20 min (see Fig. 1). However, a small amount of FePt₃ still exists in the FePt–Ag sample even after annealed at 1010 °C for 40 min (Fig. 2).

It should be noted that a Fe-rich Fe₃Pt phase should coexist with the Pt-rich FePt₃ phase in both the annealed FePt and FePt–Ag samples and its content should also decrease with increasing the anneal temperature or the anneal time. Due to the overlapping of some diffraction peaks of the Fe₃Pt and FePt phases and possible low content of Fe₃Pt at the sample surface, the Fe₃Pt cannot be identified from the XRD patterns. However, it was observed in the cross-section scanning electron microscopy images.⁸

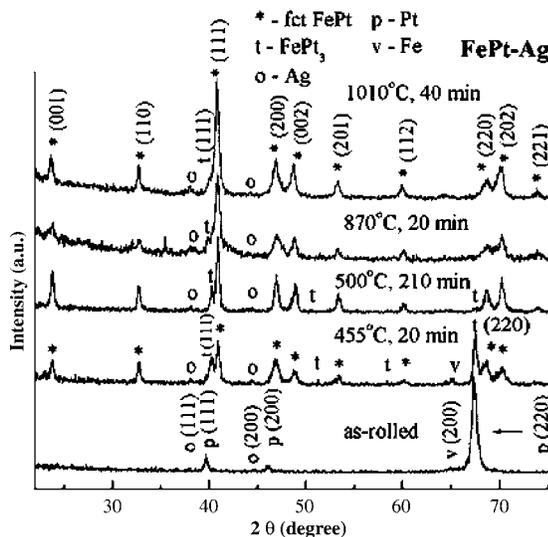


FIG. 2. XRD patterns of the FePt–Ag samples annealed with a 19 T out-of-plane field at (a) 455 °C for 20 min, (b) 500 °C for 210 min, (c) 870 °C for 20 min, and (d) 1010 °C for 40 min. XRD pattern of as-rolled Fe/Pt–Ag is also given here.

TABLE I. Magnetic properties at 300 K and average grain sizes D of the fct phase for the FePt and FePt–Ag samples. Error bars for $\mu_0 H_c$, J_r , $(BH)_{\max}$, and D are 0.5%, 0.5%, 1%, and 10%, respectively.

Samples and Anneal conditions	$\mu_0 H_c$ (T)	$(BH)_{\max}$ (kJ/m ³)	J_r (T)	D (nm)	
FePt	455 °C, 20 min	0.76	41.3	0.57	14
	455 °C, 120 min	0.75	46.0	0.56	17
	500 °C, 210 min	0.71	65.9	0.64	21
	555 °C, 120 min	0.61	44.2	0.53	22
	1010 °C, 20 min	0.38	38.4	0.57	19
FePt–Ag	455 °C, 20 min	0.27	4.2	0.31	11
	500 °C, 210 min	0.72	38.4	0.46	17
	870 °C, 20 min	0.43	36.4	0.58	12
	1010 °C, 40 min	0.18	7.7	0.42	14

As discussed above, unlike reducing the ordering temperature of hard phase in the self-assembled FePt–Ag nanoparticles and sputtered FePt–Ag thin films,^{4,5} the addition of 7.1 wt % Ag to the as-rolled Fe/Pt nanolaminate foils results in an increase of both the ordering temperature and relative volume fractions of FePt₃ and Fe₃Pt phases. This is due to the diffusion and phase formation mechanism linked to the specific nanostructures of the cold-rolled Fe/Pt and Fe/Pt–Ag foils. The formation of FePt (fct) in as-rolled nanolaminate foils should occur at interfaces of Fe and Pt at 455 °C. However, the inserted Ag layers in the as-rolled nanolaminate Fe/Pt–Ag foils acts as a barrier to further diffusion of Fe and Pt atoms which is essential to form the fct phase, resulting in Pt (Fe) rich zones and an increase of FePt ordering temperature. This role of Ag layers is dominant in the samples annealed at relatively low temperatures and short time, such as 455 °C for 20 min. With increasing the anneal temperature or the anneal time, the diffusion rate and therefore the diffusion distance of Fe and Pt atoms and density of fct FePt nuclei increase. Consequently, a more homogeneous grain nanostructure could be formed in the FePt–Ag samples, resulting in a decrease of the content of both FePt₃ and Fe₃Pt phases.

It is noteworthy that lattice parameters a , c of the fct phase are 3.854, 3.714 Å and 3.868, 3.731 Å in the FePt and FePt–Ag samples annealed at 1010 °C, respectively. Thus, the addition of Ag results in a volume expansion of the unit cells of the fct FePt lattice by 1.2%. This indicates that a part of Ag atoms have been introduced into the lattice sites of the fct FePt phase because the atomic volume of Ag (10.3 cm³/mol) is larger than those of Fe (7.1 cm³/mol) and Pt (9.1 cm³/mol).⁴ On the other hand, Ag can be observed in all the annealed FePt–Ag samples (see Fig. 2), indicating some of Ag exists at the grain boundaries. Ag has low solubility with both Fe and alloys with Pt, also has a low surface energy, and is easy to segregate at the grain boundaries.^{4,6} Thus, Ag was interleaved between Fe foils with the intension of reducing grain growth rate of the FePt phase formed during the annealing. From Table I, it is clearly seen that the addition of Ag decreases the grain sizes of the fct phase. For example, the average grain sizes of the fct phase are 21 and 17 nm for the FePt and FePt–Ag samples annealed at 500 °C for 210 min, respectively.

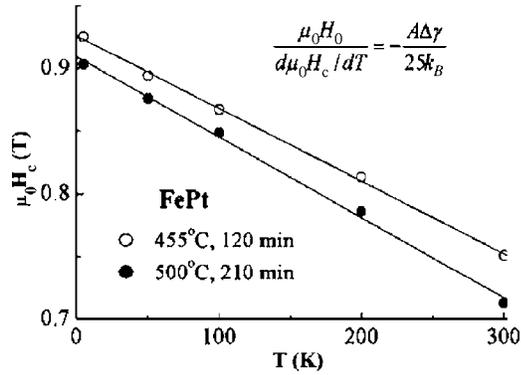


FIG. 3. Dependence of coercivity on temperature for the FePt samples annealed at 455 °C for 120 min and 500 °C for 210 min, respectively.

The domain-wall pinning makes an important contribution to the coercivity of the FePt alloys.⁹ The motion of the magnetic domain walls should be inhibited by the high anisotropy phase as “magnetic pin,” which is fct FePt phase here. The grain boundaries of the fct phase and other inhomogeneous phase ingredients, such as Ag in this paper, can also act as effective pinning sites. According to Gaunt’s domain-wall pinning model,¹⁰ the temperature-dependent coercivity $\mu_0 H_c$ satisfies the equation

$$\frac{\mu_0 H_0}{d\mu_0 H_c/dT} = -\frac{A\Delta\gamma}{25k_B}$$

where $\mu_0 H_0$ is the coercivity at 0 K, k_B is the Boltzmann constant, A represents the area of domain wall, and $A\Delta\gamma$ the increase in the wall energy associated with pinning sites. The equation shows that a large variation of domain-wall energy associated with pinning positions is required to get a high coercivity. Figure 3 gives the temperature-dependent coercivity for the two typical FePt samples, showing a good fitted result for Gaunt’s domain-wall pinning model. For the FePt samples annealed at 455 °C for 120 min and 500 °C for 210 min, $\mu_0 H_0/(d\mu_0 H_c/dT)$ is -1600 and -1417 K while $A\Delta\gamma$ is 5.5×10^{-19} and 4.9×10^{-19} J, respectively, in which $\mu_0 H_0$ was obtained through extrapolation to 0 K from Fig. 3. It can be seen that the FePt sample annealed at 500 °C for 210 min has a higher value of $A\Delta\gamma$, resulting in a higher coercivity. Similar results were obtained for other annealed FePt

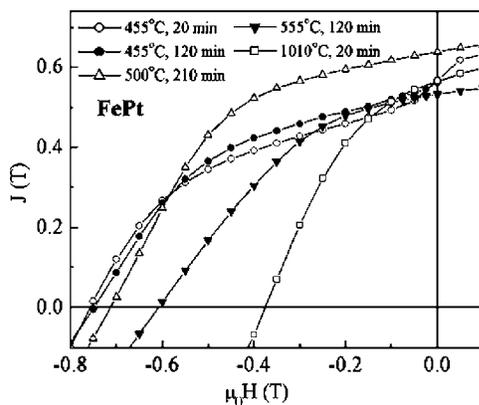


FIG. 4. Hysteresis loops at 300 K of the FePt samples of Fig. 1.

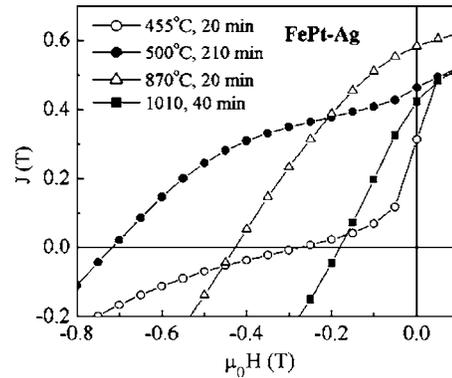


FIG. 5. Hysteresis loops at 300 K of the FePt–Ag samples of Fig. 2.

samples. In the meantime, the smaller grain size of fct FePt obtained at relatively low anneal temperatures increases the density of the obstacles of the domain-wall motion, also resulting in an increase of the coercivity. Thus, the grain growth of the fct phase and the decrease of $A\Delta\gamma$ are responsible for the monotonous decrease of the coercivity of the FePt samples with increasing the anneal temperature or prolonging the anneal time (see Table I). On the other hand, both the excessive grain growth of the fct phase and the presence of the soft Fe₃Pt and antiferromagnetic FePt₃ phases degrade the hard magnetic properties of the FePt and FePt–Ag alloys.^{1–6} So, the highest energy product $(BH)_{\max}$, remanence J_r , and best demagnetization squareness were obtained for the FePt sample annealed at 500 °C for 120 min (see Table I and Fig. 4). For this sample, the diffusion of Fe and Pt atoms completed. The fct FePt hard phase was completely formed with relatively small FePt grain size and a relatively small amount of Fe₃Pt and FePt₃ phases.

Due to the similar reasons, the best magnetic properties were obtained for the Ag-added samples annealed at 500 °C for 120 min. As mentioned above, the addition of Ag results in an obvious increase of both the ordering temperature of hard phase and relative volume fractions of Fe₃Pt and FePt₃ phases also introduces the presence of nonmagnetic Ag at grain boundaries. Thus, the $(BH)_{\max}$, J_r , and $\mu_0 H_c$ of Ag-added samples are much lower than those of Ag-free samples although the grain sizes are smaller in the Ag-added ones (see Table I and Fig. 5). But there is only one exception that Ag-added sample annealed at 500 °C for 120 min has higher $\mu_0 H_c$ than the corresponding Ag-free sample. The fct phase was completely formed in these two samples. In this case, the higher $\mu_0 H_c$ is the direct consequence of the smaller grain size of fct phase due to the Ag addition.

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