

Ordering and Magnetic Properties of Nanostructured CoPt Particles

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Abstract—The kinetics of ordering in nanostructured CoPt particles is investigated. The low activation energy (58 ± 2 kJ/mol) of the ordering process indicates that the kinetics of ordering is not limited by bulk diffusion. Coercivity grows along with the degree of ordering and reaches its maximum value of 14.2 kOe upon the complete ordering of CoPt alloy with a crystallite size of no more than that of a single domain.

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INTRODUCTION

The high magnetic hardness of the CoPt alloys is due to the establishing of long-range magnetic order, i.e., an ordered solid solution phase of the $L1_0$ type. The crystallographic magnetic anisotropy constant of this phase is enormous ($K(L1_0) = 4.7 \times 10^7$ erg cm⁻³), making CoPt a promising material for use in permanent magnets and magnetic recording media. The magnetic anisotropy constant of CoPt depends on the degree of ordering of its solid solution. This dependence for CoPt single crystals was investigated experimentally in [1, 2]. We showed that in nanostructured CoPt particles, the anisotropy constants assume intermediate values between the extreme cases of $K = K(L1_0)S$ and $K(L1_0)S/3$, depending on the number of ordering domains within one crystallite [3]. In this work, we investigate the kinetics of ordering and magnetic properties of CoPt particles, and discuss the effect ordering has on coercivity.

EXPERIMENTAL

CoPt nanoparticles were formed via the thermal decomposition of complex $[\text{Pt}(\text{NH}_3)_4][\text{Co}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ precursor compounds and annealed in a helium atmosphere at temperatures of 400, 500, and 600°C for 2, 4, 8, and 16 h [4]. X-ray diffraction (XRD) spectra were investigated in the angle 2θ range of 5° to 120° on a DRON RM4 diffractometer at the CuK_α radiation line ($\lambda = 1.5418$ Å) using a graphite monochromator. The spectrum of coarse-grained silicon powder was used as our reference line profile. The contribu-

tion to the instrumental line broadening was considered using the pseudo-Voigt function in [5]. The parameters estimated in this manner were used in whole powder pattern modeling (WPPM) with the PM2K package [6].

Magnetization curves were measured on a magnetic property measuring system (MPMS) and a physical property measuring system (PPMS) in fields of up to 90 kOe.

RESULTS AND DISCUSSION

According to our transmission electron microscopy data, the decomposed powders consisted of conglomerates of particle 3–5 nm in size. Annealing resulted in the sintering and coarsening of powder grains [3, 7, 8]. Microscopic study showed that the nanocrystallites in a conglomerate were several nanometers in size, while the conglomerate size could be as large as 500 nm. We can see in the XRD patterns (Fig. 1) that the decomposed particles had the fcc structure typical of disordered CoPt solid solution. Annealing the particles led to superstructural reflections in the XRD spectra, which become more intense as the time and temperature of annealing grew. The XRD linewidth shrank, indicating crystallite coarsening. Order parameter S was quantitatively estimated from the ratio between the intensities of superstructural and main reflections ((001) and (002))

$$S = \left(\frac{I_{(001)}}{I_{(002)}} \left(\frac{f_{\text{Co}}(s_{002}) + f_{\text{Pt}}(s_{002})}{f_{\text{Co}}(s_{001}) - f_{\text{Pt}}(s_{001})} \right)^2 \right)^{0.5}, \quad (1)$$

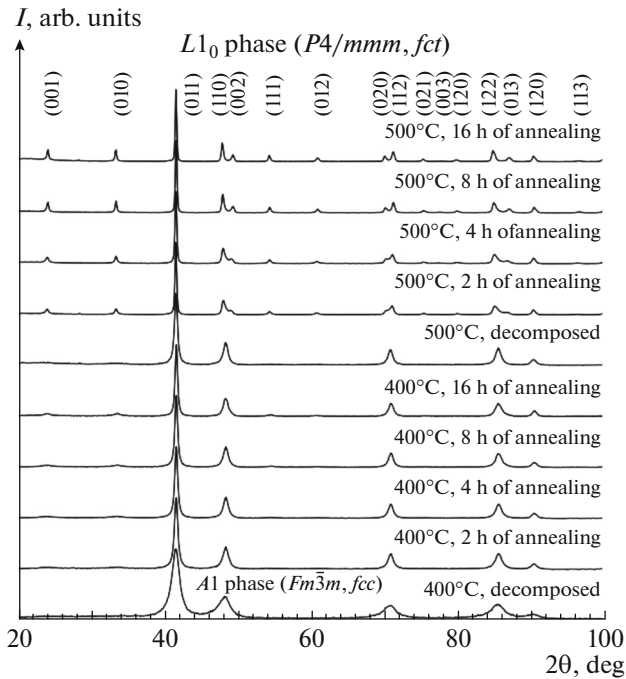


Fig. 1. X-ray diffraction spectra of decomposed and annealed powders consisting of CoPt particles.

where $s_{hkl} = (\sin \theta_{hkl})/\lambda$, and $f(s) = \sum_{i=1}^4 a_i \exp(-b_i s^2) + c$ are the atomic scattering factors [3].

The degree of ordering determined from the ratio between the intensities of the superstructural and main reflections using Eq. (1) is illustrated in Fig. 2. Estimates of the degree of ordering according to ratio c/a for the $L1_0$ structure showed that the divergence from the ideal ratio was no more than 1–3% for all of the investigated samples. This means the alloy was ordered via the formation of $L1_0$ nuclei in a disordered matrix. This was also confirmed by the high-resolution electron microscopy data and the nonzero broadening of diffraction lines caused by the antiphase boundaries. We may therefore conclude that the disorder–order phase transition was (in this case) of the first order. The increase in the order parameter (Fig. 2) determined using Eq. (1) was due to the growth of the volume fraction of ordered areas.

We used the Johnson–Melh–Avrami–Kolmogorov kinetic equation to describe the time dependences of the degree of ordering (the solid lines in Fig. 2):

$$S = 1 - \exp(-kt^n). \quad (2)$$

Using the temperature dependence of rate constants determined via the least squares method, we estimated the activation energy of the ordering pro-

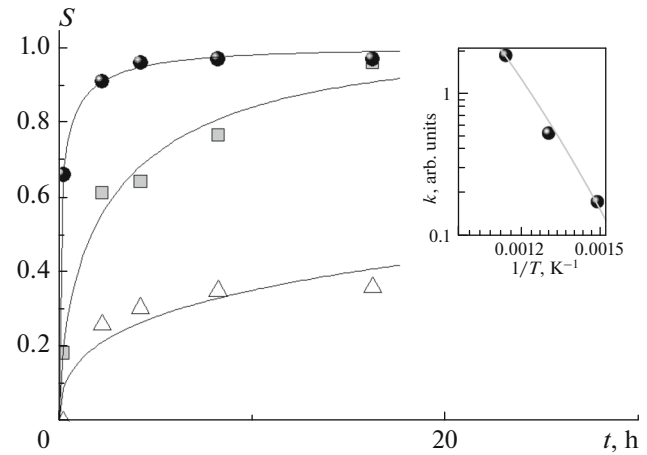


Fig. 2. Dependences of the degree of ordering in CoPt particles on the time and temperature of annealing. Dots correspond to annealing at 600°C; squares, at 500°C; triangles, at 400°C. Solid lines show the data as described using Eq. (2). The insert shows the dependence of the ordering rate constant on the reciprocal temperature.

cess. The k data obtained in coordinates $(\ln(k), 1/T)$ fit the straight line (see insert in Fig. 2) whose slope was used to determine the process's activation energy ($E_a = 58 \pm 2$ kJ/mol). Comparing this value to the activation energy of mutual diffusion in the bulk of CoPt (274 kJ/mol) led us to conclude that the kinetics of the ordering process is not limited by bulk diffusion.

The shape of the hysteresis loop of particles changes during annealing; specifically, coercivity H_c and reduced remanent magnetization (the squareness ratio of the hysteresis loop) M_r/M_s increase [3, 7, 8]. The coercivity and remanent magnetization grow upon annealing because of the formation and subsequent growth of the ordered phase with $L1_0$ structure. The data in Fig. 3 show the correlation between H_c and the order parameter. The line with the steep slope in Fig. 3 corresponds to the expected behavior of the coercivity of fully isolated univariant (containing the only ordered-phase domain) nanoparticles in the Stoner–Wohlfart model: $H_c = 2 \times 0.48K(L1_0)S/M_s$. For particles with many $L1_0$ domains, the model predicts the line with the gentler slope [3]: $H_c = 2 \times 0.48K(L1_0)S/(3M_s)$. The arrangement of experimental points below this line in Fig. 3 is due to the coercivity being determined by both the magnetic anisotropy constant and interparticle interactions [9]. The drop in H_c from 8.2 kOe upon annealing at 600°C for 16 hours to 13.7 kOe upon annealing for 8 h can in particular be attributed to the crystallite size exceeding the critical single-domain size. The maximum value of $H_c = 14.2$ kOe was reached upon annealing at 500°C for 16 hours.

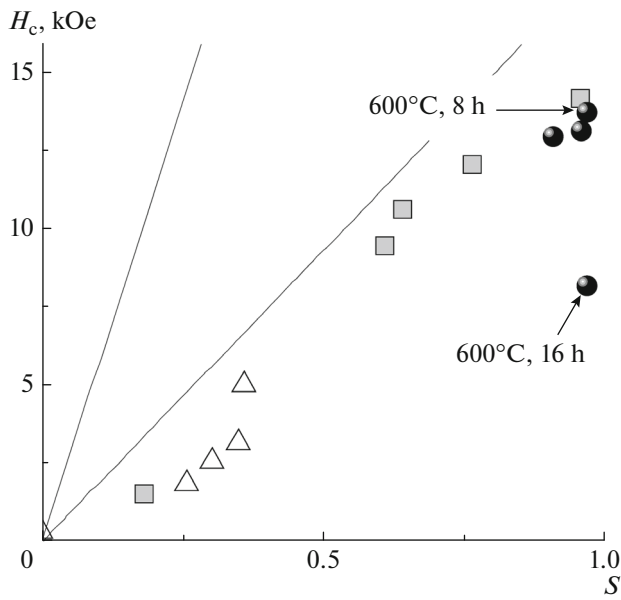


Fig. 3. Coercivity of CoPt particles with different degrees of ordering. Dots correspond to annealing at 600°C; squares, at 500°C; and triangles, at 400°C. The line with the steep slope is for $H_c = 2 \times 0.48K(L1_0)S/M_s$; the one with the gentler slope is for $H_c = 2 \times 0.48K(L1_0)S/(3M_s)$.

CONCLUSIONS

In nanostructured CoPt particles, the activation energy of the ordering process (58 ± 2 kJ/mol) is considerably lower than that of bulk diffusion. Coercivity grows along with the degree of ordering and reaches its

maximum value of 14.2 kOe upon complete ordering of the CoPt alloy with a crystallite size no larger than that of a single domain.

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