Atomic structure imaging of CoPt nanoparticles: effect of cooling rate on size-dependent atomic ordering

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Recent demands for ultrahigh density magnetic storage technology require the development of novel recording media with higher magnetocrystalline anisotropy energy (MAE), with the aim of increasing storage density and reducing a recording noise [1]. For such a purpose, Co-Pt alloy nanoparticles are one of the candidate materials: the hard magnetic properties of this alloy can be attributed to the tetragonal $L1_0$-type ordered structure with a high MAE [2, 3]. The MAE is dependent on the degree of order (long-range order parameter: LRO). Therefore, the atomic ordering and the stability of the ordered phase are the key issues for the hard magnetic properties of the $L1_0$-type alloy nanoparticles [4]. Recently, Alloyeau et al. have reported the formation of the $L1_0$ ordered phase in CoPt nanoparticles as small as 2-3 nm in diameter [5]. Their work implies a possibility of atomic ordering induced by slow cooling after annealing at temperatures below or even higher than a transformation temperature [6]. It is hence important to clarify kinetics of atomic ordering as well as thermodynamics.

The present study was done in an attempt to investigate the effect of cooling rate on the size-dependent atomic ordering of CoPt nanoparticles to find ways to improve hard magnetic properties with controlling annealing conditions. We employed aberration corrected (C_S-corrected) high-resolution transmission electron microscopy (HRTEM) to determine the atomic structures of CoPt nanoparticles.

CoPt nanoparticles were fabricated by sequential electron-beam depositions of Pt, Co and Al_2O_3 onto NaCl(001) substrates kept at 653 K. The average alloy composition was Co-61at%Pt. We carried out post-deposition *ex situ* annealing of the as-deposited film on a Mo-grid at 873 or 973 K for 1 h in a high-vacuum furnace. The mean heating rate was 10 K/min, while we adopted two different mean cooling rates; one is 1.5 K/min (hereafter, slow cooling) and the other 110 K/min (hereafter, rapid cooling). The structure and morphology of the nanoparticles were characterized using an FEI Titan80-300 TEM equipped with a spherical aberration corrector for the objective lens (300 kV, $C_S \approx 4$ µm). HRTEM images were simulated using the QSTEM software.

Figure 1 shows C_S-corrected HRTEM images and the corresponding FFT patterns of the CoPt nanoparticles with sizes of ≈3 nm in diameter. The annealing conditions are as follows: (a) 873 K-1h, slow cooling, (b) 873 K-1h, rapid cooling, and (c) 973 K-1h, rapid cooling. As can be seen, the atomic ordering was detected for nanoparticles after annealing at 873 K for 1h followed by slow cooling. In contrast, size dependence of the atomic ordering was found in the specimens followed by rapid cooling. For the specimen rapidly-cooled after annealing at 873 K, the A1 disordered phase with the face centered cubic (fcc) structure was observed in nanoparticles smaller than 3 nm in diameter. For example, nanoparticles shown in Fig. 1(b) are the disordered phase, characterized by crossed {200} lattice fringes. No superlattice reflections can be seen in the corresponding FFT pattern. The population of the disordered nanoparticles was found to be 14%. Similarly, for the specimen after annealing at 973 K followed by rapid cooling, the disordered phase was observed in the nanoparticles smaller than approximately 3.5 nm in diameter as shown in Fig. 1(c). The appearance of the disordered phase is, hence, an evidence for the size-dependence of the order-disorder transformation temperature of isolated alloy nanoparticles. Thus, the result unambiguously indicates that the order-disorder transformation temperature of CoPt nanoparticles smaller than 3 nm is reduced to a temperature at least lower than 873 K, which is in good agreement with a preceding report [5]. It is also noted that magnetic coercivity was enhanced by 20% after a slow cooling process due to the promotion of atomic ordering [7].

References

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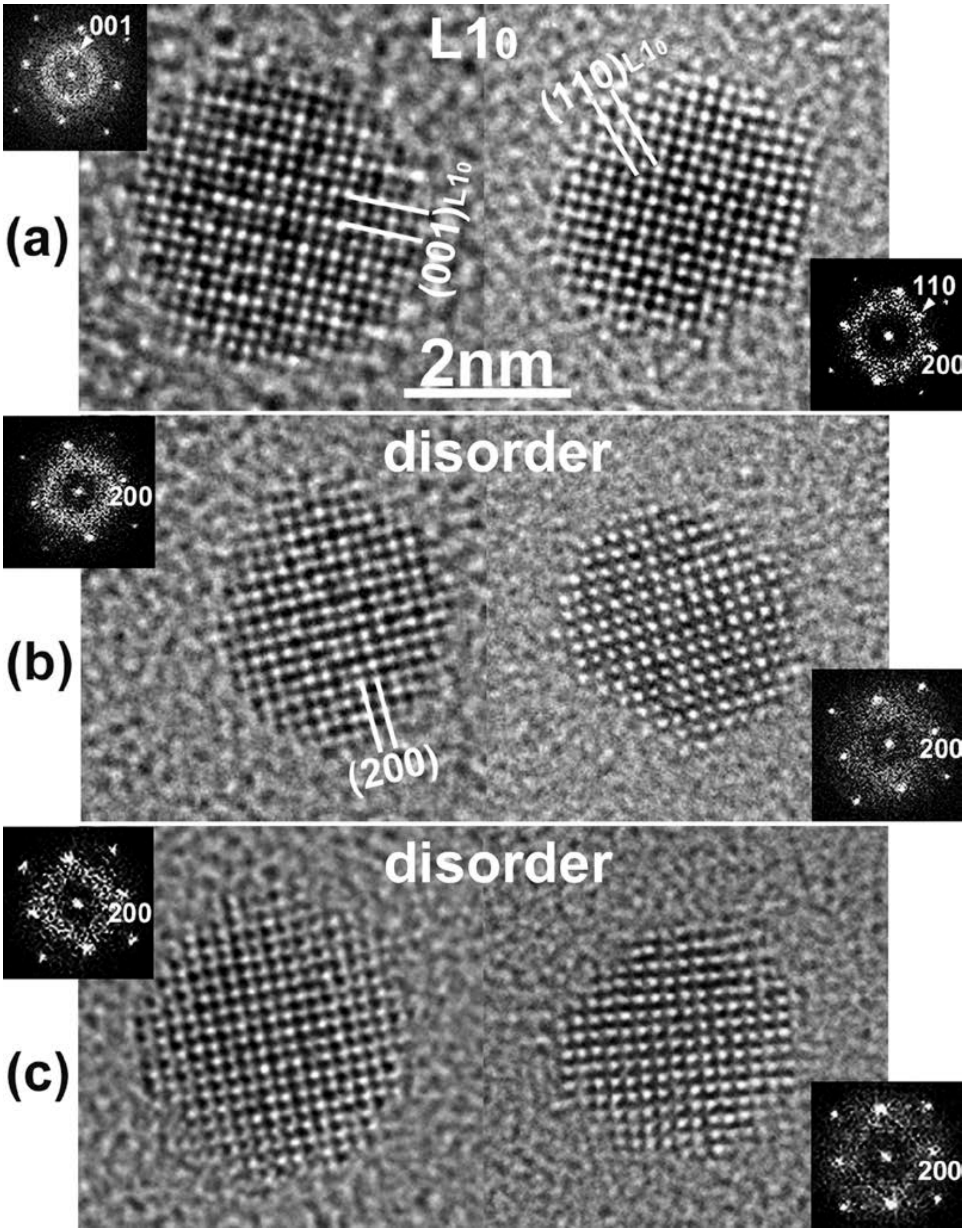

Figure 1. *C_S-corrected HRTEM images and the corresponding FFT patterns of the CoPt nanoparticles about 3 nm in diameter. The annealing conditions are as follows: (a) 873 K for 1h followed by slow cooling ($L1_0$ ordered), (b) 873 K for 1h, rapid cooling (disordered phase), (c) 973 K for 1h, rapid cooling (disordered phase).*