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Structure and compositional evolution in epitaxial Co/Pt core–shell nanoparticles on annealing

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ABSTRACT

We report on the alloying of epitaxial Co/Pt core–shell nanoparticles using transmission electron microscopy (TEM) and electron diffraction. In as-deposited nanoparticles followed by *in situ* annealing at 823 K for 10.8 ks, high-angle annular dark-field (HAADF) imaging by scanning TEM (STEM) clearly revealed formation of Co-shell/Pt-core structures due to the large atomic number (Z) difference between Co (Z = 27) and Pt (Z = 78). We identified a formation of locally ordered areas of the $L1_0$ ordered phase at the core of the nanoparticles. After *ex situ* annealing at 873 K for 0.6 ks, some of the ordered areas showed complicated contrasts in the HAADF-STEM images. Based on image simulations, we found that these atypical contrasts arise from the stacking of two orthogonal variants of the $L1_0$ phase in the electron beam direction. Furthermore, the simulation showed that image contrast strongly reflects the structure of the variant located closer to the beam entrance rather than to the bottom side. Solid solution phase was formed by further annealing at 873 K for 3.6 ks, while high-density {111} stacking faults were observed inside the Co–Pt alloy nanoparticles. Magnetic coercivity remained at values as low as ~15.9 kA/m at 300 K, irrespective of the formation of local $L1_0$ ordered areas and/or a high-density stacking faults.

1. Introduction

Magnetic alloy nanoparticles have been actively studied in the last two decades due to their excellent magnetic and magnetotransport properties. Recent demands for ultrahigh density magnetic storage technology require the development of recording media with higher magnetocrystalline anisotropy energy (MAE), with the aim of increasing storage density and reducing recording noise [1–5]. For such a purpose, Co–Pt alloy nanoparticles are one of the candidate materials: high coercivity has been reported for equiatomic Co–Pt alloy nanoparticles and/or ultrathin films [6–10], and also for those with Pt content of 10–30 at% [11–13]. The hard magnetic properties of the former equiatomic alloy can be attributed to the tetragonal $L1_0$-type ordered structure with a high MAE [14,15]. Recent reports showed formation of the $L1_0$ ordered phase in CoPt nanoparticles as small as 2–3 nm in diameter [16], while Tournus et al. reported a rather low MAE of 3.8×10^5 J/m^3 for their $L1_0$-CoPt clusters 2.6 nm in average diameter [17]. On the other hand, for the latter alloys with Co-rich composition, the origin of the hard magnetic properties was explained in three different ways: (1) formation of hexagonal close-packed (hcp) Co–Pt phase with a high MAE [18], (2) formation of dense {111} stacking faults in the hcp Co–Pt phase [19] and (3) formation of the so-called Co_3Pt ordered phase [20,21]. For the last point, although a model structure was proposed [20], the crystal structure of the ordered phase has not been clarified yet. Thus, the formation and the stability of the alloy phase(s) in Co–Pt nanoparticles are the key issue to improve their magnetic properties.

In this study we hence intend to examine the structure and alloying behaviors of Co-rich Co–Pt core–shell nanoparticles on annealing using transmission electron microscopy (TEM) and electron diffraction. The atomic structure of nanoparticles have been clearly imaged by aberration corrected high-resolution TEM (HRTEM). The formation of core–shell islands as well as their structural and compositional evolution on annealing was examined by chemically sensitive high-angle annular dark-filed (HAADF) imaging using scanning TEM (STEM).

2. Experimental procedures

Bi-metallic Co/Pt core–shell nanoparticles were fabricated by sequential deposition of Pt and Co onto NaCl(001) substrates cleaved in air [22]. The evaporation was performed by a high vacuum electron-beam deposition apparatus operated at 4 kV with a base pressure of 9×10^{-7} Pa. Pure Pt (99.95%), Co (99.98%), and Al_2O_3 (99.99%) crystals were used as evaporation sources. The substrate temperature was kept at 653 K during the deposition. At first, Pt was deposited on the substrate, which resulted in the formation of (001) oriented Pt islands. Then, Co was deposited onto the substrate with the Pt. In the sequential deposition process, Pt nanoparticles act as nucleation sites for Co

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nanoparticles, and they formed Co/Pt nanocomplex particles in the as-deposited condition [22]. These nanoparticles are mutually separated by further deposited amorphous (a-) Al_2O_3 thin film. The pressure was around $0.8–2\times10^{-5}$ Pa during the sequential deposition. After the deposition of Al_2O_3, the specimen films were heated inside the vacuum chamber for 10.8 ks at 823 K to promote island growth of nanoparticles (hereafter, nanoparticles after *in situ* annealing). A quartz thickness monitor located near the substrate stage in the vacuum chamber was used to estimate the nominal thickness of deposited layers. The amounts of Pt, Co, and Al_2O_3 deposited were equivalent to 0.8 nm, 2 nm, and 6 nm coverage, respectively. Energy dispersive X-ray spectroscopy (EDS) attached to TEM showed that the average alloy composition was Co–12 at% Pt. The specimen film was then removed from the NaCl substrate by immersion into distilled water and the floating film was mounted onto a Mo-grid with a holey carbon film for TEM observation. We carried out post-deposition *ex situ* annealing of the film on a Mo-grid at 873 K for 0.6 ks and 3.6 ks in a high-vacuum furnace ($<2\times10^{-5}$ Pa). The specimen films on the NaCl substrates were also annealed for magnetic measurements. The mean heating and cooling rates were 10 K/min and 2.5 K/min, respectively.

The structure and morphology of the Co–Pt nanoparticles were characterized using a JEOL JEM-3011 TEM (spherical aberration coefficient, $C_s = 0.6$ mm) operating at 300 kV and an FEI Titan80-300 (S) TEM operating at 300 kV with a field emission gun and a C_s-corrector for the objective lens ($C_s \approx 8$ μm). All HRTEM images were recorded by a 1 k × 1 k charge coupled device camera. HAADF-STEM images were acquired using an annular detector (Fischione model 3000) with detector half angles of 60–210 mrad. We set the beam convergence to be 10 mrad in half-angle for atomic resolution STEM imaging, taking into account the C_s (= 1.2 mm) of the prefield of objective lens (supertwin lens). Elemental analyses were carried out using an EDS attached to the Titan. HRTEM and HAADF-STEM images were simulated using QSTEM and MACTEMPAS package (Total Resolution LLC).

Magnetic properties of the Co–Pt nanoparticles on the NaCl(001) substrates were measured using a superconducting quantum interference device magnetometer (Quantum Design, MPMS-XL) in a temperature range between 10 and 300 K with a magnetic field up to 4 MA/m. The magnetic field was applied both along the film plane and along the perpendicular directions.

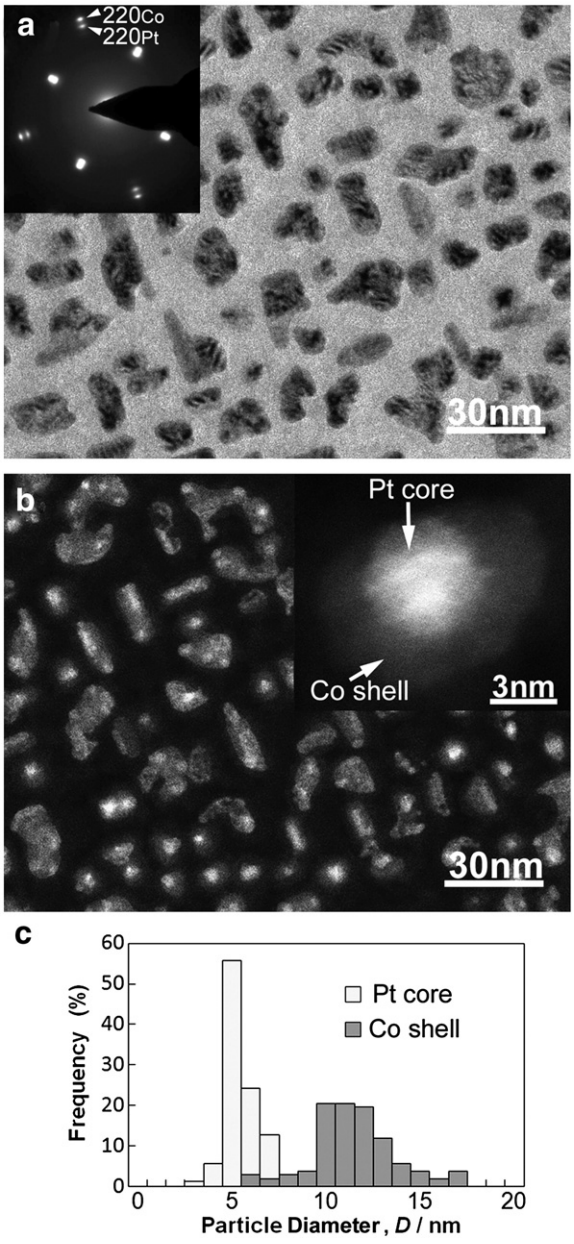

Fig. 1. (a) BF-TEM image and the corresponding SAED pattern for Co/Pt nanoparticles after *in situ* annealing. The beam incidence is [001] for both fcc-Pt and fcc-Co. (b) HAADF-STEM image of the nanoparticles with core–shell contrasts. The zone axis is [001]fcc. A magnified image of a nanoparticle is shown in the inset. (c) Particle size distribution of Pt cores and Co shells.

3. Results and discussion

3.1. Structure of core–shell nanoparticles after in situ annealing

Fig. 1(a) shows a bright-field (BF) TEM image and the corresponding selected area electron diffraction (SAED) pattern of the Co/Pt

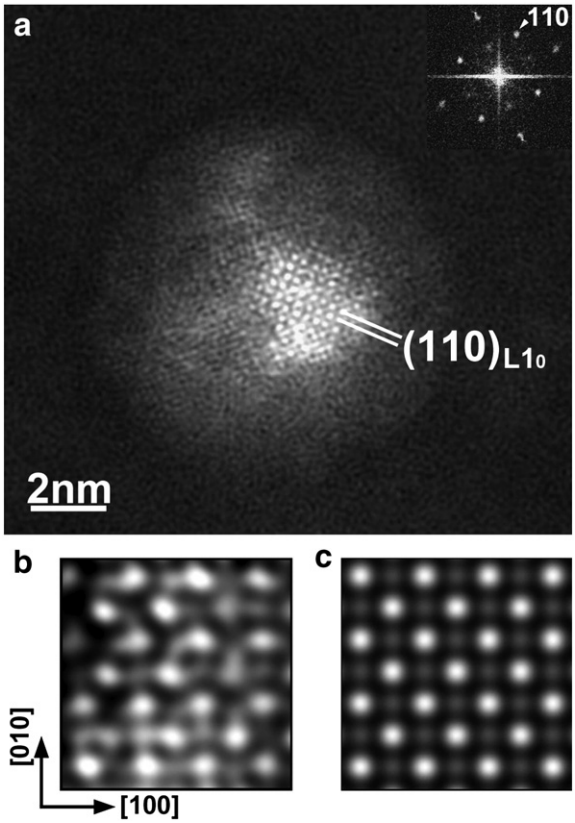

Fig. 2. (a) Z-contrast image by HAADF-STEM for a Co/Pt nanoparticle with a core–shell contrast after *in situ* annealing. Corresponding Fourier spectrum is shown in the inset. The zone axis is [001]$L1_0$. (b) Magnified image of the $L1_0$ ordered area. (c) Simulated image of the $L1_0$ ordered structure with the [001] beam incidence.