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In situ investigation of ordering phase transformations in FePt magnetic nanoparticles

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ABSTRACT

In situ high-resolution electron microscopy was used to reveal information at the atomic level for the disordered-to-ordered phase transformation of equiatomic FePt nanoparticles that can exhibit outstanding magnetic properties after transforming from disordered face-centered-cubic into the tetragonal $L1_0$ ordered structure. High-angle annular dark-field imaging in the scanning transmission electron microscope provided sufficient contrast between the Fe and Pt atoms to readily monitor the ordering of the atoms during in situ heating experiments. However, during continuous high-magnification imaging the electron beam influenced the kinetics of the transformation so annealing had to be performed with the electron beam blanked. At 500 °C where the reaction rate was relatively slow, observation of the transformation mechanisms using this sequential imaging protocol revealed that ordering proceeded from (002) surface facets but was incomplete and multiple-domain particles were formed that contained anti-phase domain boundaries and anti-site defects. At 600 and 700 °C, the limitations of sequential imaging were revealed as a consequence of increased transformation kinetics. Annealing for only 5 min at 700 °C produced complete single-domain $L1_0$ order; such single-domain particles were more spherical in shape with (002) facets. The in situ experiments also provided information concerning nanoparticle sintering, coalescence, and consolidation. Although there was resistance to complete sintering due to the crystallography of $L1_0$ order, the driving force from the large surface-area-to-volume ratio resulted in considerable nanoparticle coalescence, which would render such FePt nanoparticles unsuitable for use as magnetic recording media. Comparison of the in situ data acquired using the protocol described above with parallel ex situ annealing experiments showed that identical behavior resulted in all cases.

1. Introduction

In situ experiments using high-resolution transmission electron microscopy (HRTEM) provide a method to study the behavior of materials at the atomic scale. In situ HRTEM is especially useful for investigation of phase transformations in order to gain understanding of the microstructural changes as a function of time and temperature and to determine their mechanisms and kinetics. There are excellent review articles by Sinclair on this topic that describe the development of using heating holders to observe materials reactions with HRTEM [1,2]. In addition to revealing the atomic mechanism, these in situ experiments can in some cases quantify reaction rates that when analyzed with an Arrhenius relationship allows for activation energy determination [3].

However, care must be taken to ensure that the behavior observed in the TEM is consistent with behavior outside the TEM and, where relevant, that thin TEM specimens behave in the same way as bulk materials. Any influences of surface diffusion and electron beam-specimen interactions need to be understood to determine the applicability of the in situ data. Although, in certain experimental situations, electron beam heating is useful to activate defect motion or change the crystal shape [4,5], correct analysis of phase transformation kinetics requires the elimination of any influence of the electron beam on the reaction rate. In situ results should always be compared to ex situ experiments in order to verify the validity of the in situ results. Nevertheless, with careful experimental technique, in situ HRTEM provides information that is otherwise not available with any other experimental method.

The experiments described in this study concern ferromagnetic FePt nanoparticles. In the $L1_0$ (CuAuI) ordered state, equiatomic FePt exhibits exceptional magnetic properties with uniaxial-magnetocrystalline anisotropy (K_u) greater than 10^7 ergs/cm^3 [6]. However, mono-

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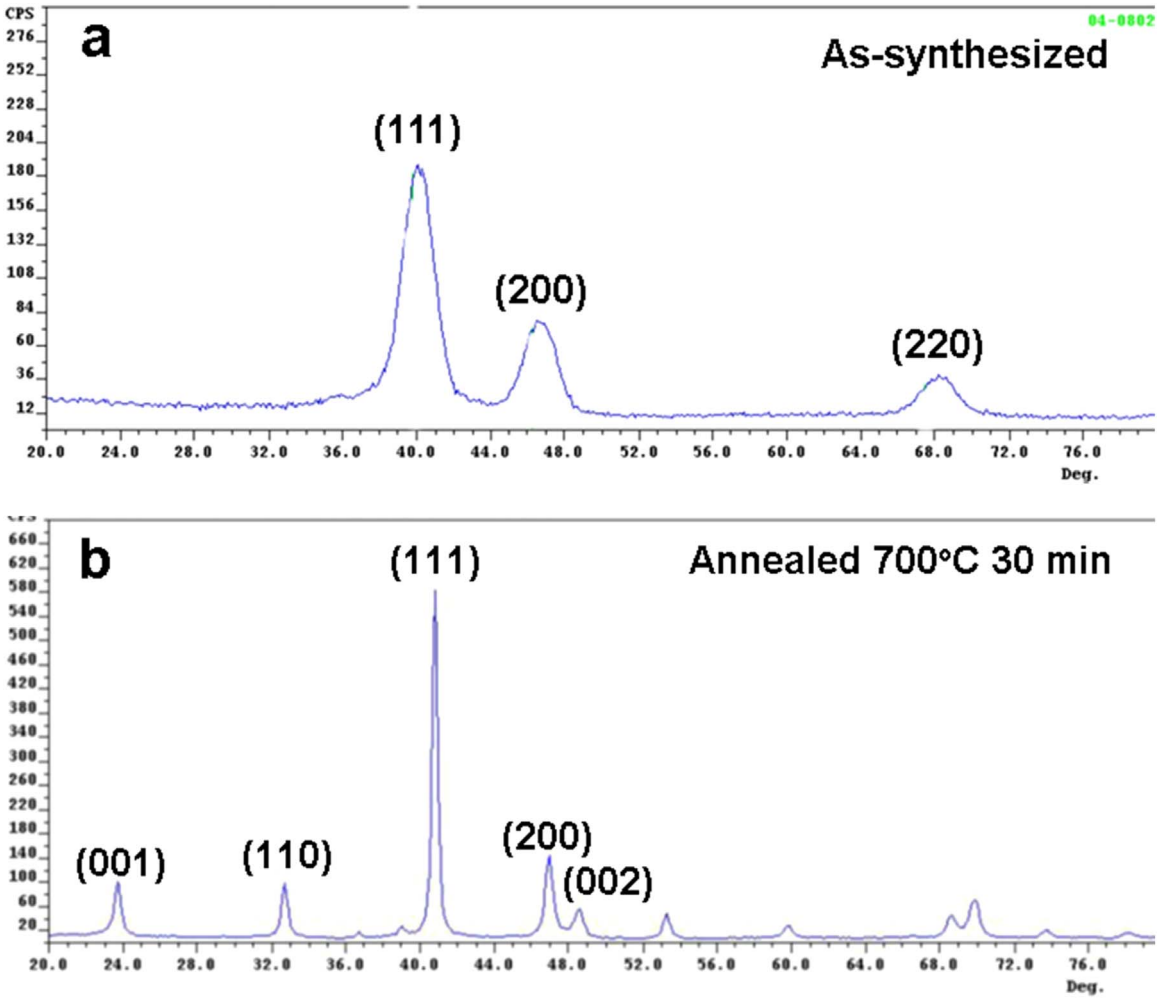

Fig. 1. X-ray diffractometer scans of intensity versus 2θ for (a) the as-synthesized disordered face-centered cubic FePt nanoparticles (b) $L1_0$-ordered FePt nanoparticles after annealing at 700 °C for 30 min.

dispersed FePt nanoparticles produced by chemical synthesis methods [7] are disordered face-centered cubic (FCC) and require annealing to chemically order into the tetragonal $L1_0$ structure. This disorder-to-order phase transformation has been studied by using x-ray diffractometry (XRD) to monitor the development of the superlattice peaks with annealing time and temperature [7–10]. Fig. 1 shows an illustrative example of XRD data from as-synthesized monodispersed FePt nanoparticles (average size 4.9 ± 0.5 nm as determined by TEM) and after annealing at 700 °C for 30 min. Clearly annealing at 700 °C for 30 min not only ordered the particles (presence of the (001) and (110) superlattice peaks) and produced a tetragonal unit cell (splitting of the (200) and (002) peaks) but the average particle size also increased, as evidenced by the reduced characteristic peak widths. Although it reveals the overall crystallographic state of the particles, XRD is limited by being biased with diffraction from the larger particles compared to the contribution from the smaller ones and provides no information concerning the actual mechanisms of the phase transformation. A more complete understanding of this transformation requires electron microscopy to observe the structural changes that occur during the annealing heat treatments.

In the disordered FCC state, the nanoparticles are superparamagnetic; however, the $L1_0$-ordered FePt nanoparticles display outstanding magnetic properties [7,8,11–13] with extremely high K_u and coercivity that can exceed 22 kOe [8]. Therefore, understanding the $L1_0$-ordering phase transformation in these FePt nanoparticles is critical for incorporating them into information storage devices that exploit their exceptional magnetic properties. The current study employs in situ heating using a TEM specimen holder with a MEMS-based heating element/specimen support and imaging by high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM), also known as atomic-number contrast or Z-STEM, to investigate the development of $L1_0$ order as well as associated changes in particle shape and particle coalescence during annealing. Parts of this work have previously appeared as extended abstracts in conference proceedings [14–19].

2. Materials and methods

The FePt nanoparticles were synthesized using a standard method that is described elsewhere [7]. A surfactant of oleic acid and oleyl amine stabilizes the FePt particle-size distribution with a standard deviation that can be as small as 5%. One drop of a suspension of FePt nanoparticles in hexane was deposited onto a Protochips “Aduro™” disposable 3-mm diameter MEMS device (“E-chip”) that serves as both the heating element and the specimen support grid (consisting of a patterned SiC membrane supporting an electron-transparent holey carbon film and fitted with microfabricated Au electrical contact pads), a custom TEM holder with electrical feed-throughs, and a progammable external stable power supply [20]. The E-chip heater allows specimens to be heated to temperatures up to 1000 °C in milliseconds through resistance heating by passing a current through the membrane. Each E-chip is calibrated in vacuum, using infrared imaging methods described in [20]. Since the distance from the center of the hole with the carbon film to the edge of the ceramic membrane heater