When atoms move around: Magnetic nanoparticles

Sato, Kazuhisa
Institute for Materials Research, Tohoku University

出版情報：Nature Materials. 8 (12), pp.924-925, 2009-12. Springer
バージョン：

Nature Materials **8** (2009) 924–925.

Magnetic nanoparticles: When atoms move around

The degree of atomic ordering in magnetic nanoparticles decreases strongly with the particles' size. The origin of such a phenomenon has been determined by high-resolution transmission electron microscopy and tomography, which shows how correct heat treatment can lead to atomic order also in very small nanoparticles.

Kazuhisa Sato

Considerable attention has recently been given to nanoparticles (NPs) of magnetic alloys like FePt, CoPt, or FePd with the CuAu I-type ($L1_0$-type) ordered structure, because of their potential applications for future ultra-high density magnetic storage media. In binary $L1_0$-type ordered alloys, two kinds of sublattices are occupied by either Fe(Co) or Pt(Pd) atoms (Fig.1a). The tetragonal $L1_0$ ordered structure gives rise to a high magnetocrystalline anisotropy along the crystallographic c-axis. However, as-synthesized NPs, typically by chemical solution methods or physical vapor deposition, are in most cases disordered solid solution with the face-centered cubic (fcc) structure. To recover the atomic order and therefore the excellent magnetic properties a high temperature annealing (typically above 600ºC) is required, so that the $L1_0$ ordered phase can be recovered by atomic diffusion. However, the procedure is not enough to attain order in small nanoparticles (below 5 nm), as confirmed by several experimental work that reveal large components of disordered phases. This puzzling dependence of atomic ordering on the nanoparticle size has been under considerable debate. On page 940 of this issue, Damien Alloyeau and co-authors report their results on atomic ordering of equiatomic Co-Pt alloy NPs 2-3 nm in sizes[1], which provide important elements to decipher the origin of this "size-dependent ordering effect".

The researchers found that the transition temperatures of these NPs are in the range between 500 and 650ºC, lower than that of the bulk alloy which can be as high as 825ºC. The

authors performed an annealing of disordered Co-Pt NPs as long as 16 hours at 500°C, and finally they found the ordered lattice inside a 2.4-nm-sized particle by high-resolution transmission electron microscopy (HRTEM). However, when the same sample of nanoparticles was annealed for 1 hour at 650°C followed by quenching to room temperature, resulted in disordering of NPs less than 3nm in sizes, implying a transition temperature lower than 650°C. The comparison between these two results proved that atomic ordering can take place even in very small NPs when the annealing temperature is lower than the size-dependent, reduced, transition temperature. This point has been expressed by Chepulskii and Butler as follows: "the experimental absence of relatively high $L1_0$ order in 3.5-nm-diameter NPs annealed at 600°C or below is primarily a problem of kinetics rather than equilibrium"[2]. The present study is then the first to experimentally prove the above point unambiguously.

Figure 1b schematically illustrates the temperature dependence of the degree of order for different sized NPs based on recent Monte Carlo simulations[1-4]. As can be seen, the transition temperature is reduced as the particle size becomes smaller. This is due to the progressively more enhanced reduced coordination at the surface. The $L1_0$-fcc transition is known to be the first order transition in the bulk alloy, while a continuous transition has been predicted for NPs less than about 5 nm in diameter. The continuous disordering has been attributed to the surface induced disorder (SID) related to Pt segregation onto the particle surface[3,4]. In fact, SID has very recently been found in strained NPs by means of aberration-corrected HRTEM[5]. Here, relationship between annealing temperatures and the reduced transition temperature is of fundamental importance. When the reduced transition temperature (T_c^{NP}) is lower than the typical annealing temperature (T_a~600°C) (NP2 in Fig.1b), the following two situations can be considered. First, if the particles are quite slowly cooled down to the ambient temperature after annealing above the transition temperature, NPs will be annealed during this slow cooling process and eventually atomic ordering will take place. In contrast, if the particles are rapidly cooled down (quenched) to room temperature just after annealing, a metastable disordered phase will remain. Therefore, the "cooling rate" is one of the key

issues when discussing a possibility of atomic ordering during the cooling process. As the transition temperature reduces (NP3), atomic migration requires a longer annealing time for ordering (annealing at $T_a' < T_c^{NP3}$ is required), and consequently the disordered phase may dominate NPs in practice. Furthermore, it is practically impossible to attain the ordered state for NP4 by heat treatment, whose transition temperature is well below RT. Indeed, an ordered phase is not always attainable by heat treatment, as in the case of Cu_3Au alloy NPs 2-4 nm in sizes, where the reduced transition temperature is well below the room temperature[6,7].

Besides the experimental proof of atomic ordering described above, the study further revealed the essential aspect of size effect: the transition temperature is uniquely determined by the smallest characteristic length of a NP. That is, only one dimension of the particle (in-plane size or thickness) smaller than 3 nm is sufficient to induce a considerable depression of the transition temperature. This work then emphasizes the necessity of taking into account 3D morphologies of NPs to understand their structural properties. Understanding the size and shape effect on ordering, which was eventually possible through basic methodologies in materials science, namely control of annealing time and temperature, and HRTEM and 3D electron tomography, not only do the result shed light on the order-disorder transition in small NPs, but present also some perspectives for designing NPs for industrial applications such as ultra-high density magnetic storage media.

Kazuhisa Sato,

is at the Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

e-mail: ksato@imr.tohoku.ac.jp

References

1. Alloyeau, D. *et al. Nature Mater.* 8, 940–946 (2009).
2. Chepulskii, R. V. and Butler, W. H. *Phys. Rev. B* 72, 134205 (2005).
3. Müller, M. and Albe K. *Phys. Rev. B* 72, 094203 (2005).

4. Yang, B., Asta, M., Mryasov, O. N., Klemmer, T. J., and Chantrell, R. W. *Acta Mater.* 54, 4201‑4211 (2006).
5. Kovács, A. *et al. Phys. Rev. Lett.* 103, 115703 (2009).
6. Yasuda, H. and Mori, H. *Z. Phys. D* 37, 181‑186 (1996).
7. Tadaki, T., Kinoshita, T., Nakata, Y., Ohkubo, T., and Hirotsu, Y. *Z. Phys. D* 40, 493‑495 (1997).

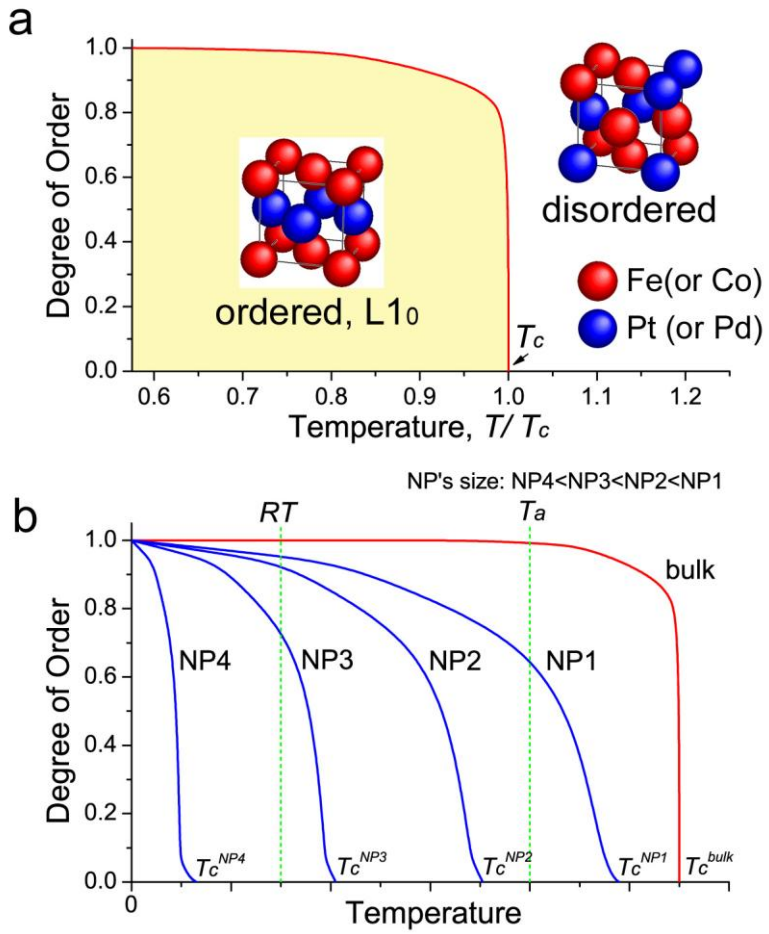

Figure 1 Temperature dependence of the degree of order. (a) The $L1_0$-fcc order-disorder transition in a bulk alloy, with structural models shown in the insets. (b) The effects of size on T_c. As the nanoparticle's size decreases there is an associated decrease in T_c. Note that NP2, NP3 and NP4 are not ordered by annealing the alloys at T_a followed by quenching to room temperature. The stability of an ordered phase in a nanoparticle will also be affected by external parameters, such as substrates or protective layers.