Fluctuation of long-range order in Co-Pt alloy nanoparticles revealed by time-resolved high-voltage electron microscopy

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Recent demands for ultrahigh density magnetic storage technology require the development of recording media with higher magnetocrystalline anisotropy energy in order to ensure thermal stability of magnetization as well as ultrahigh recording density. For such a purpose, equiatomic CoPt alloy nanoparticles (NPs) are one of the candidate materials. The hard magnetic property of this alloy is attributed to the tetragonal $L1_0$-type ordered structure; the anisotropy energy is dependent on the degree of order of the ordered structure [1]. Therefore, formation of the ordered CoPt phase is the key issue for practical applications. In this study, we observed initial stage of atomic ordering in CoPt NPs triggered by high-energy electron irradiation using a direct electron detection camera.

Thin films of disordered Co-45at%Pt alloy NPs were synthesized by Co, Pt, and C targets using rf-magnetron sputtering onto NaCl(001) substrates kept at 620 K. Electron irradiation experiments and the simultaneous *in-situ* heating observation were carried out using a JEOL JEM-1000EES UHVEM (1 MV) equipped with a Gatan K2IS electron direct detection CMOS camera.

Electron-irradiation-enhanced ordering occurred at 573 K with 1 MeV electrons at a dose rate of 8.9×10^{24} e/m^{2}s. Figure 1 shows successive TEM images of a Co-Pt alloy NP acquired at 400 frames/s (2.5 ms/frame). High-speed imaging revealed fluctuations of the c-axis orientation of the $L1_0$ - type ordered structure [2]. The c-axis orientation reversal occurred at 2.5-msec intervals. Thus, the atomic ordering rate at 573 K is deduced to be 3×10^{-17} m^2/s, which is 10^{13} times higher than that estimated for interdiffusion in a bulk Co-Pt alloy. The high effective diffusivity corresponds to a value expected at 1160 K, which is just above the order-disorder transition temperature of a bulk alloy. A vacancy concentration C_v at 573 K under 1 MeV electron irradiation was estimated to a value $\sim 10^6$ times higher than that at thermal equilibrium at 573 K, assuming the formation entropy of a vacancy $S_f \sim 1.5k_B$ and the formation energy of a vacancy $E_f \sim 1.5$ eV. This high mobility of atoms derives from a different mechanism than that in bulk diffusion by heat treatment. The observed kinetic ordering temperature of 573 K is significantly lower than that reported previously (>800 K). The low-temperature atomic ordering may have been caused by the enhancement of atom migration via excess vacancies introduced by high-energy electron irradiation. In conclusion, we have demonstrated that time-resolved electron imaging can directly reveal rapid spatiotemporal fluctuations [3].

[1] K. Sato et al. *Advances in Imaging and Electron Physics* **170** (2012) 165.
[2] K. Sato and H. Yasuda, *Appl. Phys. Lett.* **110** (2017) 153101.
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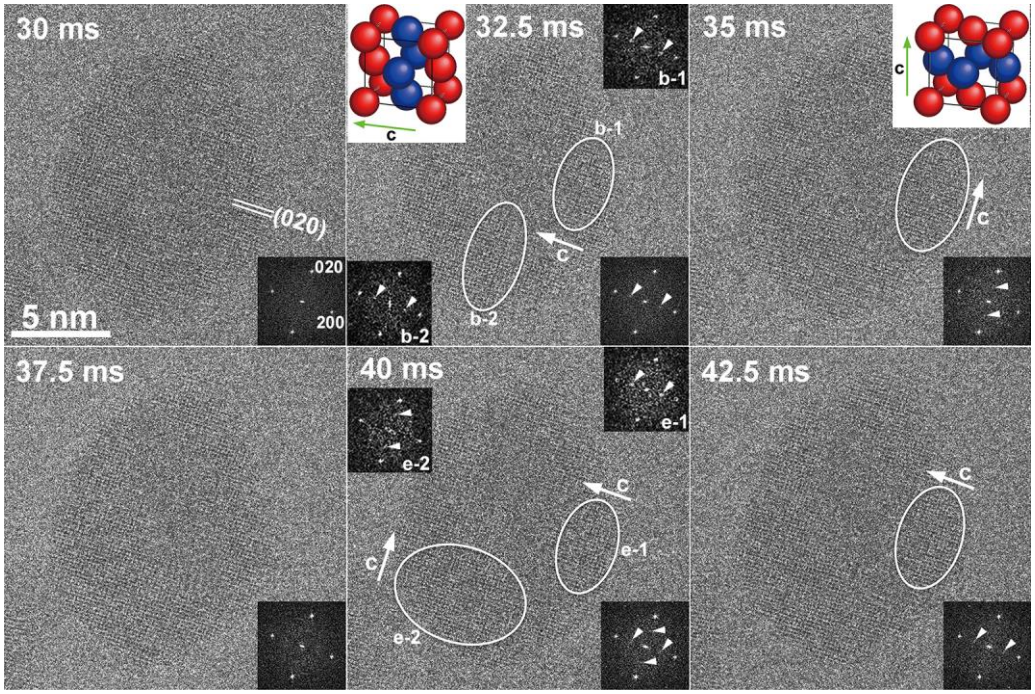

Fig.1 TEM images of a Co-Pt alloy NP acquired at 400 fps (2.5 ms / frame). Atomic ordering was detected after electron irradiation at a total dose of approximately 1×10^{26} e/m^2.