Structures and microscopic miscibility for nanoparticles of palladium-ruthenium-based alloys

O. Yamamuro(A), H. Akiba(A), K. Kusada(B), D. Wu(B), H. Kitagawa(B), D. Keen(C)
(A)ISSP-NSL Univ. Tokyo, (B)Kyoto Univ., (C)ISIS, RAL

Nanometer-size particles of alloys are attracting researchers in various scientific and industry fields. Recently we are focusing attention on PdRu alloys since they are expected to be high-performance and low-cost catalysts to remove CO and NOx in exhaust gas of cars. Pd and Ru atoms form bulk solid solutions only at much higher temperatures than room temperature (RT). This is mainly because Pd has an fcc structure while Ru has an hcp one. We have found that PdxRu1-x with a diameter of 5-7 nm are miscible in the whole composition range around RT [1]. However, the fcc and hcp phases coexist in a single nanoparticle. The present large problem is that the catalytic activity decreases due to the vaporization of Ru atoms at higher temperatures. In this study, we have performed the neutron powder diffraction (NPD) experiments on PdRuM (M = Rh, Pt, Ir) nanoparticles to investigate the miscibility improvement by adding the third metals M. The third metal may stabilize the alloys state due to the mixing entropy effect. These nanoparticles are covered with a protective polymer polyvinylpyrrolidone (PVP) to avoid adhesion between the nanoparticles. The NPD measurements were performed using the high-intensity neutron powder diffractometer (Polaris) installed at RAL, ISIS. NPD is powerful to distinguish between neighboring atoms in the periodic table such as Pd and Ru.

Figure 1 shows the atomic pair correlation function G(r) of Pd0.5Ru0.5 and Pd0.33Ru0.33M0.33 (M = Rh, Pt, Ir) nanoparticles obtained by the Fourier transform of the S(Q) data. The contribution from PVP has been subtracted. The red and green bars represent the positions and intensities calculated from the fcc and hcp structures. Both fcc and hcp peaks appeared in Pd0.5Ru0.5, Pd0.33Ru0.33Rh0.33 and Pd0.33Ru0.33Ir0.33, while only the fcc peaks in Pd0.33Ru0.33Pt0.33. This result demonstrates that adding Pt atoms is the most effective to stabilize the fcc structure and improve the miscibility of the alloy nanoparticles. Furthermore, we have found that the presence of much interface between fcc and hcp phases enhances the catalytic performance in PdRuM nanoparticles.

[1] K. Kusada et al., J. Am. Chem. Soc. 136, 1864 (2014).

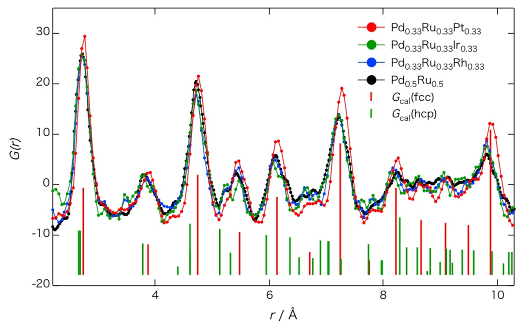

Fig. 1. Atomic pair correlation functions G(r) of Pd0.5Ru0.5 and Pd0.33Ru0.33M0.33 nanoparticles.