XRD and XAFS Analyses for Metal Nanocomposites Used in Anomalous Heat Effect Experiments

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Anomalous heat effect (AHE) has recently been reported to be well reproducible in a series of collaborative experiments performed at elevated temperatures 200 ~ 350℃ using metal nanocomposites and hydrogen isotope gas [1 - 5]. A variety of samples were studied and AHE was found dependent on samples. For example, a remarkable AHE was observed for PNZ6 with a composition of $Pd_{0.032}Ni_{0.318}Zr_{0.65}O_{0.24}$. However, no AHE was observed for Pd/TMPS-4R in which Pd nano-particles with sizes ~4nm were included in the pores of the mesoporous silica matrix TMPS-4R.

In this paper, structural changes of PNZ6 and Pd/TMPS-4R with increasing temperature under hydrogen atmosphere were studied by in-situ XRD (X-ray diffraction) and XAFS (X ray absorption fine structure) analyses using facilities of Aichi Synchrotron Radiation Center. The analysed PNZ6 and Pd/TMPS-4R samples were a part of the materials that were used for the heat evolution experiments at Kobe University [5] and Tohoku University[2,4], respectively.

The in-situ XRD analyses were performed at 15keV under hydrogen atmosphere of ~ 0.4MPa, while raising temperature from room temperature (RT) up to ~600℃. XAFS profiles for K-edge Ni and K-edge Pd were taken under flowing hydrogen at 100 cc/min, while raising temperature from RT up to ~ 600 ℃.

For PNZ6, following results were obtained: i) before hydrogen exposure, PNZ6 dominantly consisted of $NiZr_2$ and ZrO_2, ii) after hydrogen exposure, the peak from $NiZr_2$ was divided into two peaks at 120℃, suggesting the formation of two hydride phases $NiZr_2H_{\sim 1}$ and $NiZr_2H_{\sim 5}$, iii) at 200 ~ 300 ℃, PNZ6 dominantly consisted of $NiZr_2H_{\sim 5}$ and ZrO_2, iv) at 400℃, the formation of ZrH_2 started, v) at temperatures higher than 500℃, ZrH_2 and $Ni_{10}Zr_7H_6$ formed with a decomposition of $NiZr_2$.

The XAFS data were qualitatively consistent with the XRD results. From the Pd- and Ni- K edge XAFS data, it was suggested that nano-scale metallic Pd-Ni alloy particles exist in the mixed matrix of $NiZr_2$ and ZrO_2 even just after the partial oxidation treatment.

It was inferred that nano-scale Ni-Pd alloy particles enhance kinematics of hydrogen absorption and desorption of $NiZr_2$ which have a high hydrogen storage capacity. The remarkable AHE observed in PNZ6 may be correlated with such complex structure of nanoscale Ni-Pd alloy particles dispersed in a mixed matrix of highly hydrogen absorptive $NiZr_2$ and hydrogen inactive ZrO_2.

References

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