Hydrogen induced structural change in various materials using the atomic pair distribution function analysis

H. Kim,[1] K. Sakaki,[1] K. Asano,[1] M. Yamauchi,[2] A. Machida,[3] T. Watanuki,[3] and Y. Nakamura [1]

[1] Energy Technology Research Institute, National Institute of Advanced Science and Technology, Tsukuba, Ibaraki 305-8565, Japan

[2] Department of Chemistry, Kyushu University, Fukuoka, 812-8581, Japan

[3] Quantum Beam Science Directorate, Japan Atomic Energy Agency, Sayo, Hyogo 679-5148, Japan

Summary

Modern scientifically interesting functional materials are heavily disordered, nano-sized or nano-structured. Although obtaining structural information is an essential part for understanding their fascinating properties, because of their poorly defined Bragg peaks, conventional crystallography method can not be applied. Here, we apply the atomic pair distribution function (PDF) analysis, a powerful local structural probing technique, to study Au and Cu atomic ordering in AuCu nanoparticles and structural disorder induced by the hydrogenation of AB_3-type intermetallic compounds RNi_3 (R=Ca, Y and La).

key words:

Hydrogen storage materials, local structure, nanoparticles, AB_3-type intermetallic compounds

1. Objectives

AuCu nanoparticles

Atomically ordered intermetallic AuCu nanoparticles (ordered nanoparticles) have been successfully synthesized [1] but relatively high annealing temperature (300°C) often causes coagulation of nanoparticles. It has been reported that under hydrogen atmosphere the ordering of Au and Cu atoms could be promoted even at much lower annealing temperature (180°C) [2]. Such ordered AuCu nanoparticles showed different catalytic activity from disordered nanoparticles (non-annealed nanoparticles). However, diffraction peaks from the ordering of Au and Cu atoms were too weak to provide a strong evidence that such improvement in catalytic activity is due to the atomic ordering. Therefore, we would like to apply the PDF analysis to investigate the degree of the ordering of Au and Cu atoms in AuCu nanoparticles and the role of hydrogen in promoting atomic ordering.

RNi_3 (R=Ca, Y and La) and $Mg_{1-x}Ca_xNi_3$

AB_3-type intermetallic compounds RNi_3 (R=Ca, Y and La) have a super lattice structure where $CaCu_5$-type (AB_5) and $MgZn_2$-type (AB_2) cells are alternately stacked along the c-axis [3]. Although all bulk $CaNi_2$, YNi_2 and $LaNi_2$ become amorphous after hydrogenation (while $CaNi_5$, YNi_5 and $LaNi_5$ remain crystalline), $CaNi_3$, YNi_3 and $LaNi_3$ remain crystalline. This means that AB_5 prevents amorphization of AB_2 cells in AB_3 structure. However, rapid hydrogenation sometimes induces amorphization of $LaNi_3$ indicating interface between AB_2 and AB_5 is somewhat

fragile. Therefore, it would be interesting to see changes in the local structure (whether there is any local distortion or not), especially interface between AB_2 and AB_5 of hydride phase of RNi_3 (R=Ca, Y and La) to study the stability of AB_2 in AB_3.

In addition, change in A element or partial substitution on A leads to great modification in its hydrogenation properties such as the number of plateau in pressure-composition isotherm (PCT). For instance, when we partially substitute Mg for Ca in $CaNi_3$, two narrow plateaus becomes one wide one. The mechanism behind such change in hydrogenation properties is not fully understood. Therefore, we would like to investigate changes in the local structure of hydride phase of $Mg_{1-x}Ca_xNi_3$ by changing Mg substitution using PDF.

2. Methods

Powder samples of AuCu nanoparticle and hydride samples of AB_3-type intermetallic compounds were packed in kapton capillaries with a diameter of 1.0 mm. Data were collected at BL22XU at SPring-8 [4] with an incident X-ray energy of 70.09 keV (λ=0.1769 Å) at room temperature using RA-PDF setup [5]. An image plate detector (R-AXISV from Rigaku) was mounted orthogonal to the incident beam with a sample-to-detector distance of 300 mm. The signal from an empty container (a kapton capillary) was subtracted from the raw data, and various other corrections were made [6]. The X-ray PDFs were obtained using the program PDFgetX2 [7]. For local structural studies the PDFgui program [8] was used for real space modeling.

3. Results and Discussion

AuCu nanoparticles: It has been suggested that the catalytic activity of AuCu nanoparticles are closely related to the degree of Au and Cu ordering. To investigate the ordering of Au and Cu atoms, we employed PDF analysis since analyzing diffraction data of nanoparticles is difficult due to the finite size effect. X-ray PDFs of AuCu nanoparticles annealed under various conditions are shown in Figure 1. The annealing effect on the structure of nanoparticles can be seen in PDFs. The sample annealed at 250°C under the H_2 gas environment shows PDF peaks even above 40 Å, which is the average particle size, indicating particle growth.

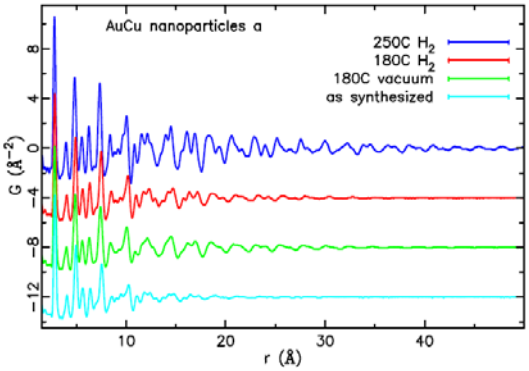

Figure 1. X-ray PDFs of AuCu nanoparticles annealed under various conditions.

All PDFs, including that of the as-synthesized sample, were better explained the by the ordered model, where Au and Cu layers are alternatively placed along ***c***-direction, than disordered model, where Au and Cu atoms are randomly distributed in the face centered cubic (fcc) structure; the ordered model reproduced relative PDF peak intensities below 8 Å better than the disordered model. The representative PDF fit is shown in Figure 2.

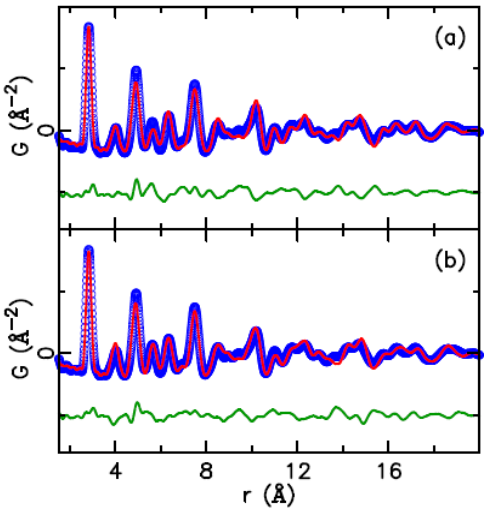

Figure 2. PDF refinement results of AuCu nanoparticle annealed at 180°C under the H_2 gas environment using (a) disordered and (b) ordered models.

AB_3 hydrides: Figure 3 shows the X-ray PDFs of $CaNi_3H_4$, YNi_3H_4 and $LaNi_3H_4$. Depending on A atom, changes in structure after hydrogenation are significantly different; $CaNi_3$ shows the well ordered structure even after hydrogenation but YNi_3 seems to become disordered. Significant change was observed in $LaNi_3$. Sharp PDF peaks were only seen in r < 20 Å. It indicates that $LaNi_3H_4$ becomes heavily disordered or even possibly becomes amorphous.

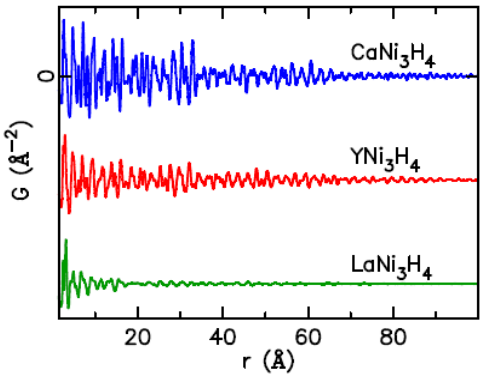

Figure 3. X-ray PDFs of $CaNi_3H_4$, YNi_3H_4 and $LaNi_3H_4$.

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