Insight into the local structure and lattice defect formation in La(Ni,Cu)_{5+x}

during the hydrogen absorption process

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Summary

We have carried out an in-situ X-ray total scattering experiment on $La(Ni,Cu)_{5+x}$ to investigate its local structural evolution during the hydrogenation process using the atomic pair distribution function (PDF) analysis. Data were collected at several pressure points at room temperature at BL22XU at SPring-8. Our preliminary Rietveld refinement results showed that the phase transformation was not observed upon hydrogenation and all the diffraction data were explained by the average hexagonal structural model (space group *P6/mmm*). However, the thermal factors for all atomic positions were larger than usual. Our preliminary PDF refinement results suggest that the peaks at ~3 Å cannot be explained by the average structural model even though fit in higher *r* region than 10 Å was good enough. This is probably closely related to local deviation of Ni atoms at 3*g* site near the dumbbell from the ideal position. The detailed local structure analyses are underway.

Key words: Hydrogen storage, local structure, total scattering, pair distribution function

1. Objectives

We have investigated unusual lattice defect behavior in $La(Ni,Cu)_{5+x}$ intermetallic compounds. Our previous study using XRD and positron annihilation showed that $LaNi_5Cu$ absorbed hydrogen without phase transformation and vacancies started to be formed from certain hydrogen content in absorption process and introduced vacancies were recovered during desorption at room temperature [1]. We have proposed that these unusual lattice defect behavior has relationship with the formation of dumbbell pairs which were composed by extra Ni or Cu atoms. Using the atomic pair distribution function (PDF) analysis, we can trace the local structural changes, especially changes in the environment of extra Cu atoms and correlate them with positron lifetime measurement results to find out the interaction between extra Cu and lattice defects. Therefore, we propose to carry out the in-situ hydrogen gas loading X-ray total scattering experiments on $La(Ni,Cu)_{5+x}$ for the PDF analysis.

2. Methods

A synchrotron X-ray total scattering experiment was conducted at Japan Atomic Energy Agency (JAEA) beam line of BL22XU [2] at SPring-8. LaNi_{4.4}Cu and LaNi_{4.6}Cu powder sample was packed in an in-situ gas loading sample holder made of a kapton capillary with a diameter of 1.4 mm, a valve and couplings. The sample was activated by heating at 423 K under vacuum for 1 h before hydrogenation. Data were collected at several pressure points using RA-PDF setup [3]. All the measurements were carried out at room temperature and an incident X-ray energy was 70 keV (= 0.17768 Å). An image plate detector (R-AXISV from Rigaku) was mounted orthogonal to the incident beam



Fig.1 Rietveld refinements of XRD patterns of LaNi_{4.4}Cu (a) and LaNi_{4.6}Cu (b) before hydrogenation.

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 [4] before obtaining the PDFs using the program PDFgetX2 [5]. For local structural studies the PDFgui program [6] was used and for average structural studies the RIETAN-FP program [7] was used.

3. Results and Discussion

The crystal structure of a stoichiometric LaNi₅ is hexagonal with space group P6/mmm. La (1*a* site) is on (0,0,0), Ni (2*c* site) on (0.3333, 0.6667, 0) and Ni (3*g* site) on (0.5, 0, 0.5). When the composition becomes over-stoichiometry, a part of La is replaced by the dumbbell composed of two B atoms (Ni and Cu) occupying at (0, 0, *z*) called 2*e* site [8]. Then the atomic position of B atoms at 2*c* site near the dumbbell shifts toward the dumbbell. This new position is (*x*, 2*x*, 0) called 6*l* site. In this assumption, the atomic position of Ni (3*g* site) is unaffected by the dumbbell.

Figure 1 showed Rietveld refinements of synchrotron X-ray diffraction patterns of LaNi_{4.4}Cu and LaNi_{4.6}Cu before hydrogenation using the *P6/mmm* structural model. These samples were single phase. The lattice constants of LaNi_{4.4}Cu and LaNi_{4.6}Cu were a = 5.01965 Å and c = 4.02597 Å and a = 5.00778Å and c = 4.03012 Å, respectively. It is known that the lattice constant for *c* axis expands and that for *a* axis contracts by the replacement of La by the dumbbell. Our result shows the same tendency.

During hydrogenation the Bragg peaks continuously shifted toward lower 2θ with increase of hydrogen pressure in both alloys as shown in Fig.2. These results indicate that the alloys absorbed hydrogen but the phase transformation from a solid solution phase to a hydride phase did not occur. Figure 3 showed Rietveld



Fig.2 Change in XRD patterns of LaNi_{4.4}Cu (a) and LaNi_{4.6}Cu (b) during hydrogenation.



Fig.3 Rietveld refinements of XRD patterns of LaNi_{4.4}Cu (a) and LaNi_{4.6}Cu (b) in a full hydride phase.

refinements of synchrotron X-ray diffraction patterns of the hydride of LaNi_{4.4}Cu and LaNi_{4.6}Cu using the *P6/mmm* structural model. The lattice constants of the hydride of LaNi_{4.4}Cu and LaNi_{4.6}Cu were a = 5.30923 Å and c = 4.18616 Å and a = 5.25069 Å and c = 4.16256 Å, respectively. The volume expansions were around 16.3% and 13.5%, respectively. The Rietveld refinements showed that the thermal factors for all atomic sites increased with increase of hydrogen pressure. These results suggest that the deviation of the atomic positions from their ideal positions became significant upon hydrogenation.

The PDF refinement results using LaNi_{4.4}Cu and LaNi_{4.6}Cu X-ray patterns are shown in Fig. 4 and Fig.5, respectively. The average structural model (space group *P6/mmm*) was used. The refinement range was 1.5 < r < 80 Å. A scale factor, lattice constants, isotropic atomic displacement parameters (U_{iso}) and a peak sharpening parameter [4] were refined until the best fit was obtained. The model explained the PDF



Fig.4 PDF refinement of LaNi_{4.4}Cu before hydrogenation; (a) up to 80 Å (b) enlarged view



Fig.5 PDF refinement of LaNi_{4.6}Cu before hydrogenation; (a) up to 80 Å (b) enlarged view

patterns of LaNi_{4.4}Cu and LaNi_{4.6}Cu well. However, the atomic displacement parameters were slightly larger than usual. These values increased with hydrogen pressure similar to the values estimated by Rietveld refinements. In addition there are some differences between data and calculation especially at ~3 Å shown by an arrow and LaNi_{4.6}Cu had larger difference than LaNi_{4.4}Cu. These results suggest that the atomic arrangement of LaNi_{4.4}Cu and LaNi_{4.6}Cu is somewhat distorted by the dumbbell. As described above, in the current structure model, the B atoms at 3g are assumed to be unaffected by the dumbbell. Therefore, this is probably closely related to local deviation of Ni atoms at 3g site near the dumbbell from the ideal position. Further analyses of the local distortion and the local structural evolution during the hydrogenation process are underway.

4. References

- [1] K. Sakaki et al. (in preparation).
- [2] T. Watanuki et al., Philos. Mag. 87, 2905-2911 (2007).
- [3] P. J. Chupas et al., J. Appl. Crystallogr. 36, 1342-1347 (2003).
- [4] T. Egami and S. J. L. Billinge, *Underneath the Bragg Peaks: Structural Analysis of Complex Materials*: Pergamon Press Elsevier: Oxford, England, 2003.
- [5] X. Qiu et al., J. Appl. Crystallogr. 37, 678 (2004).
- [6] C. L. Farrow et al., J. Phys.: Condens. Matter 19, 335219 (2007).
- [7] F. Izumi and K. Momma, Solid State Phenom. 130, 15-20 (2007).
- [8] M. Latroche, J.-M. Joubert, A. Percheron-Guegan and P. H. L. Notten, Journal of Solid State Chemistry, 146 (1999) 313-321.