EXAFS characterization of LaNi₅, LaCo₅ and their hydrides

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Introduction

LaNi₅ and LaNi₅ based alloys are important for hydrogen storage materials, such as an electrode in Ni-metal hydride batteries and hydrogen-fuel cells. The crystal structure of LaNi₅ is CaCu₅-type (space group P6/mmm). Its hydride, LaNi₅H₇, has hexagonal structure of space group P6₃mc. LaCo₅ also has CaCu₅-type structure, while hexagonal structure distorts to orthorhombic structure when LaCo₅ is hydrogenized. Hydride of LaCo₅ is represented as LaCo₅H₃ rather than LaNi₅H₇ for LaNi₅, which leads to smaller hydrogen absorption for LaCo₅ compared with LaNi₅. Their hydrogenation characteristics may correspond to the difference of local structure between LaCo₅ and LaNi₅ [1].

In this paper, the local structures around Ni, Co and La for LaNi₅, LaCo₅ and their hydrides are clarified with EXAFS and the mean-square fluctuation of inter-atomic distance, σ², is given from EXAFS spectrum due to estimate the influence of the structural fluctuation on the hydrogen absorption and the structural transition.

Experiments

Samples of LaNi₅ and LaCo₅ are prepared by arc-melting the constituent elements under an argon atmosphere and annealed at 1223 K for 5 days. These samples are hydrogenized under 4MPa hydrogen at 353K.

For XAFS measurements, BN pellets are prepared adjusting optimum absorption thickness. XAFS spectra of the Ni (Co) K-edge and La L III-edge were measured by a transmission method from 20 K to 300K using a double Si(111) monochromator. UWXAFS programs are used to analyze the XAFS data and FEFF program is used for multiple scattering calculations.

Results and discussion

Fig.1 shows Ni K-edge EXAFS spectra at 20K for LaNi₅ and LaNi₅H₇, and Co K-edge for LaCo₅ and LaCo₅H₃. The EXAFS spectrum of LaNi₅ exhibits relatively larger amplitude than LaCo₅, while the phase of spectrum is almost same as that for LaCo₅, because these compounds have same CaCu₅-type crystal structure. Small EXAFS amplitude of LaCo₅ is supposed that the local structure around Co in LaCo₅ has relatively large fluctuation probably due to weak Co-Co bonding compare with Ni-Ni one for LaNi₅, which can be associated with transformation from hexagonal to orthorhombic structure through hydrogenation.

Fig.2 shows the EXAFS spectra of the La LIII-edge represented as k³χ(k) vs. k at 20K for LaNi₅, LaCo₅, and their hydrides. EXAFS k³χ(k) spectra of the La LIII-edge are shown in Fig.2. The amplitude of spectrum for LaNi₅H₇ drastically attenuated from that for LaNi₅. Consequently, σ²(La-Ni) increases from 0.48×10⁻⁴ [nm²] for LaNi₅ to 1.85×10⁻⁴ [nm²] for LaNi₅H₇.

Although the XRD patterns of hydrides show long-range structural order, EXAFS spectra indicate that the local structure of hydrides involves large fluctuation of inter-atomic distance. It is interesting that the phase of spectrum for LaNi₅H₇ is almost same as that for LaNi₅, which disagrees with the calculated spectra for LaNi₅H₇. It is indicated that the transformation from LaNi₅ to hydride is an isotropic expansion with large structural fluctuation.

Reference


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