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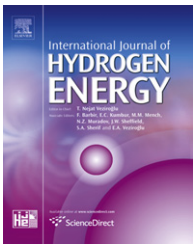

Development of sample holder for *in situ* neutron measurement of hydrogen absorbing alloy

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ABSTRACT

We developed a sample holder for *in situ* measurement of hydrogen absorbing alloy. In order to prevent the hydrogen absorption by vanadium, copper is coated with 2 μm thickness on inner surface of the vanadium holder. The effect of copper coating and the performance of the holder were evaluated by neutron diffraction and PDF profiles. The lattice parameters *a* and *c* of La_2Ni_7 with Ce_2Ni_7-type structure were refined as 0.505921(4) and 2.468608(4) nm by Rietveld analysis. The Cu–Cu correlation peak around $r = 0.255$ nm was not observed in the PDF profile. Thus the holder is useful for *in situ* measurement of hydrogen absorbing alloy. The diffraction and PDF profiles of $La_2Ni_7D_x$ ($0 < x < 10.5$) were collected using a deuterium pressure of 3.7 MPa, and the changes of crystal and local structures were clearly observed.

1. Introduction

Some metal hydrides absorb and desorb at under ambient temperature and low pressure. Applying this property La_2Ni_7 based alloy is used as a cathode of Ni–metal hydride battery [1]. The bcc solid solution alloy Ti–Cr–V–Mo is expected to be applied for hydrogen storage tank in fuel cell vehicle [2].

Hydrogen atoms are located at interstitial sites of metal matrix and absorption–desorption property is closely related to the position and occupancy of the hydrogen atom. Neutron diffraction can directly determine the hydrogen position and has been used to refine the crystal structure of metal hydride [3–6]. Iwase et al. reported the crystal and local structures in $(Ti_{0.45}Cr_{0.35}Mo_{0.20})$-D system by *ex situ* neutron powder diffraction [7]. From the result of Rietveld refinement, the deuterium atoms occupy the tetrahedral (T) sites in both the CaF_2-type phase (MD_2 phase) and the bcc phase (primary solid solution phase). The metal–metal and metal–deuterium correlations length and the nearest neighbor coordination number around deuterium are obtained by pair

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distribution function (PDF) analysis and radial distribution function (RDF) analysis. The deuterium atoms occupy the T sites surrounded mainly by Ti atoms. Nakamura et al. reported the crystal structures and distribution of deuterium in $LaNi_{5-x}Al_xD_{y\ (y\ =\ 5-7)}$, $LaNi_{4.78}Sn_{0.22}D_{6.1}$ and $La_4MgNi_{19}D_{24}$ by *in situ* powder neutron diffraction [8]. Neutron diffraction data were collected on a time-of-flight (TOF) neutron diffractometer. In order to eliminate unwanted scattering from stainless steel sample holder, diffraction data were collected using the 90°bank together with a cadmium mask (see Fig. 1 of Ref. [8]).

PDF analysis is a powerful tool for structural investigation [9]. PDF is derived from Fourier transformation of the structure factor $S(Q)$, where $Q\ (=4\pi\sin\theta/\lambda)$ is the momentum transfer. To get the PDF profile, the measurement of wide Q range is needed. When the 90°bank is used, sufficiently wide Q range cannot be obtained. Vanadium holder is often used for neutron diffraction because the coherent neutron scattering length of vanadium is small. However, vanadium absorbs a large amount of hydrogen [10]. For this reason, stainless steel sample holder had been used for *in situ* measurement of the metal-hydrogen system.

This study aims to develop a new sample holder for *in situ* measurement of crystal and local structures of La_2Ni_7 deuteride. In order to clarify the relation between hydrogenation properties and structural change, *in situ* neutron measurement is an indispensable tool. We attempted to observe diffraction and PDF profiles at the same time. The present paper describes performance of the developed sample holder and structural changes of the La_2Ni_7-D system with increasing deuterium content.

2. Experimental

The sample holder is composed of three parts, cylindrical vanadium can, titanium cap and SS304 flange joint (Fig. 1). The purity of vanadium is 99.94%. The cylindrical vanadium can was made by machining and was connected to the titanium cap by arc welding. The vanadium can is 70 mm long with inner diameter of 8 mm and wall thickness of 0.3 mm. O-ring or metal O-ring was used between titanium cap and SS304 flange joint. In order to prevent hydrogen absorption by vanadium, the inside of the vanadium can was coated with copper. Fig. 2 shows the SEM photograph of the copper coating removed from the holder. The thickness of copper coating is 2 μm. The copper coating was made by electroless plating.

La_2Ni_7 alloy was prepared by arc-melting of La and Ni metals (99.9%) in Ar atmosphere. The obtained ingot was annealed at 1153 K for 65 h under vacuum of 2.0×10^{-2} Pa and quenched into ice water.

The intensity $I(Q)$ of TOF neutron data were collected at room temperature on the neutron powder diffractometer NPDF installed at the Lujan Center, Los Alamos Neutron Science Center (LANSCE) in Los Alamos National Laboratory (LANL). The Rietveld refinement program GSAS [11,12] was used to analyze the data. $I(Q)$ was corrected for background, absorption and multiple and incoherent scatterings, in order to obtain the structure factor $S(Q)$ by using a PDF analysis program PDFgetN [13]. The reduced pair distribution function

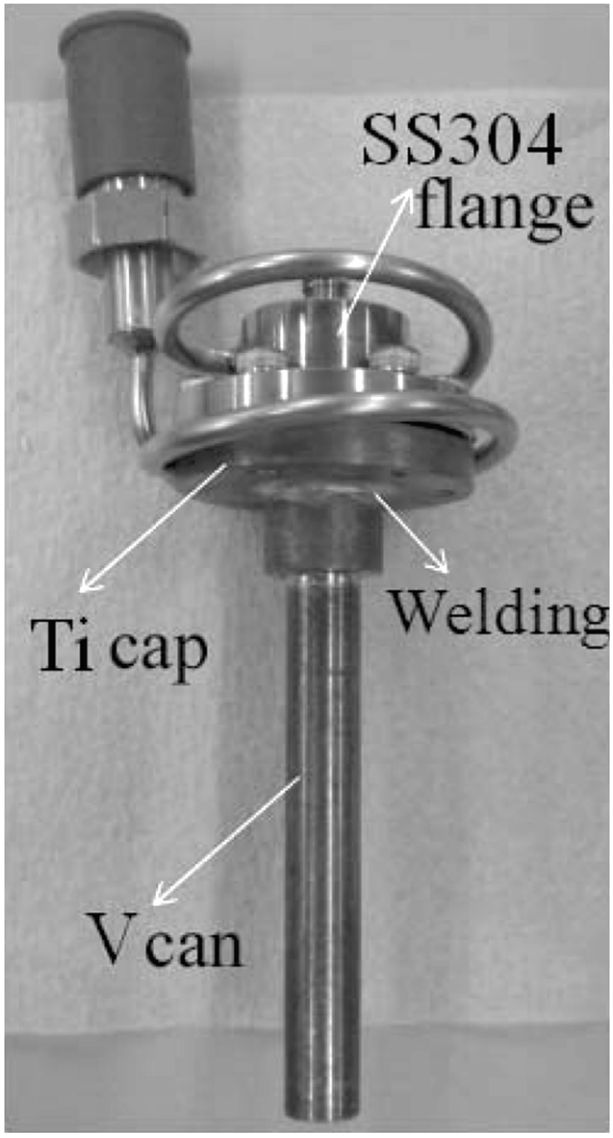

Fig. 1 – Vanadium sample holder with copper coating. The vanadium can was connected to the titanium cap by arc welding.

$G(r)$ was derived from the Fourier transformation of $S(Q)$. $G(r)$ is obtained as follows:

$$G(r) = 4\pi r[\rho(r) - \rho_0] = \frac{2}{\pi}\int_0^\infty Q[S(Q) - 1]\sin(Qr)dQ$$

where $\rho(r)$ is the microscopic pair density, ρ_0 is the average density and Q is the magnitude of the scattering vector. The scattering data were terminated at $Q_{max} = 350\ nm^{-1}$.

The neutron data were measured using the sample holder shown in Fig. 1. A 4.8 g sample was placed in the holder. Deuterium gas pressure and deuterium content of the sample was controlled using PCT machine. Deuterium was introduced gradually into the holder up to a pressure of 3.7 MPa. The *P–C* isotherm was measured using the Sieverts method with no pre-treatment for activation. The deuterium content of the sample was refined by PCT machine.