MLF Experimental Report	提出日 Date of Report 2015/3/6
課題番号 Project No. 2014A0329 実験課題名 Title of experiment Crystal structure analyses for new hydrogen storage materials when absorbing/desorbing hydrogen 実験責任者名 Name of principal investigator Hiroshi NOZAKI 所属 Affiliation Toyota Central R&D Labs., Inc.	装置責任者 Name of responsible person Toshiya Otomo 装置名 Name of Instrument/（BL No.） NOVA/BL21 実施日 Date of Experiment 2014/6/10-13, 11/21-23

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。（適宜、図表添付のこと）
Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.

MH1: $TiMn_{1.5}$

MH2: $TiMn_{1.3}Cr_{0.2}$

MOF-1: $C_{12}H_{12}CuN_2O_4$

2. 実験方法及び結果（実験がうまくいかなかった場合、その理由を記述してください。）
Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.

1. Metal hydride

The samples, $TiMn_{1.5}$ (with large hysteresis) and $TiMn_{1.3}Cr_{0.2}$ (with small hysteresis), were prepared by heat treatment (1200°C 4 hours in argon atmosphere) after pure metals were alloyed with arc melting method. The in-situ neutron diffraction (ND) measurements were performed by high intensity total scattering diffractometer (NOVA) equipped pressure-composition (P-C) isothermal measuring apparatus using deuterium gas.

Hysteresis phenomenon, which absorption and desorption pressures are different, appears in many hydrogen storage alloys. In the practical use of hydrogen storage alloys, the development of small hysteresis alloys is one of the important issues because wide range pressure control is needed in large hysteresis alloys. It is known that the substitution of Mn by Cr reduces the hysteresis in Ti-Mn alloys. However, the mechanism of hysteresis reduction in hydrogen storage alloys is not clarified sufficiently. As compared with X-ray diffraction, ND intensity for hydrogen atom is very high than that for metal atom. Therefore, the structural changes in hydrogen absorption-desorption process has been studied by in-situ ND measurement in order to clarify the mechanism of hysteresis phenomenon.

2. 実験方法及び結果（つづき） Experimental method and results (continued)

Figure 1 shows the result of P-C isothermal measurement of the $TiMn_{1.5}$ sample. Figure 2 shows the ND patterns at each point on the P-C isothermal curve. In the hydrogen absorption process, the diffraction peak intensity of hydrogen-poor Laves phase (α-phase, $TiMn_{1.5}D_x$ x~0.5) decreases and that of hydrogen-rich Laves phase (β-phase, $TiMn_{1.5}D_x$ x~2.0) increases according to absorption of hydrogen. The reverse change occurs in the hydrogen desorption process. The peaks of each phase shift depending on hydrogen content. In future, the crystal structural changes (the site position and occupancy of deuterium mainly) in the absorption and desorption process, will be studied by Rietveld analysis.

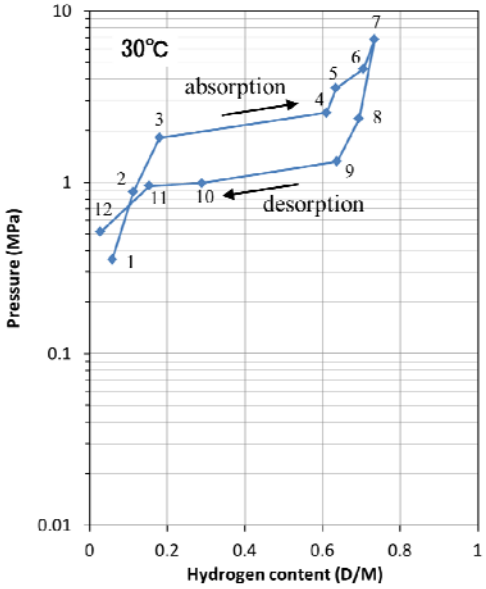

Fig.1 Pressure composition isothermal curve of the $TiMn_{1.5}$ sample in neutron diffraction measurement.

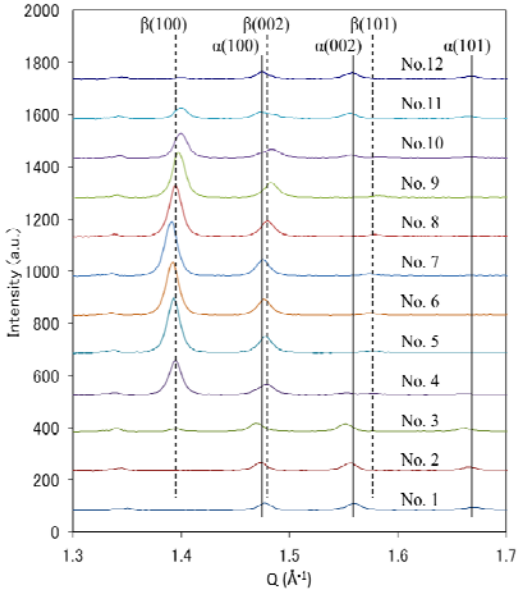

Fig.2 Neutron diffraction patterns of the $TiMn_{1.5}$ sample measured at each stage of Fig.1.

2. Metal-organic framework material

The $C_{12}H_{12}CuN_2O_4$ single crystals, which belongs to metal-organic framework (MOF) [1], was synthesized by a self-organization from a mixture of $Cu(HCO_2)_2{\cdot}4H_2O$ [2] and C_5H_5N. Then, the powder sample was prepared by crushing the single crystals. The powder sample was filled into the cylindrical sample holder made of sapphire. The in-situ ND patterns were recorded on NOVA under D_2 gas atmosphere. The ND patterns under vacuum and 8 MPa of D_2 pressure are shown in Fig. 3 together with the simulated pattern using the crystallographic parameters based on the ref. [1]. There are several unknown diffraction peaks in the ND patterns. This means that the MOF sample was probably decomposed before ND measurement. Mixture of MOF and unknown phases complicates the certain discussion at least at the present stage. We speculate that the MOF sample was decomposed by absorbing water in air after crashing the single crystals or by evacuating the inner-space of the sample holder before pressurizing with D_2 gas. As an alternative effort, we have to convey the sample as synthesized, and crash it just before measuring the ND pattern if needed.

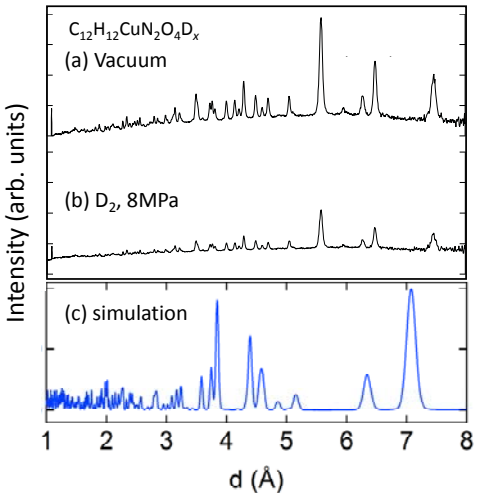

Fig. 3 ND patterns under vacuum and D_2 pressure of 8 MPa with the simulated pattern.

[References]

[1] T. Takami et al., APL Materials **2**, 096104 (2014).

[2] H. Kiriyama, Bull. Chem. Soc. Jpn. **35**, 1199 (1962).