Hydrogen storage by earth abundant metals – high-pressure synthesis of Al_3FeH_4

Compounds of metal and hydrogen are called metal hydrides, and among them, alloys that can easily release and absorb hydrogen near ambient pressure–temperature conditions are called hydrogen storage alloys. There are well-known guidelines for obtaining hydrogen storage alloys. These guidelines concern alloying metals with high and low hydrogen affinities [1]. Here, metals with high hydrogen affinities refer to elements that can easily form metal hydrides with hydrogen-to-metal atomic ratios (H/M ratios) of 0.5 or higher near ambient pressure. In contrast, metals with low hydrogen affinity refer to elements that cannot form such hydrides near ambient pressure.

It is also known that hydrogen affinity can be well classified on the basis of the periodic table. Figure 1 shows the relationship between a certain part of the periodic table and hydrogen affinity. It is clear from Fig. 1 that elements in groups 1 through 5 have high hydrogen affinities, while those in groups 6 through 13 have low hydrogen affinities. It has been reported that the hydrogen affinity of metals is related to their softness [2].

Hydrogen storage alloys must contain at least one metal with a high hydrogen affinity. However, as shown in Fig. 1, except for Mg, all metals with high hydrogen affinities are expensive, making it difficult to reduce costs. In addition, the choice of lightweight elements is also limited, making it difficult to increase the hydrogen density per weight. Thus, under the conventional search guidelines for hydrogen storage alloys, it is considered difficult to obtain a material that can solve the problems of hydrogen storage alloys, such as gravimetric hydrogen density and cost.

With the aim of realizing hydrogen storage alloys that do not contain expensive rare metals, we have been searching for hydrides consisting only of metals with low hydrogen affinities, which do not follow the synthesis guidelines for hydrogen storage alloys, under high pressures. We found that an alloy of aluminum and iron can form hydrides under high pressures and that the resulting hydride has the potential to absorb hydrogen even near ambient pressure [3].

The starting material was the $Al_{13}Fe_4$ alloy prepared by arc melting at ambient pressure. The obtained ingot was crushed into a coarse powder and compacted into a disk shape. The disk-shaped sample was placed in a sample capsule made of boron nitride. The sample was pressurized to 9 GPa at room temperature and then heated to 750°C in fluid hydrogen. The sample was kept in hydrogen for 2 h, cooled to room temperature, and depressurized to the ambient pressure.

The hydrogenation of the sample was achieved using a high-pressure cell developed by Fukai and Okuma [4]. A capsule made of NaCl was used for hydrogen sealing. An internal hydrogen source made of NH_3BH_3 was placed in the hydrogen sealing capsule along with the sample. The sample in the boron nitride capsule, through which hydrogen can permeate but not other byproducts from the internal hydrogen source, was hydrogenated. We observed structural changes of the sample during the hydrogenation reaction *in situ* using synchrotron radiation X-ray diffraction (SR-XRD) measurement at SPring-8 **BL14B1** to detect the occurrence of a novel hydrogenation reaction.

Figure 2 shows the X-ray powder diffraction profiles obtained when the $Al_{13}Fe_4$ alloy was kept in a hydrogen fluid under high pressures. Figure 2(a) shows the change in the profile when the alloy was kept at 600°C at 6 GPa. The bottom profile was obtained after the alloy was pressurized to 6 GPa at room temperature. Excluding diffraction lines from high-pressure cell parts, all peaks can be indexed to the ambient-pressure phase of the $Al_{13}Fe_4$ alloy, indicating that no pressure-induced structural phase transition occurred. When the alloy was heated, no significant structural changes were observed except for peak sharpening and increases in the intensities of some peaks owing to the relaxation of anisotropic strain introduced by solid compression. $Al_{13}Fe_4$ alloy cannot be hydrogenated at 600°C and 6 GPa.

Figure 2(b) shows X-ray diffraction profiles of the alloy hydrogenated at 750°C and 9 GPa. Decreases in the intensities of Bragg peaks from the alloy and the appearance of new peaks were observed above

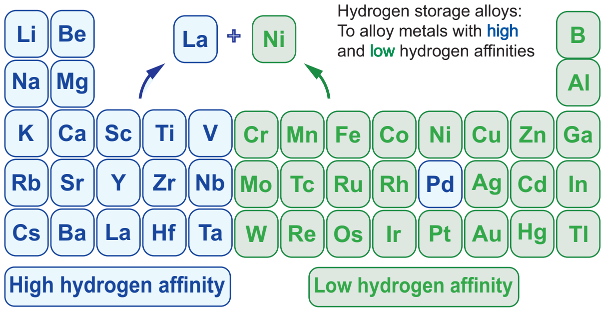

Fig. 1. Relationship between hydrogen affinities of metallic elements and the periodic table, where elements in groups 1 to 5 have high hydrogen affinities and those in groups 6 to 13 have low affinities. Hydrogen storage alloys are obtained by alloying metals with high and low hydrogen affinities.

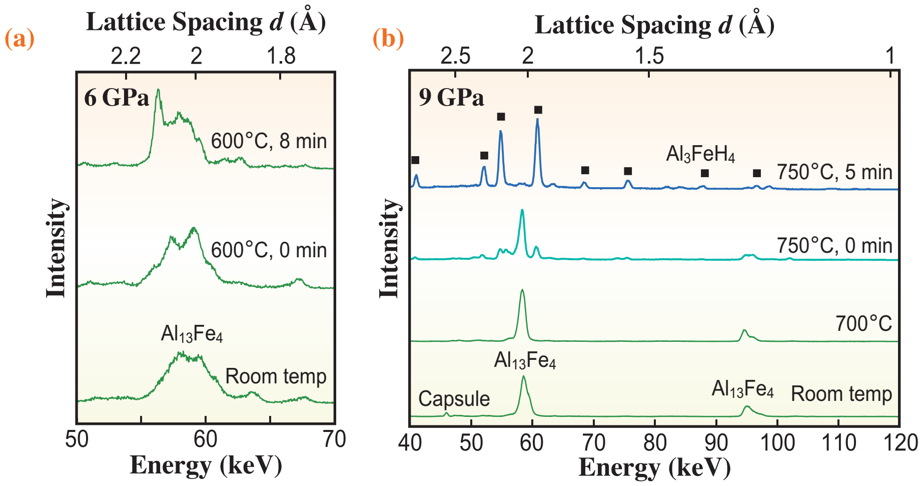

Fig. 2. *In situ* powder X-ray diffraction profiles measured when $Al_{13}Fe_4$ alloys were hydrogenated at **(a)** 6 GPa and **(b)** 9 GPa.

650°C. When the alloy was kept at 750°C, the peaks from the alloy disappeared after 5 min, and only the peaks from the new structural phase appeared. It was determined that the new structural phase was the new hydride Al_3FeH_4 on the basis of the results of characterizing the recovered hydride under ambient conditions. The schematic of the crystal structure of Al_3FeH_4 is shown in Fig. 3.

It was also clarified that Al_3FeH_4 is thermodynamically stable under near-ambient conditions by the analysis of the recovered sample. In other words, $Al_{13}Fe_4$ alloy can absorb hydrogen at around ambient pressure and has potential for hydrogen storage application. In contrast to its thermodynamical stability, a high pressure above 7 GPa is currently necessary to hydrogenate the alloy. This is because a chemically stable oxide layer on the alloy prevents the hydrogenation reaction. Now, we are attempting to hydrogenate the alloy at around ambient pressure by suppressing the effect of the surface oxide layer.

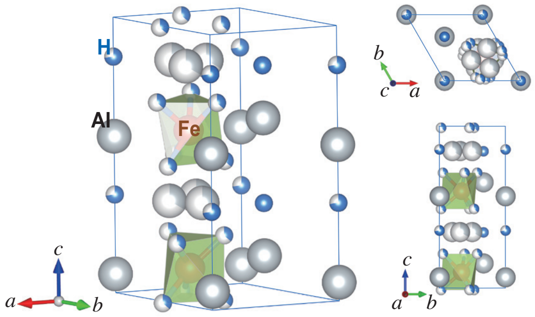

Fig. 3. Schematic of the crystal structure of Al_3FeH_4. The crystal structure was drawn using the VESTA program [5].

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