

A new class of aluminum-based interstitial hydrides, Al_2CuH_x

Safe and efficient hydrogen storage is widely recognized as one of the key technological challenges to realize a hydrogen-based economy. Hydrogen can be stored as a pressurized gas, cryogenic liquid, and solid fuel via chemical or physical combination with other materials; hydrogen forms hydrides with some materials leading to solid-state storage, which provides an important safety advantage over pressurized gas and cryogenic liquid storage methods.

For automotive applications, materials should be mainly composed of light elements ($Z \le 20$) to reach a high gravimetric hydrogen capacity. In this context, many studies of complex aluminum hydrides have been reported, in which aluminum and hydrogen atoms form complex anions as shown in Fig. 1(a). However, complex aluminum hydrides suited for practical application have not yet been developed. Apart from complex aluminum hydrides, aluminumbased alloy hydrides, i.e., aluminum-based interstitial hydrides (Fig. 1(b)), have not been reported. Pure aluminum and its alloys have low affinity for hydrogen and are difficult to hydrogenate, though their interstitial hydrides are expected to show excellent properties for hydrogen storage. In the present study, we demonstrate the formation of an aluminum-based interstitial hydride AI_2CuH_x [1], which belongs to a new class of aluminum-based hydrides. Its interstitial nature is investigated.

Figure 2(a) shows the crystal structure of the Al₂Cu alloy [2]. A square antiprism consisting of eight aluminum atoms and one copper atom is the structural unit of the crystal structure. One-dimensional chains created by the face-sharing antiprisms share edges to form the crystal structure with interstitial spaces. The starting material was Al₂Cu alloy powder. The sample was pressurized to 10 GPa and heated in hydrogen

fluid at temperatures of up to 900°C. The structural changes and hydrogenation reaction of the sample were observed *in situ* by synchrotron radiation X-ray diffraction measurements at beamline **BL14B1** [3].

Figure 3 shows a series of X-ray diffraction profiles taken when the sample was heated at 10 GPa in hydrogen fluid. The Al₂Cu structure was maintained below 880°C. The sample decomposed into pure aluminum and Al₂Cu₃ at 880°C. No hydrogenation reaction occurred at this stage. The sample was cooled to 800°C after the decomposition reaction. The diffraction profile gradually changed as shown in Fig. 3; new Bragg peaks appeared as indicated by arrows in Fig. 3. They were indexed with an enlarged unit cell of the Al₂Cu alloy, suggesting volume expansion caused by the hydrogenation reaction of the Al₂Cu alloy.

The sample was recovered at ambient conditions. Hydrogen evolved at around 150°C when the recovered sample was heated at ambient pressure. After the hydrogen evolution, the sample had the original Al₂Cu structure. Here, it was confirmed that the aluminum-based hydride Al₂CuH_x was formed by the hydrogenation reaction at 10 GPa and 800°C. The hydrogen content was roughly estimated to be $x \approx 1$ on the basis of mass measurements performed during the dehydrogenation reaction.

It is worth mentioning that the hydrogenation reaction proceeded only after the decomposition reaction at 10 GPa and 880°C. The Al₂Cu alloy was not hydrogenated when the sample was heated from room temperature to 800°C at 10 GPa. The surface oxide layer on the alloy was considered to inhibit the hydrogenation reaction. The oxide layer was removed by the decomposition reaction, which allowed the hydrogenation reaction upon the subsequent cooling



Fig. 1. Schematic of the crystal structure of (a) typical complex aluminum hydride (LiAlH₄) and (b) interstitial hydride (hypothetical). Aluminum and hydrogen atoms form complex anions in the complex aluminum hydride, whereas the metal lattice of the interstitial hydride remains intact during a hydrogenation reaction.



Fig. 2. Schematic of the crystal structure of (a) Al_2Cu alloy and (b) Al_2CuH_x . Positions of hydrogen atoms were determined only by first-principles calculations.

of the sample. Such a complex synthetic route is difficult to find without the aid of *in situ* synchrotron radiation X-ray diffraction measurement.

Figure 2(b) shows the crystal structure of Al_2CuH_x , which was determined by powder X-ray diffraction measurement and first-principles calculations (note that the positions of hydrogen atoms were determined only by first-principles calculations). The structural change of the Al_2Cu alloy caused by the hydrogenation reaction can be explained as follows. The Al_8Cu square antiprisms twist to enlarge the interstitial spaces consisting of four aluminum atoms. Hydrogen atoms are located at the center of the enlarged interstitial sites to form the interstitial hydride Al_2CuH_x . The electronic structure of Al_2CuH_x determined by first principles calculations also illustrates the interstitial nature of the hydride [1].

The aluminum-based interstitial hydride $Al_2CuH_x(x \sim 1)$ has been successfully synthesized by hydrogenating Al₂Cu alloy at high temperatures and pressures. Al₈Cu square antiprisms in Al₂Cu twisted during the hydrogenation reaction, which enlarges the interstitial spaces enabling the accommodation of hydrogen atoms. The properties of interstitial hydrides are favorable for hydrogen storage materials because the hydrogenation and dehydrogenation reactions should proceed simply and their thermodynamic properties are tunable by the addition of other elements to the alloy. Both the experimentally and theoretically obtained results in the present study will be useful for exploring other aluminum-based interstitial hydrides. These findings will help expand the variety of aluminum-based alloy hydrides, which, in turn, will help in developing practical hydrogen-storage materials.



Fig. 3. Series of *in situ* synchrotron radiation X-ray diffraction profiles of the sample during heat treatment at 10 GPa. Bragg peaks denoted by triangles, circles, and squares originated from Al₂Cu, Al₂Cu₃, and pure aluminum, respectively. Arrows indicate Bragg peaks originated from the formed hydride.

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References

H. Saitoh, S. Takagi, N. Endo, A. Machida, K. Aoki,
S. Orimo and Y. Katayama: APL Mater. 1 (2013) 032113.
A. Meetsma et al.: J. Solid State Chem. 83 (1989) 370.
W. Utsumi et al.: J. Phys. Condens. Matter 14 (2002) 10497.

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