

Synthesis of CaNiH_3 based hydrides by mechanical alloying

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CaNiH_3 , which has been discovered through the study about the decomposition of CaNi_3 in hydrogen atmosphere, has a high hydrogen storage capacity (1.5 in molar ration of hydrogen to metal or 3.0 mass%). The synthesis of the hydride is, however, accompanied by nickel metal, which makes detailed analyses about hydrogenation properties and crystallographic structures difficult. In the present study, mechanical grinding/alloying was applied to obtain the detailed information about this new hydride. Two kinds of samples, with and without Pd, were prepared at 400 rpm with a ball-mill machine under a hydrogen atmosphere of 0.6MPa. The constituent phases and their crystal structures of these samples were analyzed by Rietveld profile refinement. It was found that the samples thus obtained were approximately single-phase structure composed of CaNiH_3 type hydride phase.

Key words: Ca-Ni-Pd, hydrogen storage materials, mechanical grinding/alloying, Rietveld profile refinement

1. INTRODUCTION

Hydrogen storage materials are one of the most promising media to store and/or transport hydrogen gas. They usually have higher volumetric hydrogen storage density than liquefied hydrogen and can be utilized as hydrogen storage under the moderate conditions such as room temperature and atmospheric pressure. However, the gravimetric hydrogen density is low because the metal constituents are usually heavy. Thus the materials with higher gravimetric hydrogen density have been being searched and developed extensively.

We discovered a new hydride CaNiH_3 through the study about disproportionation of CaNi_3 under hydrogen atmosphere [1]. This hydride contains about 3 mass% of hydrogen and is composed of inexpensive elements, so it can be one of the promising candidates for hydrogen storage materials.

The problem of this hydride as a hydrogen storage material is that the corresponding metal phase CaNi is unstable and it easily decomposes to form CaH_2 and nickel metal when it desorbs hydrogen [1]. Thus the reversible hydrogenation of CaNiH_3 has not been reported and therefore the study has to be done about rehydrogenation of the decomposed sample. In our previous paper [2], it has been shown by a semi-empirical calculation [3] that the addition of Pd or Pt into CaNiH_3 should be effective to stabilize the metal phase, but no ternary phase composed of Ca, Ni and Pd was prepared by conventional melting and sintering methods.

From the point of view of structural analysis, the nickel metal which coexists with CaNiH_3 when it is obtained through the decomposition of CaNi_3 hydride

causes the disturbance to obtain the detailed information about the new hydride because the lattice constant of the nickel metal is approximately equal to that of the hydride. So it is necessary to establish the method to prepare the samples without coexistence of nickel metal for detailed analyses of the hydride.

In the present study, we focused on the synthesis of the samples composed of only CaNiH_3 , without containing nickel metal. If it is successfully done, it can be expected to obtain detailed information about the crystal structure of the hydride and the information about how to synthesize the hydride can help to achieve the rehydrogenation of the material.

2. EXPERIMENTAL DETAILS

Starting materials were granular Ca (Rare Metallic Co. Ltd., 99.5%), Pd wire (Nilaco Co. Ltd.) and CaNi ingot (Japan Metals & Chemicals Co. Ltd.). The bulk composition of the starting CaNi alloy was $\text{CaNi}_{0.96}$ and its constituent phases, which were identified by X-ray diffraction, were Ca, CaNi_2 and CaNi_3 . If Pd is added in the form of metal into the starting CaNi alloy, to prepare the samples with the bulk compositions of $\text{CaNi}_{1-x}\text{Pd}_x$, the addition of Ca is also necessary. But Ca powder which is necessary for mechanical alloying is highly flammable. Thus the use of powder was avoided for safety reason and instead the synthesis of Ca-Pd alloys from Ca and Pd ingots was adopted. Ca and Pd metal ingots were weighed to obtain the nominal composition of $\text{Ca}_{1.05}\text{Pd}_1$ and melted in a SiO_2 crucible under argon atmosphere of 0.1MPa in an induction melting furnace, where Ca was weighed taking the Ca loss due to the reaction with SiO_2 into account. The constituent phase

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of the CaPd sample was identified to be CaPd by X-ray diffraction.

Mechanical grinding/alloying was applied for the preparation of hydride samples. 2 grams of CaNi powder obtained by mechanical crushing of the original ingot or the mixture of 1.5 grams of CaNi and 0.5 gram of CaPd was put into the pot made of Cr-steel with 30 Cr-steel balls with 10mm in diameter. The pot was evacuated and then filled with hydrogen gas up to 0.6 MPa before starting milling. Mechanical grinding/alloying was performed with the P-6 milling instrument made by Fritsch under the conditions of rotational speed of 400 rpm and milling time of 144 ks. Hydrogen gas was refilled into the pot after 3.6 ks of milling in order to supply enough hydrogen to the sample so that it could form the CaNiH_3 type hydride.

The constituent phases in the samples thus prepared were analyzed by X-ray diffraction. In order to correct the diffraction angle, high purity silicon powder (Aldrich Co. Ltd.) was mixed with the sample powder in the measurement. Since the samples were easily oxidized due to oxygen in the air, masking tape was used to protect the samples against oxidation during the measurement. Some of the X-ray diffraction profiles were refined with the Rietan 97 beta program [4].

Much effort was paid to prevent the samples from oxidation. The handling of the samples was performed in a globe box filled with purified argon gas. Only when raw materials were set into the crucible and the samples were picked up from the furnace in induction melting, the samples were exposed to the air for a short time. Except for the operations described above, raw materials before melting and samples after melting were vacuum packed not to react with oxygen in the air.

3. RESULTS AND DISCUSSION

Fig. 1 shows the measured and refined X-ray diffraction profiles for the hydrogenated CaNi sample milled for 144 ks. It was found that strong diffraction peaks were from the aimed phase, CaNiH_3 , except for those from silicon which was mixed into sample powder to correct diffraction angle. The crystal structure of this hydride was the CsCl-type for metal constituents ($Pm\bar{3}m$ symmetry in space group) and the lattice constant was 0.3553(1) nm, where the value in parentheses means standard deviation. This value is consistent with the one previously reported, 0.35518(2) nm [1] within an experimental error. Nickel metal whose diffraction peaks overlap those from CaNiH_3 , was also observed as a secondary phase but its relative amount was much smaller than that of the phase observed in the sample obtained by disproportionation of CaNi_3 under hydrogen atmosphere. The Rietveld profile refinement exhibited that the amount of the nickel metal phase was only 14.7 % in mass fraction. Some Ca-rich phase such as CaH_2 would be observed in this profile, taking the bulk composition of the sample into account. The reason why CaH_2 was not observed in the samples is unclear but it might be significantly deformed or nano-structured during mechanical grinding. Thus the CaH_2 phase was not observed in all the samples mechanically ground under hydrogen atmosphere.

Fig. 2 shows the measured and calculated X-ray diffraction profiles for the sample obtained by

mechanical alloying of the mixture of the CaNi and CaPd starting alloy powder under hydrogen atmosphere, where the Rietveld profile refinement was conducted under the assumption that Pd atoms substitute for Ni ones in all the constituent phases. All the strong diffraction peaks were identified as the phase with the CsCl structure for the metal constituents and silicon. The CsCl-type phase $\text{CaNi}_{0.814}\text{Pd}_{0.186}\text{H}_y$ has the lattice constant of 0.3583 nm, which is larger than that of CaNiH_3 . The secondary phase nickel-palladium alloy phase with the face-centered cubic structure was observed as well as in the CaNi sample mechanically ground but its relative amount was only 2.7 % in mass fraction, which means that mechanical grinding/alloying is the effective way to synthesize samples with an approximately single phase structure composed of the CaNiH_3 -type phase. The results obtained by the Rietveld profile refinement of the X-ray diffraction profiles for the two samples are summarized in Table I.

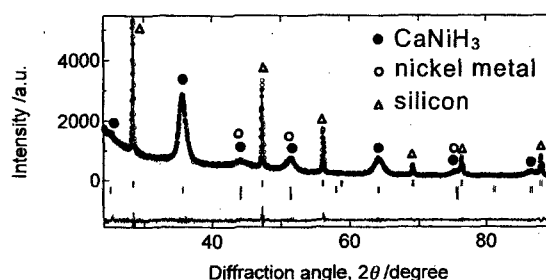


Fig. 1 X-ray diffraction profile measured for the sample obtained by mechanical grinding of the CaNi starting alloy at 400 rpm for 144 ks under the hydrogen atmosphere of 0.6MPa and the refined profile with the Rietan 97 beta program. The profiles observed (open circle) and calculated (line) are respectively shown in top, the peak positions of calculated silicon, CaNiH_3 , and nickel metal in middle and difference in bottom.

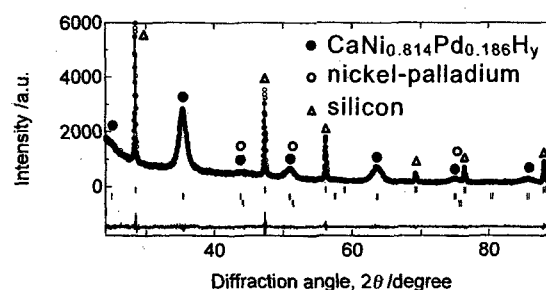


Fig. 2 X-ray diffraction profile measured for the sample obtained by mechanical grinding of the mixture of CaNi and CaPd starting alloys at 400 rpm for 144 ks under the hydrogen atmosphere of 0.6MPa and the refined profile with the Rietan 97 beta program. The profiles observed (open circle) and calculated (line) are respectively shown in top, the peak positions of calculated silicon, $\text{CaNi}_{0.814}\text{Pd}_{0.186}\text{H}_y$, and nickel-palladium alloy in middle and difference in bottom.

According to the calculation of formation enthalpy based on the semi-empirical model proposed by Miedema [3], CaPd is much more stable than CaNi because Pd has stronger affinity with Ca than Ni [2], which implies the hydrides of Ca-Pd alloys are more disproportionation-resistant than those of Ca-Ni ones. In

fact, CaPdH_2 , which is one of the hydride phases of CaPd , retains its structure at 673K under the hydrogen atmosphere of 1MPa. These facts imply that Pd tends to form alloys and hydrides together with Ca and that, as a result, stabilize the CaNiH_3 -type hydride, with which the result that the relative amount of the face-centered cubic phase is less in the Pd-containing sample than in the CaNi sample is consistent.

Table I Summary of the results obtained by the Rietveld profile refinement of the X-ray diffraction profiles measured for the samples mechanically ground under hydrogen atmosphere, shown in Figs. 1 and 2. Values in parentheses mean standard deviation

Sample	CaNi	CaNi+CaPd
Major phase	CaNiH_3	$\text{CaNi}_{0.814}\text{Pd}_{0.186}\text{H}_y$
Space group**	$Pm\bar{3}m$	$Pm\bar{3}m$
Lattice constant (nm)	0.3553(1)	0.3583(1)
Mass fraction	0.853	0.973
R_1 (%)	0.55	0.78
R_F (%)	0.41	0.52
Minor phase	Ni	$\text{Ni}_{0.814}\text{Pd}_{0.186}$
Space group	$Fm\bar{3}m$	$Fm\bar{3}m$
Lattice constant (nm)	0.3550(5)	0.3553(7)
R_1 (%)	1.05	0.82
R_F (%)	0.55	0.44
R_{wp} (%)	4.86	5.14
R_e (%)	4.32	4.36

The lattice constant of the $\text{CaNi}_{0.814}\text{Pd}_{0.186}\text{H}_y$ phase is larger than that of the original CaNiH_3 phase, which is because the atomic radius of Pd (0.137 nm) is larger than that of Ni (0.125 nm). But the value of the Pd-containing phase (0.3583 nm) is not as large as the one (0.3600 nm) calculated under the assumption that the lattice constant of the Pd-containing hydride phase linearly increases with an increase in Pd content from CaNiH_3 to CaPdH_3 , where the lattice constant of CaPdH_3 , which has not been reported on its existence yet, is estimated to be 0.3806 nm from the lattice constants of CaPd (0.3510 nm) and CaPdH_2 (0.3707 nm) [2]. One may think that Pd atoms insufficiently substitute for Ni ones in the hydride phase and concentrate to the face-centered cubic phase. However, that is inconsistent with the above-mentioned discussion and experimental result that the lattice constant of the face-centered cubic phase negligibly changes with Pd addition, which might indicate that this phase little contains Pd. Not only Pd substitution but also hydrogen content in hydride phase can affect lattice constant of hydride phase, implying that the hydrogen content y of $\text{CaNi}_{0.814}\text{Pd}_{0.186}\text{H}_y$ might be less than 3. In fact the maximum hydrogen content of the CaNi and CaPd hydride phases is respectively 1.5 [1] and 1.24 in molar ratio of hydrogen to metal [2]. If the lattice constant is calculated based on the assumption described above and using the values of CaNiH_3 and CaPdH_2 (0.3707 nm), it is estimated to be 0.3582 nm, in good agreement with the experimental value, supporting decrease in hydrogen

content of the Pd-containing hydride phase.

In the present study, the aimed sample with a single phase of the CaNiH_3 type hydride was obtained by mechanical grinding/alloying, which allows us to examine this hydride in more details. Further studies are now being conducted to obtain information about its crystal structure including the positions of hydrogen (deuterium) atoms and hydrogenation properties in order to achieve its reversible hydrogen absorption/desorption. The results will be reported in other papers.

4. CONCLUSIONS

In order to establish the way to synthesize a new hydride CaNiH_3 without the coexistence of impurity phases, mechanical grinding/alloying was applied and the hydride phases obtained were analyzed on crystal structures. The obtained results are summarized below:

- A new hydride $\text{CaNi}_{0.814}\text{Pd}_{0.186}\text{H}_y$ ($y < 3$) in which Pd partially substitutes for Ni is firstly synthesized. Its crystal structure for metal constituents is a cubic CsCl-type and $Pm\bar{3}m$ in space group, as well as CaNiH_3 , and its lattice constant is 0.3583(1) nm, larger than the original hydride.
- Mechanical grinding/alloying is an effective way to synthesize CaNiH_3 and its related hydride substituted by Pd for Ni without the coexistence of impurity phases.
- Pd can contribute to the stabilization of CaNiH_3 -type hydride by substituting for Ni due to its strong affinity with Ca.

ACKNOWLEDGEMENT

The authors greatly appreciate the INAMORI Foundation for the financial support of the present study.

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(Received October 10, 2003; Accepted October 31, 2003)

** Space group for constituent metals