Hydrogen Vibrational Excitation Spectra of CaF₂-Type Metal Hydrides Synthesized from Ti-Based BCC Solid Solution Alloys

Yumiko Nakamura¹*, Takashi Kamiyama² and Etsuo Akiba¹

¹National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba 305-8565, Japan
²Faculty of Engineering, Hokkaido University, Sapporo 060-8628, Japan

Hydrogen vibrational excitation was studied for CaF₂-type metal hydrides synthesized from Ti-based BCC solid solution alloys using inelastic incoherent neutron scattering (IINS). The first three peaks were isolated but the higher excitation peaks were not clear. Analysis of the spectra using curve-fitting with Gauss functions reflects a trumpet-type potential. The relation between metal-hydrogen distance and vibrational excitation energy for the above two hydrides and inelastic incoherent neutron scattering (IINS). The patterns of the spectra were compared with a series of CaF₂-type binary metal hydrides. All the hydrides of the Ti-based alloys had lower vibrational excitation energies than the binary metal hydrides for the corresponding metal-hydrogen distances. [doi:10.2320/matertrans.MA201014]

(Received October 13, 2010; Accepted November 26, 2010; Published April 1, 2011)

Keywords: hydrogen storage, BCC solid solution alloy, CaF₂ structure, vibration, inelastic neutron scattering

1. Introduction

Hydrogen storage materials have attracted great interest for a use in fuel cell vehicles. Among these materials, metal-based storage materials, so called metal hydrides, generally have the advantages of a large capacity per volume, and favorable kinetics and cyclic stability, but the disadvantage of a low capacity per weight. Ti- or V-based solid solution alloys with a BCC structure are known to have the largest reversible hydrogen capacity at around room temperature, close to 3 mass%.¹⁻³ This kind of alloys form dihydrides with the atomic ratio of hydrogen and metal is close to two.

Hydrogenation properties of metal-based materials are considered to depend on hydrogen occupation in their interstitial sites in the metal lattice. Properties of solid solution alloys seem to be basically similar to those of pure metals with the same crystal structure, but different from those of intermetallic compounds represented as AB₂, AB₃, AB₂M, AB₂B, etc. The difference among hydrides of pure metals, solid solution alloys and intermetallic compounds may consist in local structure, particularly surroundings of interstitial hydrogen atoms. Hydrogen atoms are in local vibration in the potential made by surrounding metal atoms. Vibrational excitation energy spectra reflect the shape of potential well of interstitial hydrogen, which is related to the local coordination of metals to hydrogen. Comparing vibrational excitation energy among different metal hydrides will provide useful information about the variation in the local structure.

Vibrational excitation spectra of interstitial hydrogen have been studied for hydrides of pure metals (binary metal hydrides).⁴⁻⁵ In particular, a series of dihydrides of CaF₂-type, denoted as MH₂, have been investigated. Ross et al. found that vibrational excitation energies E depend on metal-hydrogen distances R as E = AR⁻³/² (A: constant).⁵ Fukai and Sugimoto proposed that another equation E = AR⁻¹ can also describe the correlation as well as the equation above.⁶ Both reports indicate that the vibrational excitation energies mostly depend on metal-hydrogen distances independently of the metal elements.

In this study we investigated hydrogen vibrational excitation spectra of dihydrides synthesized from three Ti-based BCC solid solution alloys using incoherent inelastic neutron scattering (IINS). The patterns of the spectra were compared with that reported for TiH₂ to discuss the shape of the vibrational potential. The dependence of the vibrational excitation energy on the metal-hydrogen distance was discussed in comparison with the relation proposed for binary metal hydrides. A relation between the vibrational excitation energy and the hole size of the interstitial sites was also discussed.

2. Experimental

2.1 Preparation of samples

Alloy ingots of Ti₁₀V₄₁Mn₀₉ and Ti₀₇V₁₂Cr₁₁ were prepared by arc melting. Dihydride samples of Ti₁₀V₄₁Mn₀₉ and Ti₀₇V₁₂Cr₁₁ were prepared by hydrogenation of the powdered alloys at 5 MPa at room temperature. The hydrogen content was measured to be 1.48 H/M for Ti₁₀V₄₁Mn₀₉ and 1.59 H/M for Ti₀₇V₁₂Cr₁₁ by chemical analysis using hydrogen analyzer (LECO, RH-402). The synthesized dihydride phases were confirmed using X-ray diffraction. About 6 g of each sample was put between two aluminum plates (0.2 mm thick) and wrapped with aluminum foil (50 micrometers thick). The thickness of the sample layer was 1.0–1.2 mm. Ti₁₁₋₄Cr₁₄M₀₃ alloy was prepared by arc melting and annealing at 1743 K for 60 s followed by water quench. It was crushed into powder and hydrogenated at 5 MPa and 298 K. The hydrogen content was estimated to be about 1.6 H/M from the P-C isotherm. About 5 g of the powder was put into an aluminum flat cell. The thickness of the sample layer was around 1.0 mm.
2.2 IINS measurement

Hydrogen atom in a certain vibration level \( E_1 \) can be excited to an upper level \( E_n \) (\( n = 2, 3, 4, \text{ etc.} \)) by receiving energy equal to \( (E_n - E_1) \) from neutron. This interaction between neutron and hydrogen atom causes inelastic neutron scattering. An IINS spectrum, scattering intensity versus energy transfer \( \varepsilon \), shows several peaks at \( \varepsilon_{n-1} = E_n - E_1 \). When a hydrogen atom is located in symmetric tetrahedral or octahedral sites surrounded by the same element, the vibration is harmonic in a parabolic potential, where the energy levels have a constant interval \( 4) \) (Fig. 1).

IINS measurements were performed in He atmosphere at 10–25 K using the time-of-flight type crystal analyzer spectrometer, CAT \(^7\) at KENS (Tsukuba, Japan). The spectrometer is an inverted-geometry type with white neutron incident beam. Scattered neutrons of fixed energy \( E_f = 4.0 \text{ meV} \) were selected by the analyzer crystal (PG) and detected by the \(^3\)He counter. Difference in energy between the incident and detected neutrons provides the energy transfer from neutron to the sample. The counting time was about 36–48 h. Spectra were analyzed by fitting with convolution of Gaussian curves to evaluate each peak position corresponding to the excitation energy.

3. Results

The IINS spectrum of Ti\(_{1.0}V_{1.1}\)Mn\(_{0.9}\)H\(_{4.5}\) is shown in Fig. 2(a). The pattern was similar to that reported for hydrides with typical CaF\(_2\) structure such as TiH\(_2\) \(^7\) (Fig. 3), where hydrogen atoms occupy the tetrahedral sites in FCC metal sublattice. In the spectrum the first three peaks were isolated but the higher excitation peaks were not clear. The result of curve-fitting up to the third peak is shown in Fig. 2(b) and Table 1. The excitation energy obtained from the peak position was \( \varepsilon_1 = 133.1(5) \text{ meV} \), \( \varepsilon_2 = 268(2) \text{ meV} \), and \( \varepsilon_3 = 394(3) \text{ meV} \), where calculated standard errors in the last digit are in the parentheses. Assuming that the vibration is completely harmonic, \( \varepsilon_2 \) and \( \varepsilon_3 \) will be equal to \( 2\varepsilon_1 = 266 \text{ meV} \) and \( 3\varepsilon_1 = 399 \text{ meV} \), respectively, with a constant interval of 133 meV (=\( \varepsilon_1 \)). The values obtained from the analysis well agree with these values, taken the errors into account. This confirms that the hydrogen vibration in Ti\(_{1.0}V_{1.1}\)Mn\(_{0.9}\)H\(_{4.5}\) is almost harmonic.

The IINS spectrum of Ti\(_{0.7}V_{1.2}\)Cr\(_{1.1}\)H\(_{4.8}\) shows a similar profile (Fig. 4(a)). The excitation energy was \( \varepsilon_1 = 141.3(4) \text{ meV} \), \( \varepsilon_2 = 275(1) \text{ meV} \) and \( \varepsilon_3 = 406(3) \text{ meV} \) for the first three peaks (Fig. 4(b) and Table 1). The interval between \( \varepsilon_1 \) and \( \varepsilon_2 \) was 134 meV and that between \( \varepsilon_2 \) and \( \varepsilon_3 \)
was 130 meV. These values are smaller than \( \varepsilon_1 \) indicating that the interval decreases with the degree of the states, even if the error values are taken into account. From this result, the shape of the vibrational potential for Ti\(_{0.7}V\)\(_{1.2}\)Cr\(_{1.1}\)H\(_{4.8}\) is deformed from parabolic to trumpet-type.

Figure 5 shows the IINS spectrum of Ti\(_{1.0}V\)\(_{1.3}\)Mn\(_{0.9}\)H\(_{4.5}\). The pattern was assumed to be similar to those of the other two samples although the peaks were less clear because of the insufficient statistics. The first and second excitation energy was \( \varepsilon_1 \sim 148 \) meV and \( \varepsilon_2 \sim 280 \) meV. \( \varepsilon_1 \) is higher than that obtained for Ti\(_{1.0}V\)\(_{1.1}\)Mn\(_{0.8}\)H\(_{4.5}\) and Ti\(_{0.7}V\)\(_{1.2}\)Cr\(_{1.1}\)H\(_{4.8}\).

### Table 1

Parameters obtained from Gaussian fits to the IINS spectra of Ti\(_{0.7}V\)\(_{1.2}\)Cr\(_{1.1}\)H\(_{4.8}\) and Ti\(_{0.7}V\)\(_{1.2}\)Cr\(_{1.1}\)H\(_{4.8}\).

<table>
<thead>
<tr>
<th>Sample, ( n )</th>
<th>peak position*/meV</th>
<th>FWHM*/meV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti(<em>{1.0}V)(</em>{1.3})Mn(<em>{0.9})H(</em>{4.5})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1st</td>
<td>133.1(5)</td>
<td>51(1)</td>
</tr>
<tr>
<td>2nd</td>
<td>268(2)</td>
<td>75(4)</td>
</tr>
<tr>
<td>3rd</td>
<td>394(3)</td>
<td>78(8)</td>
</tr>
<tr>
<td>Ti(<em>{0.7}V)(</em>{1.2})Cr(<em>{1.1})H(</em>{4.8})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1st</td>
<td>141.3(4)</td>
<td>40.5(8)</td>
</tr>
<tr>
<td>2nd</td>
<td>275(1)</td>
<td>59(2)</td>
</tr>
<tr>
<td>3rd</td>
<td>406(3)</td>
<td>114(8)</td>
</tr>
</tbody>
</table>

*calculated standard errors in parentheses.

### Figure 6

The relation between metal-hydrogen distance \( R \) and vibrational excitation energy \( \varepsilon \). Squares: a series of CaF\(_2\)-type binary metal hydrides, MH\(_2\); the data from Ref. 5). Circles: dihydrides of Ti-based solid solution alloys (this study); 1: Ti\(_{1.0}V\)\(_{1.3}\)Mn\(_{0.9}\)H\(_{4.5}\), 2: Ti\(_{0.7}V\)\(_{1.2}\)Cr\(_{1.1}\)H\(_{4.8}\), 3: Ti\(_{1.1}\)-Cr\(_{1.4}\)Mo\(_{0.3}\)H\(_{4.5}\).

### 4. Discussion

The relation between metal-hydrogen distance \( R \) and vibrational excitation energy \( \varepsilon \) was reported in a series of CaF\(_2\)-type binary metal hydrides, MH\(_2\) by Ross et al.\(^7\). \( \varepsilon \) was considered to be proportional to \( R^{-1} \) or \( R^{-2/3} \).\(^6,7\) Our results for dihydrides of Ti\(_{1.0}Mn\(_{0.9}\)V\(_{1.1}\), Ti\(_{0.7}V\)\(_{1.2}\)Cr\(_{1.1}\) and Ti\(_{1.1}\)-Cr\(_{1.4}\)Mo\(_{0.3}\) are plotted with the reported data in Fig. 6. All the data from this study are located under the belt of the plots for the binary metal hydrides. Among the three hydrides the plot of Ti\(_{1.1}\)Cr\(_{1.4}\)Mo\(_{0.3}\)H\(_{4.5}\) is located closest to the relation for the binary hydrides, particularly close to the point for TiH\(_2\).

“Hole size” is often used as an indicator of possibility of hydrogen occupation for interstitial metal hydrides.\(^8\) A hole size corresponds to a radius of a sphere which can be inserted into an interstitial site when the surroundings metal atoms are regarded as solid spheres. We assumed that this value is related more closely to the vibrational potential than the metal-hydrogen distance because the hole size reflects the size of space which hydrogen atoms can occupy; a smaller hole size would make the potential curve narrower and raise the excitation energy. To confirm this prospect, the hole size for each of the three hydrides and TiH\(_2\) was calculated using
the lattice parameter of the hydride and the weighted average Goldschmidt radius of the constituent elements: 0.051 nm (Ti$_{1.0}$V$_{1.1}$Mn$_{0.0}$H$_{4.5}$), 0.048 nm (Ti$_{0.7}$V$_{1.2}$Cr$_{1.1}$H$_{4.8}$), 0.048 nm (Ti$_{1.1}$Cr$_{1.4}$Mo$_{0.3}$H$_{5.5}$), and 0.045 nm (TiH$_2$). The result shows the tendency of hydrogen in a smaller hole size to present a higher vibration excitation energy as a whole. However, Ti$_{1.1}$Cr$_{1.4}$Mo$_{0.3}$H$_{5.5}$ and Ti$_{0.7}$V$_{1.2}$Cr$_{1.1}$H$_{4.8}$ have a similar hole size but different vibrational excitation energies. This clearly suggests that chemical composition also affect the vibrational potential in addition to the size factor when hydrides synthesized from solid solution alloys are treated. Fernandez et al. reported IINS study of hydrogenated C15 Laves phases.\(^9\) The vibrational energies were well described by a potential obtained from summation of a Born-Mayer type equation of each constituent element, i.e. \(V(R) = \Sigma C_i \exp(-R/\rho_i)\), where \(R\) is hydrogen metal distance, \(C_i\) and \(\rho_i\) are potential parameters depending on each metal element. In their report, Cr caused a shallower potential than Ti and Zr. By analogy with this, interstitial sites surrounded by more Mn and Cr atoms may make a shallower potential and lower excitation energies. Mo has a different effect. Adding Mo to Ti-based BCC solid solution alloys is known to raise equilibrium pressure of hydrogenation significantly.\(^10\)

A larger Mo content provides a higher equilibrium pressure, which has been understood as Mo reduces hole sizes of the interstitial sites.\(^11\) Not only the atomic radius but also the larger number of electrons of Mo are likely to give the deeper (or sharper) vibrational potential and result in the higher excitation energies.

TiH$_2$, Ti$_{1.0}$V$_{1.1}$Mn$_{0.0}$H$_{4.5}$, and Ti$_{0.7}$V$_{1.2}$Cr$_{1.1}$H$_{4.8}$ showed different peak width in their spectra. TiH$_2$ shows sharp and well-isolated peaks, while peaks of the other two di-hydrides are broader and less clear. This peak broadening can be attributed to the following factors. (1) Distribution of the site energy of hydrogen atoms: In solid solution alloys, the atoms of the constituent elements are assumed to be randomly distributed as a whole. Interstitial tetrahedral sites are formed by combination of four atoms selected from the constituent elements. Different combination will provide different potential. (2) Asymmetric local structure: If interstitial hydrogen is surrounded by Ti, V, and Cr or Mn, the vibrational potential will arise more sharply on the Ti side and less sharply on the Cr or Mn side, considering their potential parameters.\(^9\) This will make the vibration asymmetric. Our local structure study of Ti$_{1.0}$V$_{1.1}$Mn$_{0.0}$H$_{2.5}$ using neutron total scattering suggested that the hydrogen atoms in the tetrahedral sites are slightly displaced from the center of the tetrahedron,\(^15\) which may be related to the asymmetric vibration. The asymmetric vibration splits the degenerate energy levels for the three directions, which splits the peaks in the IINS spectra. Small peak splitting may appear as peak broadening.

5. Conclusion

Hydrogen vibrational excitation was studied for dihydrides of Ti$_{1.0}$V$_{1.1}$Mn$_{0.9}$, Ti$_{0.7}$V$_{1.2}$Cr$_{1.1}$, and Ti$_{1.1}$Cr$_{1.4}$Mo$_{0.3}$ using inelastic incoherent neutron scattering (IINS). Hydrogen in the tetrahedral site in Ti$_{1.0}$V$_{1.1}$Mn$_{0.9}$H$_{4.5}$ and Ti$_{0.7}$V$_{1.2}$Cr$_{1.1}$H$_{4.8}$ is in almost harmonic vibration. The shape of the vibrational potential for Ti$_{0.7}$V$_{1.2}$Cr$_{1.1}$H$_{4.8}$ is slightly deformed from parabolic to trumpet-type. The three hydrides of this study have lower excitation energies than those expected from the metal-hydrogen distances based on the relation proposed for binary metal hydrides. Hydrogen in a smaller hole size tends to present a higher vibration excitation energy as a whole, but the chemical composition also affects the vibrational potential for hydrides of solid solution alloys in addition to the size factor.

Acknowledgements

The authors thank Drs. K. Kubo and H. Itoh of Japan Steel Works, Ltd. for providing the Ti$_{1.1}$Cr$_{1.4}$Mo$_{0.3}$ alloy sample.

REFERENCES